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Preface

The papers included in this issue of *ECS Transactions* were originally presented in the symposium “Electrocatalysis 9: Symposium in Honor of Radoslav Adzic”, held during the 233rd meeting of The Electrochemical Society, in Seattle, WA, from May 13-17, 2018.

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Facts about ECS

The Electrochemical Society (ECS) is an international, nonprofit, scientific, educational organization advancing the theory and practice of electrochemistry and solid state science and technology, and allied subjects. The Society was founded in Philadelphia in 1902 and incorporated in 1930. There are currently over 8,400 members from around the globe representing 13 technical division and 23 geographical sections and a growing student membership program with almost 70 student chapters. The Society is also supported by more than 800 corporations, government agencies and academic institutions through institutional membership, corporate programs and subscriptions.

The technical activities of the Society are carried on by divisions. Sections of the Society host symposia, programs and events focused on their respective geographic regions. Major international meetings of the Society are held in the spring and fall of each year. At these meetings, the divisions and partnered organizations hold general sessions and sponsor symposia on specialized subjects.

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Journal of The Electrochemical Society — (JES) is the flagship journal of The Electrochemical Society and the oldest peer-reviewed journal in its field. Since its founding in 1902, JES has evolved into one of the most highly cited and prestigious journals in electrochemistry and materials science with a cited half-life of greater than 10 years.

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The Electrochemical Society Interface — *Interface* is a quarterly news magazine that provides a forum for the lively exchange of ideas within the scientific community. Published online with free access in the ECS Digital Library, issues engage readers with a featured scientific research section, and summaries of research breakthroughs, and industry and Society news.

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For more information on these and other Society activities, visit the ECS website:

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Chapter 1

General Electrocatalysis

Use of E-ALD by SLRR of Cu UPD Layers for the Growth of Pd Thin Films in One-Cell Configuration

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This work illustrates the application of electrochemical atomic layer deposition (E-ALD) by surface limited redox replacement (SLRR) in one-cell configuration for the growth of Pd thin films using underpotentially deposited Cu (Cu_{UPD}) as a sacrificial metal. The growth of Pd films on Au was monitored by open circuit chronopotentiometry while the roughness evolution and thickness of accordingly deposited Pd films were assessed by H_{UPD} and Cu_{UPD} cyclic voltammetry and stripping experiments, respectively. The growth of smooth Pd films was observed for about 15 equivalent monolayers (MLs) of Pd followed by a rapid transition to dendritic growth. A comparison with counterpart results of Pd SLRR deposition in a flow-cell suggests that the dendritic growth in one-cell is associated with establishment of mass-transport limitations. To address this shortcoming a modified protocol introducing SLRR-cycle disruption and forced convection was applied to demonstrate the growth of 26 MLs thick, smooth and continuous Pd film.

Introduction

The research and development work has intensified lately on the thin-films of metals on different substrates. The ultrathin metal films can exhibit quantum size and surface effects that enable them to show unique physical and chemical properties that bulk counterparts never exhibit (1). Due to its reversible and selective ability to adsorb and absorb large volumes of hydrogen, palladium thin films can be used in H storage, as hydrogen sensors (2) as well as in the fuel cell industry as catalyst (3, 4). Thin films of Pd or Pd-based alloys with other metals like Pt, are considered to be among the (hetero)catalysts for oxygen reduction (5). The use of Pd as catalyst facilitates the commercialization of the fuel cells which have been using the costly but rare Pt metal (6). The fabrication of thin films via atomic layer deposition (ALD) on different substrates employs various techniques (7) such as physical vapor deposition (8), molecular beam epitaxy (9), chemical vapor deposition (10), magnetron sputtering (11) and electrochemical deposition (12, 13). Most of these techniques are very expensive and unsustainable due to ultrahigh vacuum conditions. The electrodeposition approaches are more economical and operate under ambient conditions (13). Electrochemical atomic layer deposition (E-ALD) has utilized the surface limited redox replacement (SLRR) (14-17) technique to achieve epitaxial and conformal thin films of metals or alloys. This technique involves the underpotential deposition (UPD) of a less noble element (Cu, Pb or H) to form a sacrificial layer on a conductive substrate such as polycrystalline Au_{poly} electrode followed by a redox replacement reaction, at open circuit potential (OCP), with

more noble metal (Au, Pd, Pt, Rh Cu or Ag). The latter exchange reaction enables growth of conformal noble metal thin films whose thickness depends on the number of deposition and redox replacements performed i.e. number of SLRR cycles (14-18). The Pd ultrathin film deposition via the SLRR has been extensively studied by J. Stickney et al in an automated flow cell system (4, 19-21). Having identified Cu as the better sacrificial metal relative to Pb, Stickney and co-workers optimized the growth conditions coming up with best growth results in a solution with chloride/palladium ion concentration ($[Cl^-]/[Pd^{2+}]$) ratio of 500. This involved minimizing the differential redox displacement associated with a concentration gradient across the flow cell working electrode that resulted from high activity at the ingress and vice versa. The rate of redox exchange was reduced, and 3D growth thus minimized. The best results were 75 SLRR cycles with up to 95% exchange efficiency and minimal roughness development (4). The automated flow cell system suffers a few drawbacks such as high maintenance and relatively high operation cost. An alternative to the flow-cell approach is the one-cell configuration that features simplicity and offers the comfort of having all chemicals for E-ALD by SLRR at once in the same cell (22). While addressing some drawbacks of other SLRR routines, the one-cell approach also suffers some limitations among which is an inevitable transitioning to diffusion-limited growth in the course of thicker film deposition (23). Such transitioning has been recently believed to facilitate systems growing in a quasi-2D mode to proceed eventually to a dendritic growth mode.

In this work, we present a study on the SLRR growth of Pd thin films in one-cell configuration using Cu as a sacrificial metal. Along with detailed optimization effort assessing the impact of absolute and relative concentrations of Pd^{2+} and Cl^- ions on the deposition outcome (kinetics and morphology), of interest to this work has been the transitioning to dendritic growth and development of means to minimize its adverse effects on the Pd growth in general. More specifically, the growth of Pd is conducted and studied by potential pulse routines and open circuit chronopotentiometry (OCCP). The film roughness is assessed by H_{UPD} and Cu_{UPD} cyclic voltammetry (CV) experiments and the film thickness (deposition efficiency) was determined by anodic stripping of Pd films following all test and characterization routines.

Experimental

Electrode Preparation

The working electrodes for all electrochemical and morphological characterization experiments in this work are polycrystalline Au_{poly} discs of 6 mm diameter and thickness of 2 mm. Their preparation involves mechanical polishing down to 1 μm using water-based, de-agglomerated alumina slurry (Buehler). After which, they are rinsed with water before being immersed in warm concentrated HNO_3 to remove any polishing residual particles and then followed by thorough rinsing with Barnsted NanoPure® water ($>18M\Omega$). Next, the Au disks are electropolished via protocol described elsewhere (24) (ref 28 paper 1). The final step of preparation involves carefully annealing the crystals to red-hot in a propane torch for minimum 5 min before cooling rapidly in ultrapure nitrogen atmosphere to avoid surface oxidation. The process is terminated with a droplet of the Barnsted NanoPure® water to prevent surface contamination. These electrodes are mounted on to a conductive vacuum holder and immersed in a hanging meniscus configuration in a three-electrode cell system for characterization and consequently thin film growth. All electrochemical experiments were performed in three electrode cells using solutions made from and ultra-high purity grade chemicals as received from the

vendors and Barnsted NanoPure[®] water. A saturated mercury-mercurous sulfate electrode (MSE) is used as reference electrode in most experiments except those stated otherwise. Also, a Pt wire serves as the counter electrode (CE) in all experiments. All potentials in the manuscript are presented versus MSE (except the Cu_{UPD} characterization experiment) and all current densities are normalized with respect to the geometric area of the electrode.

Initial Characterization of Au Electrodes

The Au electrodes are characterized using Pb_{UPD} cyclic voltammetry(23) (CV) to determine the quality of their surfaces before Pd deposition as well as to determine the electrochemical surface area (ECSA). The solution composition for Pb_{UPD} experiments is given elsewhere(23). The CV measurements were performed using Model AFCBP Bipotentiostat (Pine Instruments) interfaced with a PC through the PineChem software (Version 2.80). Pb wire was used as a pseudo-reference electrode.

Pd Ultrathin Film Growth

The formation of the ultrathin layers of Pd on Au was performed via different number of SLRR events in a one cell configuration. The optimized deposition solution made of 0.3 mM PdCl₂ (Aldrich, 99.99%), 30 mM HCl (J.T. Baker[®], 36.5-38 %), 3 mM CuSO₄ (Aldrich, 99.995%) and 0.1 M H₂SO₄ (GFS Chemical, redistilled 95-98%) was purged with ultrapure N₂ for at least 30 min. One SLRR cycle involves the formation of a conformal submonolayer or monolayer of Cu_{UPD} by application of a potential pulse for 1 s followed by a redox replacement step by the more noble metal – Pd, occurring at open circuit potential(25). The cycles could be run continuously non-stop or could be broken into groups of four runs then four again until the total equals the intended number of cycles. These thin-film growth processes for palladium were administered and monitored using a Princeton Applied Research (PAR) Model 273 Potentiostat/Galvanostat coupled with Corrware Software. Data was collected by PicoLog software.

Electrochemical Testing and Characterization

The Cyclic Voltammetry employing H_{UPD} and Cu_{UPD} were used to electrochemically characterization of the as-grown Pd thin films. The H_{UPD} CV was conducted in 0.5 M H₂SO₄ (GFS Chemical, highest purity grade, redistilled) within a potential range that minimizes H absorption i.e. 0.1 V to -0.67 V (vs MSE) at a sweep rate of 50 mV.s⁻¹. We conducted the Cu_{UPD} characterization via CV in 3 mM CuSO₄ (J.T. Baker, 99.8%), 0.1M H₂SO₄ solution using Cu wire as pseudo-reference electrode at a sweep rate of 20 mV.s⁻¹. The administration and monitoring of these Pd thin films was done using the instruments and software used for Pb_{UPD} characterization mentioned early.

Anodic Stripping of Pd Films

When characterization of the thin-films of palladium on gold is done, anodic stripping of the same films is done by a linear sweep voltammetry (LSV) in a 0.1 M HCl (J.T. Baker[®], 36.5-38%) solution over a potential range -0.3 to 0.4 V against MSE as a reference electrode. The LSV sweep rate 3mV.s⁻¹ and was controlled by Model AFCBP Bipotentiostat (Pine Instruments) interfaced with a PC through the *Aftermath Data Organizer* software.

Results and Discussion

Initial Au Electrode Characterization

The structure of deposited Pd on Au surfaces depends on the quality of the substrate. The quality of the Au electrode surface must therefore be very good. To determine this, the Au electrodes used in this work are characterized by Pb_{UPD} (Figure 1a) and Cu_{UPD} CV curves (Figure 1b) which both show shapes and features typical for a polycrystalline Au samples with strongly dominating (111) surface orientation. Work on electrodes of the same or comparable quality was also reported in our previous publications (23). It must show the typical peaks the represent low-index Au facets of (111), (110) and (100) to indicate the readiness of the substrate for the deposition step. Many systems that use UPD galvanic replacements to grow epitaxial thin layers of metals on different conductive substrates have utilized Cu or Pb as the sacrificial elements (7, 14, 16, 19, 26).

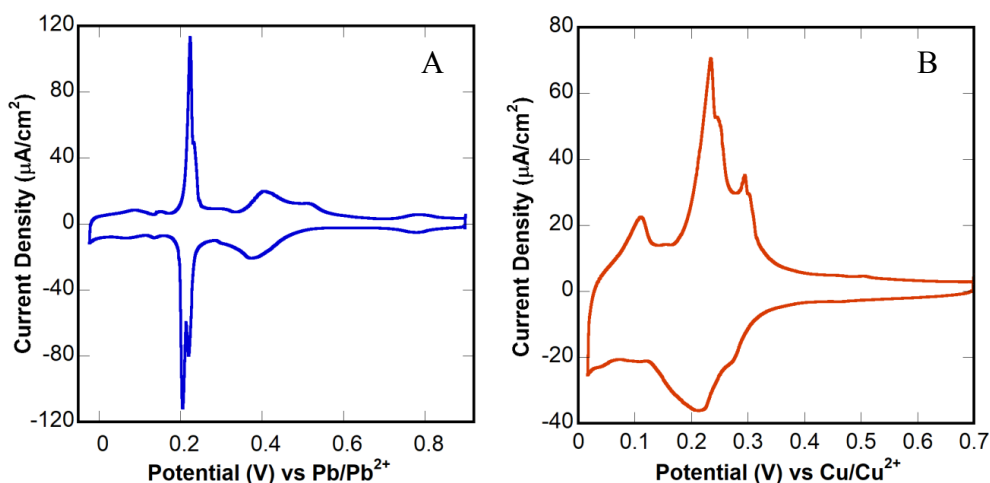


Figure 1. CV curves of Pb_{UPD} (A), and Cu_{UPD} (B) on Au_{poly} electrode. Sweep rate: 20 mV.s⁻¹

For Pd thin film growth of Au, Cu was found to be a better sacrificial element compared to Pb since Pb alloyed strongly with Pd and thus the growing thin film of palladium remains with high percent of Pb contaminant compared to Cu residues(19). The growth of the thin films of Pd on Au via the flow cell system (19) had some issues with differential deposition of Pd with most of deposition occurring at the ingress where the activity of Pd is highest and thus the rate of exchange reaction was higher relative to the solution exchange time (4). To facilitate uniformity of the thin film, EDTA was used to complex Pd ions at an optimized ratio of $[Pd^{2+}]/[EDTA] = 1$, this resulted in slowing down the process, growing more homogenous films at the expense the amount of deposit (replacement efficiency)(4). A more labile complexing agent was used to both realize smooth and homogenous Pd thin films without sacrificing the amount deposited. Based on several work done by Uosaki et al (13) and Kolb (27), the chloride complexes of palladium ($PdCl_4^{2-}$) are more labile compared to EDTA complexes of Pd^{2+} ions. They promote formation of high-quality deposits and they shift the standard reduction potential of Pd^{2+} by ~0.3 V negative due to decreased concentration of free Pd^{2+} ions. Robinson et al(4) reported the optimized complexation ratio of chloride to palladium ions to be $[Cl^-]/[Pd^{2+}] = 500$ showing that the greater the ratio the more homogeneous and uniform the grow was in their flow cell system.

[Pd²⁺] Impact on the Growth

Taking into account previous developments our work was initiated with SLRR deposition of Pd in one-cell configuration from solution featuring ratio of $[Cl^-]/[Pd^{2+}] = 8$ and with using Cu as the sacrificial element (28). Also, the solution was made of 0.3 mM PdCl₂, 2.4 mM HCl, 4.0 mM CuSO₄ and 0.1 M H₂SO₄. Figure 2 (A) and (B) represent the H and Cu underpotential characterization CVs on the as grown Pd ultrathin layers on

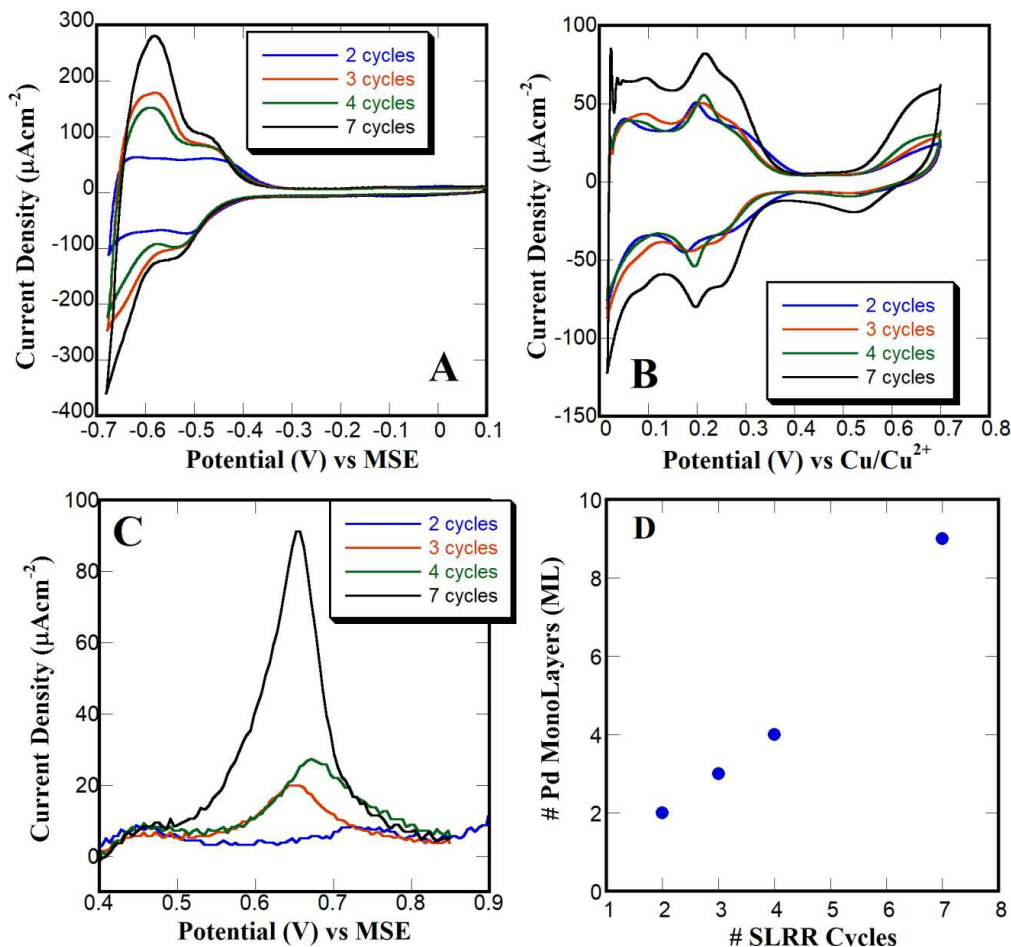


Figure 2. CV curves of H_{UPD} at sweep rate of 50 mVs⁻¹ (A), and Cu_{UPD} at sweep rate of 20 mVs⁻¹ (B) on Pd films deposited on Au_{poly} electrode with different number of SLRR cycles. Anodic stripping curves for as deposited Pd films at sweep rate of 3 mV.s⁻¹ (C), and thickness of the films in equivalent MLs as a function of SLRR cycles (D).

Au_{poly} respectively. As can be seen, based on the Cu_{UPD} analysis the roughness (preferential 3D growth) starts to develop only after 4 cycles before the 7th cycle and this is seconded by H_{UPD} though not very distinctive since H_{UPD} on Pd can absorb H and this impairs its efficiency as a measure of roughness development. The stripping graph (Fig 1C) and the relationship of number of monolayers to the number of SLRR cycles (Fig 1D) also support the observation resulting from the CV characterization. More specifically, the departure from linearity observed for the deposit's thickness after 7 SLRR cycles is attributed to sudden roughening that could be a result of initiation of dendritic growth. Favorable conditions for transitioning to such growth would be generated when the Pd concentration at the interface of working electrode held in the

hanging meniscus contact with the electrolyte is different than the one in the bulk of the solution. Then, the growth process will be affected by the diffusion limitation resulting from a hindered mass transport to the electrode surface with the increasing number of SLRR cycles. Normally, the dendritic growth nucleation takes place on top of existing 3D clusters, where the Pd concentration is high enough to promote locally a faster deposition (29, 30).

The potential transitioning from quasi 2D growth to a dendritic one impacts inevitably the potential transient associated with SLRR deposition in one cell configuration. Figure 3, (A) and (B), presents typical potential transients reflecting the

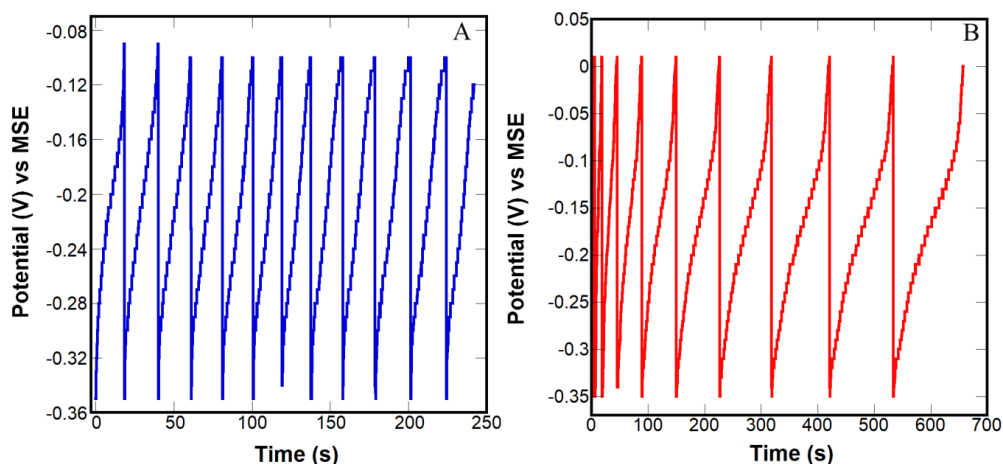


Figure 3. Potential transients following the SLRR deposition of Pd films in one-cell setup in a solution with Pd^{2+} ion concentration of 0.3 mM and $[\text{Cl}^-]/[\text{Pd}^{2+}]$ ratio of 100 (A), and 500 (B).

potential changes in the course of each SLRR cycle at different $\text{Cl}^-/\text{Pd}^{2+}$ concentration ratios. Apparently, the timing of one cycle is directly dependent on the concentration of Pd^{2+} ions and indirectly by the ratio between the $[\text{Pd}^{2+}]$ and $[\text{Cl}^-]$ ion as they both form a complex that makes the Pd less available to the growth process (compare Fig. 3 A and B). Also, if no mass transport issues are experienced by the growth process all cycles should have identical timing (Fig. 3A). Some difference could be expected only in the beginning when the Au surface is not completely covered by Pd (Fig. 3B). Overall, as also seen in Figure 3B, the potential transients during SLRR deposition in one cell could be used as early indicator of potential growth mode transitioning manifested by prolonging of single-cycle duration. These observations could be cross-compared later with those from the CV and stripping experiments and (as needed) ultimately validated by direct imaging, such as SEM and/or STM/AFM (not presented in this work).

Our optimization of the SLRR deposition routines in one cell continued with preserving the $[\text{Cl}^-]/[\text{Pd}^{2+}]$ ratio of 8 but increasing by a factor of 2 the absolute concentrations of said ions. Unfortunately, no significant difference was registered during the characterization tests (not presented). In a marginal improvement the transition to roughening occurred between the 6th and 10th cycle instead of 4th and 7th in the experiment presented in Figure 2. Overall, the CV curves and the departure from linearity in the stripping tests confirm the transitioning from layer-by-layer to 3D growth in that case as well. Apparently, substantially higher concentration of Pd^{2+} ions is needed to provide favorable conditions for longer quasi-2D growth.

[Cl⁻]/[Pd²⁺] Ratio Impact on the Growth

After obtaining similar results with higher concentrations, solutions with high [Cl⁻]/[Pd²⁺] of 100, 170 and 500 were used. Based on the work done by Stickney et al (4) in a flow cell system, the best [Cl⁻]/[Pd²⁺] ratio is 500. Experiments were therefore performed with this ratio. Figure 4 (A), (B) and the inset therein present results of characterization of the accordingly grown Pd thin films. The Cu_{UPD} CVs show virtually no roughness development at all. However, further analysis of the stripping results shows very low efficiency of the growth process as the maximum number of monolayers from 20 SLRR cycles was less than 3. This result can be

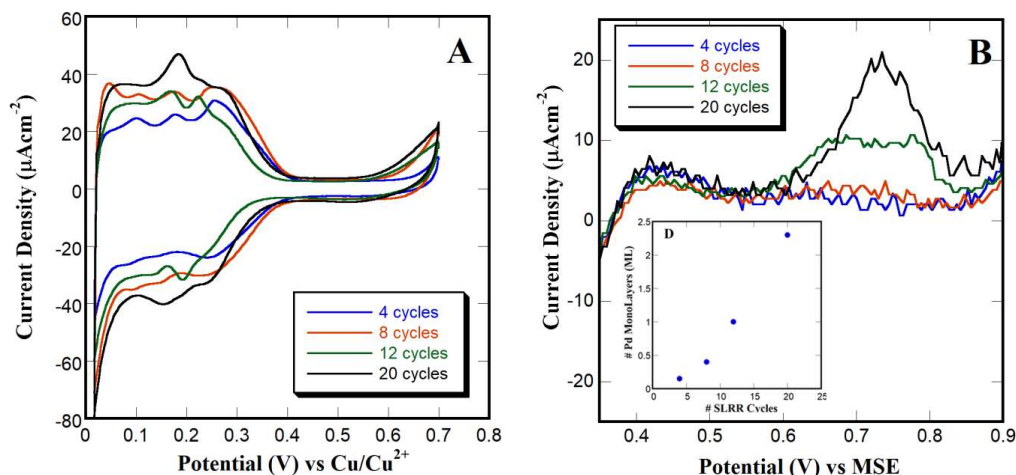


Figure 4. CV curves of Cu_{UPD} at sweep rate of 20 mVs⁻¹ on Pd films deposited on Au_{poly} electrode with different number of SLRR cycles (A). Anodic stripping curves at sweep rate of 3 mVs⁻¹ for as deposited Pd films (B), and dependence of the film thickness in equivalent MLs on the number of SLRR cycles (inset D).

understood in light of the reported in Stickney's paper increased complexation of Pd²⁺ at higher concentration of Cl⁻ ions. This in turn slows down the growth process, since the Pd²⁺ ions are less available to be exchanged with the Cu sacrificial atoms. In more detail, the formation constant, β₄ for PdCl₄²⁻ is 10^{11.53}. Therefore, the complex is very stable, and as a result the free Pd²⁺ ion concentration is very low (31). This in turn indirectly boosts the impact of otherwise suppressed side reactions like ORR, and effectively leads to very low overall deposition efficiency. A proof in favor of this explanation could be found in Figure 3B and its inset both showing the very low quantities of Pd stripped off eventually from the Au substrate.

A further optimization process of the [Cl⁻]/[Pd²⁺] ratio at fixed Pd²⁺ ion concentration yielded best results regarding the SLRR deposition outcome at ratios in the range of 100 to 170. Figure 5 (A) and (B) presents results from CV characterization of accordingly grown Pd thin films. The analysis shows that there was smooth growth up to the 12th cycle and a substantial roughness evolution after 20th cycle of SLRR growth. Figure 5(C) and the integrated stripping charges presented in 5(D) simply confirm the growth of the thin films being smooth up to the 12th cycle that accounts for about 16 MLs thick Pd deposit. This is evidenced by the perfectly linear trend of charge increase within that range of SLRR cycles. Alike with previous results (Figure 2), the persistent transition

towards 3D, dendritic growth takes place also in this deposition run occurring between the 12th and 20th cycles, i.e. after ~ 15 MLs.

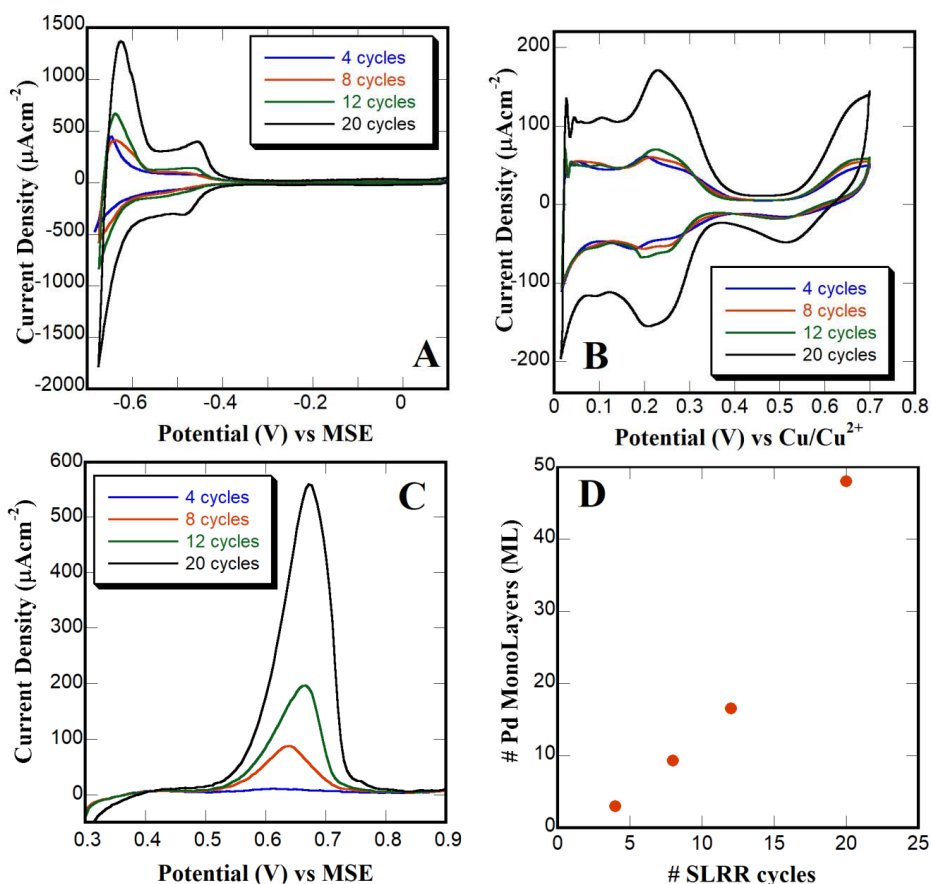


Figure 5. CV curves of H_{UPD} at sweep rate of 50 mVs⁻¹ (A), and Cu_{UPD} at sweep rate of 20 mVs⁻¹ (B) on Pd films deposited on Au_{poly} electrode with different number of SLRR cycles. Anodic stripping curves for as deposited Pd films at sweep rate of 3 mVs⁻¹ (C), and thickness of the films in equivalent MLs as a function of SLRR cycles (D).

SLRR Deposition with Disruption of the Growth Process:

A straightforward analysis of all of the so far reported results on the E-ALD by SLRR growth of Pd in one-cell configuration suggests that the transitioning of said systems to 3D, dendritic growth is practically inevitable, and it occurs sooner or later depending mainly on the concentration of the growing metal ion. At the same time no evidence for such transition could be found in the experiments of Stickney et al in the same system, but carried out in an automated flow-cell setup (4). This significant difference suggests lack of transport limitations in the E-ALD by SLRR administered in the latter environment. This inference is seconded by the significantly shorter time needed for a single SLRR cycle in flow cell compared to one-cell configuration under identical other growth conditions. Indeed, this is not surprising given the naturally existing identical starting conditions before each SLRR cycle in the flow-cell setup as oppose to the steadily decreasing growing metal concentration in the near electrode vicinity in one-cell configuration (23). To that end, we decided to optimize the deposition process in one-cell by disrupting the growth after several successive SLRR cycles along with introducing electrolyte convection during the break. Then, the growth was resumed again for a set of

successive cycles until the next interruption. Figure 6 presents summary of the characterization of one such optimized deposition experiment performed by SLRR in one-cell configuration. The growth in that case was administered in multiples of four successive SLRR cycles with a 30-second growth interruption accompanied with forced electrolyte convection. The CV characterization by both H_{UPD} and Cu_{UPD} reveals virtually no roughness increase even after 24 SLRR cycles of growth. It is noteworthy that this

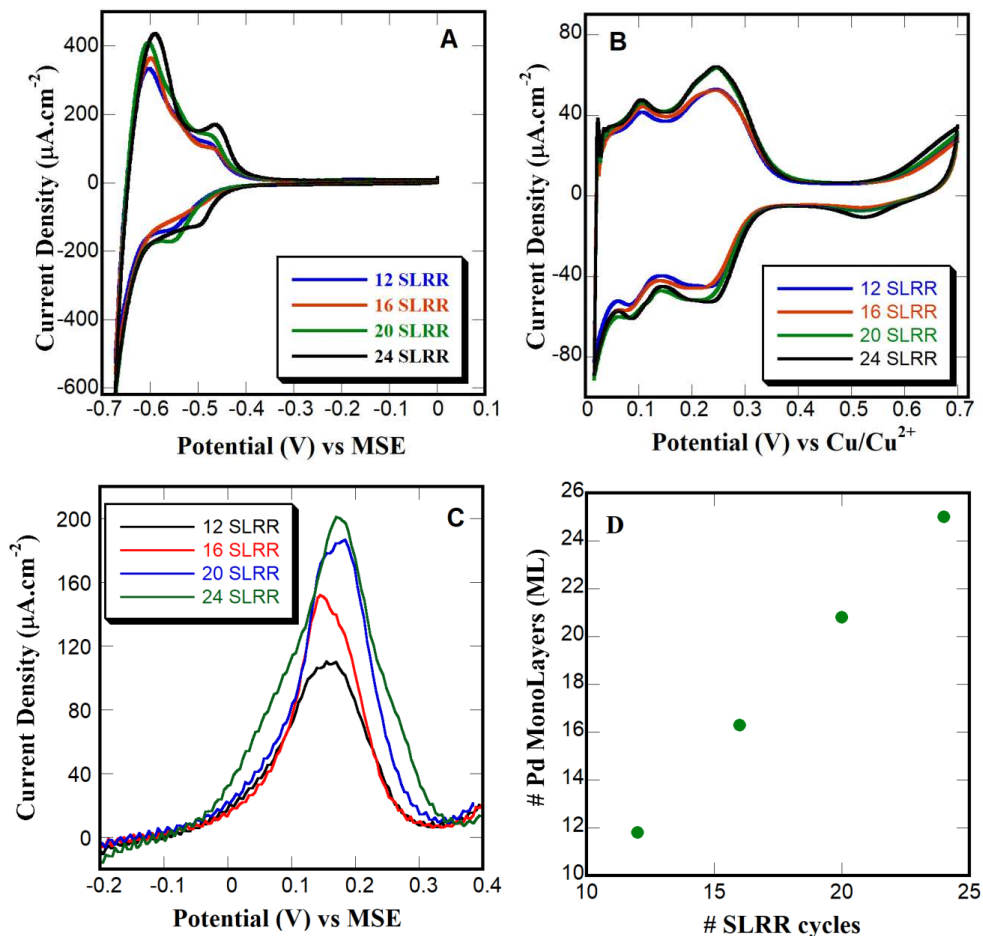


Figure 6. CV curves of H_{UPD} at sweep rate of 50 mVs^{-1} (A), and Cu_{UPD} at sweep rate of 20 mVs^{-1} (B) on Pd films deposited on Au_{poly} electrode with different number of disrupted SLRR cycles and forced convection. Anodic stripping curves for as deposited Pd films at sweep rate of 3 mVs^{-1} (C), and thickness of the films in equivalent MLs as a function of SLRR cycles (D).

constitutes about twice thicker continuous Pd film with a smooth morphology. While this result is comparable with results obtained in flow cell (4), no even a single experiment carried out in conventional one-cell configuration mode (without interruption and convection) came even close to this quality of growth in our previous optimization attempts. This result is seconded by the stripping experiments (Figure 6, C and D) suggesting almost perfectly linear increase of the grown layer thickness up to 26 MLs deposited by 24 SLRR cycles in one-cell configuration.

Conclusions

The work presented herein demonstrates the suitability of one-cell configuration setup for the growth of Pd thin films on polycrystalline Au electrodes using E-ALD by SLRR of Cu_{UPD} sacrificial layer. A critical comparison of this activity with the similar one where the Pd films were grown in an automated flow-cell setup suggests that a key limitation of the one-cell approach is an inevitable transitioning to dendritic growth owing to establishment of mass-transport controlled deposition at some point of the process duration. The uninterrupted SLRR growth in one-cell was optimized to yield smooth and continuous films of thickness up to 15 MLs at Pd²⁺ ion concentration of 0.3 mM and [Cl⁻]/[Pd²⁺] ratios of between 100 and 170. A major improvement was achieved by implementing a modified SLRR protocol for deposition in one-cell with interruption of the successive SLRR cycles and applying forced electrolyte convection. Thus, the growth of smooth and continuous films was extended to Pd deposits with a thickness of 26 MLs.

Acknowledgments

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Impacts of Ions on Oxygen Reduction Reaction Kinetics on Platinum and Palladium Surfaces

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Fundamental understandings on the impacts induced by anions and cations on oxygen reduction reaction (ORR) are of great interest in designing more efficient catalysts and identifying reasons for discrepancies in activities measured in different protocols. In this paper, the specific adsorption of various anions and cations on platinum and palladium catalysts and their effects on the ORR kinetics were summarized. It was found that ClO_4^- had a negligible impact on the ORR activity of Pt/C possibly due to its weak adsorption. Nafion ionomers can significantly poison the bulk Pt surfaces, but its impact on Pt/C is negligible. Self-dissociation of citrate anion was found to occur on both Pt/C and Pd/C.

Introduction

The reaction kinetics of oxygen reduction reaction (ORR) is rather sluggish even on noble metal-based catalysts (Pt, Pd, etc.) in low temperature fuel cells.(1) Besides the types of catalytic materials,(2–4) the electrolytes that are used in evaluating the ORR activity also significantly affect the performance of the evaluated material due to specific adsorption of ions. Fundamental understandings on the behaviors of those ions (SO_4^{2-} , Cl^- , ClO_4^- , Nafion ionomer, citrate, etc.) on different surfaces are of importance to the development of more active catalysts.(5) More studies are required to clarify the effects caused by ions on ORR activity. In this work, the ClO_4^- , citrate, and Nafion impacts on ORR activity of platinum and palladium were carefully studied.

Experimental

ClO_4^- Impact

Approximately 10 mg of Pt/C (46%, TEC10E50E, TKK) was ultrasonically dispersed in a mixing solvent consisting of 8 mL of water (Milli-Q® UV-plus), 2 mL of isopropanol (VWR Chemicals), and 40 μL of 5% Nafion (Aldrich) for 10 min. 10 μL of the suspension was deposited on a pre-cleaned glassy carbon RDE tip (5 mm in diameter, Pine Instruments) and allowed to dry in air. A leak-free Ag/AgCl electrode (with sat. KCl solution) calibrated by a reversible hydrogen electrode (RHE) was used as reference. A Pt wire was used as the counter electrode. A 0.1 M HClO_4 + 0.1 M NaClO_4 solution was prepared from ultrapure NaOH (VWR Chemicals) and HClO_4 (GFS Chemicals, Veritas double distilled, $\text{Cl}^- \leq 0.1$ ppm, $\text{SO}_4^{2-} \leq 1$ ppm) to control the impurity content below 50 ppb. For comparison, one more 0.1 M HClO_4 + 0.1 M NaClO_4 solution was prepared from NaClO_4 with a lower purity (Aldrich, ACS Reagent, 98%) and HClO_4 (GFS Chemicals, Veritas double distilled) to allow a slightly higher impurity level (maximum

400 ppb). The electrode was cycled between 0.02 and 1.2 V vs RHE for 10 cycles in an argon-saturated 0.1 M HClO₄ at 100 mV s⁻¹. Then a stable cyclic voltammetry (CV) curve was recorded at 50 mV s⁻¹. The polarization curves for ORR were recorded in oxygen-saturated solutions following the order of 0.1 M HClO₄, 0.1 M HClO₄ + 0.1 M NaClO₄, and 0.2 M HClO₄ using the same electrode at a scanning rate of 10 mV s⁻¹ at 1600 rpm. CV curves were recorded in Ar-saturated solutions following the same order.

Nafion Impact

The Nafion effect on ORR activity was evaluated on both a flat polycrystalline Pt RDE tip (5 mm in diameter, Pine Instrument) and 46% Pt/C deposited on a glassy carbon electrode. The Pt electrode was polished using the 50 nm Al₂O₃ powder, followed by potential cycling between 0.05 and 1.4 V in an Ar-saturated 0.1 M HClO₄ solution for 40 cycles at a scanning rate of 100 mV s⁻¹. Then a stabilized CV curve was recorded between 0.05 and 1.2 V at 50 mV s⁻¹. The polarization curves for ORR were recorded in an O₂-saturated 0.1 M HClO₄ solution. Then the polycrystalline Pt electrode was washed with ultrapure water for several times and 5 μ L of diluted Nafion solution (80 μ L of 5% Nafion in 4 mL of H₂O and 1 mL of isopropanol) was dropped on the electrode and dried in air. The estimated thickness of the Nafion layer was 113 nm according to the density of solid Nafion (1.5 g cm⁻³). The Nafion covered Pt electrode was cycled in an Ar-saturated 0.1 M HClO₄ solution until a stable CV curve was obtained. The ORR polarization curve was recorded in an O₂-saturated 0.1 M HClO₄ solution. The process was repeated to obtain a thicker layer of Nafion (~226 nm) by dropping the same volume of Nafion solution. Nafion effect was also evaluated in 0.1 M NaOH solutions following similar procedures.

A special protocol was developed in order to prepare a smooth Nafion-free thin Pt/C catalyst film on the glassy carbon electrode. Approximately 10 mg of Pt/C was ultrasonically dispersed in a mixing solvent consisting of 2 mL of water and 8 mL of isopropanol for 10 min. 10 μ L of the suspension was deposited on the pre-cleaned glassy carbon RDE tip and allowed to dry in a vacuum oven with a low pressure (0.2 bar) for 3 min. The CV and ORR polarization curves were recorded in 0.1 M HClO₄ solutions following the procedures described above. Then the electrode was carefully washed with water to remove residual electrolyte. 5 μ L of diluted Nafion solution was dropped on the electrode and allowed to dry in air. The estimated ionomer to carbon (I/C) ratio was 0.67. Then the ORR polarization curve was recorded after cycling the electrode in an Ar-saturated 0.1 M HClO₄ solution for 5 cycles. The electrode with a higher I/C ratio (1.33) was prepared by dropping another 5 μ L of diluted Nafion solution on the same electrode following the previous procedure.

Citrate Impact

The catalyst ink (Pt/C and Pd/C) was prepared according to the same recipe mentioned above. The electrode was cycled between 0.02 (0.07 V for Pd/C) and 1.2 V vs RHE for 10 cycles in an argon-saturated 0.1 M NaOH (VWR Chemicals) solution at 100 mV s⁻¹. Then a stable cyclic voltammetry (CV) curve was recorded at 50 mV s⁻¹. The polarization curves for ORR were recorded in oxygen-saturated solutions following the order of 0.1 M NaOH and 0.1 M NaOH + x mM (x = 0.1 to 100) sodium citrate using the same electrode at a scan rate of 10 mV s⁻¹ at 1600 rpm. CV curves were recorded in Ar-saturated solutions on another working electrode prepared following the same order.

Results and Discussion

ClO₄⁻ Impact

We firstly assessed the concentration effects of HClO₄ on the CV and ORR polarization curves. Figure 1a shows the CVs of the same sample (Pt/C coated RDE tip) in Ar-saturated 0.1 M (black solid line) and 0.2 M HClO₄ (blue dotted line) solutions. A higher concentration of ClO₄⁻ does not affect the shape of the CV of Pt/C implying that ClO₄⁻ might not be adsorbed on Pt surface in the potential window between 0.05 and 1.2 V. The overlapping of ORR polarization curves in Figure 1b also supports this argument. Similar experiment conducted in strong adsorbate-contained ((bi)sulfate anions) solutions shows different result (Figure 1c and d). Changes on both CV and ORR polarizations are clearly observed after increasing the concentration of electrolyte. Specifically, the H adsorption/desorption region between 0.05 and 0.35 V are narrowed in CV, along with a 10 mV negative shift on ORR half-wave potential. This result further supports the argument that ClO₄⁻ does not or only weakly adsorb on Pt surfaces. To exclude possible effect from pH change, similar experiments were conducted in 0.1 M HClO₄ + 0.1 M NaClO₄ solutions (red dashed line in Figure 1) with impurity level below 50 ppb. Clearly, the CV of Pt/C does not change in Figure 1a. While the limiting current is slightly lower due to a slower O₂ diffusion rate in 0.1 M HClO₄ + 0.1 M NaClO₄ than that in pure HClO₄ solutions. The poisoning of ClO₄⁻ anions on the kinetics of ORR was also negligible in the mixed kinetics and mass-transport controlled region between 0.8 and 1.0 V. It should be noted that an extremely low impurity level of electrolyte is critical to obtain reliable results. In a controlled experiment, the same measurement was conducted in a 0.1 M HClO₄ + 0.1 M NaClO₄ solution containing ~400 ppb SO₄²⁻ and ~300 ppb Cl⁻ at maximum prepared from NaClO₄ with a lower purity level. As shown in Figure 1e and f, besides the narrowed H adsorption/desorption region and attenuated OH formation on CV, a considerable 12 mV negative shift of the half-wave potential on ORR curves was observed compared to the one obtained in a 0.1 M HClO₄ solution. Despite strong evidences of specific adsorption of ClO₄⁻ on Pt surfaces(6–8), our result demonstrates that its impact on the ORR activity of Pt/C catalyst is negligible. It is possible that the interaction of ClO₄⁻ with Pt surfaces is too weak to compete with the adsorption of O₂ and other oxygen containing species, and consequently has a negligible impact on ORR kinetics.

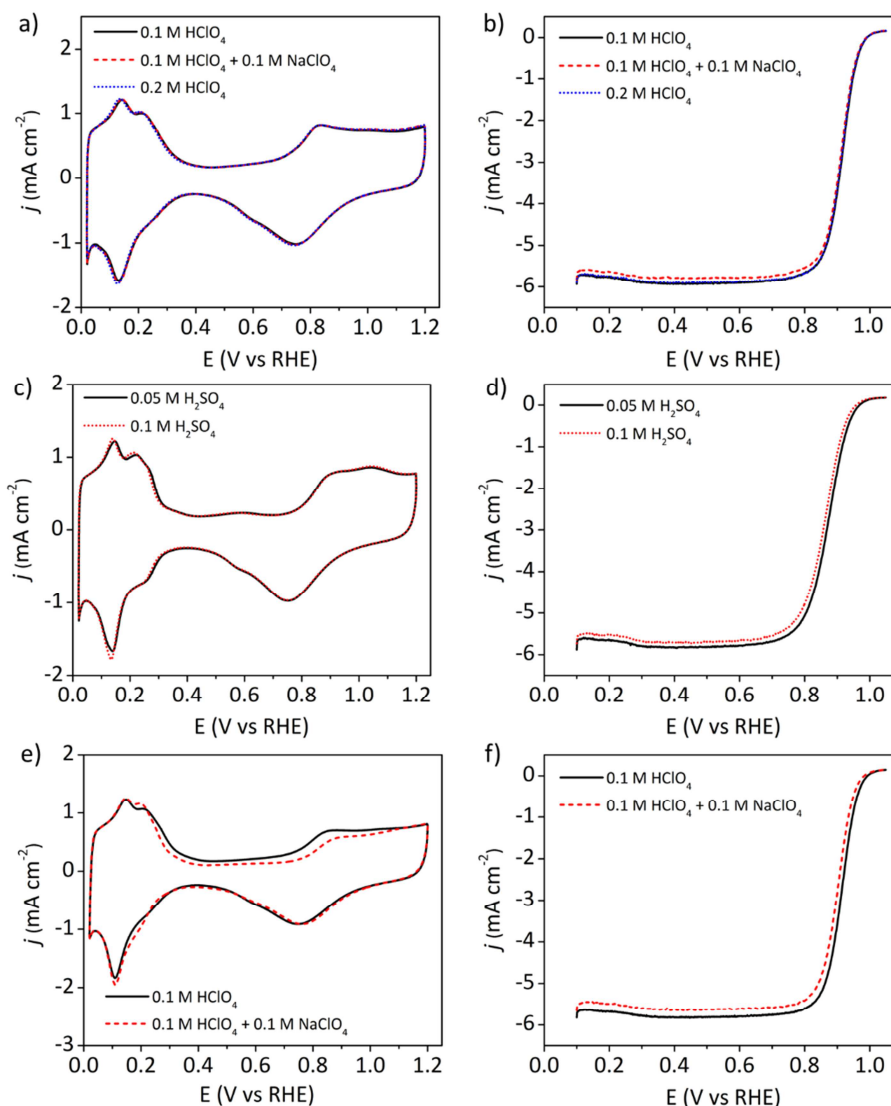


Figure 1. Comparisons of cyclic voltammograms for Pt/C supported on a glassy carbon electrode in a) Ar-saturated 0.1 M HClO₄ (black solid line), 0.1 M HClO₄ + 0.1 M NaClO₄ (red dashed line) and 0.2 M HClO₄ (blue dotted line) solutions at a scan rate of 50 mV s⁻¹, and b) O₂-saturated 0.1 M HClO₄ (black solid line), 0.1 M HClO₄ + 0.1 M NaClO₄ (red dashed line) and 0.2 M HClO₄ (blue dotted line) solutions at a scan rate of 10 mV s⁻¹ with a rotating speed of 1600 rpm, c) Ar-saturated and d) O₂-saturated 0.1 M H₂SO₄ (black solid line) and 0.2 M H₂SO₄ (red dashed line) solutions, e) Ar-saturated and f) O₂-saturated 0.1 M HClO₄ (black solid line) solution and 0.1 M HClO₄ + 0.1 M NaClO₄ (red dashed line) solutions with a higher impurity level.(9)

Nafion Impact

The possible impact of Nafion ionomer on the ORR activity of Pt/C has been studied by several groups(10–12). In the current study, the impact of Nafion on ORR activity was firstly evaluated on a polycrystalline Pt electrode. The CVs of a flat Pt electrode without (black solid line) and with a Nafion layer (red dashed line) are compared in Figure 2a. The CV curve of a Nafion capped Pt electrode shows distinct features as compared to the bare Pt surface.

The impacts of Nafion capping on ORR activity are significant as shown in Figure 2b. A considerable 24 mV negative shift of ORR half-wave potential and the reduction of limit current density by $\sim 0.35 \text{ mA cm}^{-2}$ are observed with one layer of Nafion on the Pt electrode. Doubling the amount of Nafion does not lead to a further shift of the half-wave potential, although a smaller limiting current density is observed due to the larger resistance on O_2 diffusion in a thicker Nafion layer. The specific activity is significantly reduced by $\sim 55\%$ with one Nafion layer, which echoes previous findings on severe poisoning effect of Nafion ionomer on Pt surfaces.(13) A thicker Nafion layer does not cause further reduction of activity possibly due to the full coverage of the first Nafion layer, which is in consistency with the CVs in Figure 2a.

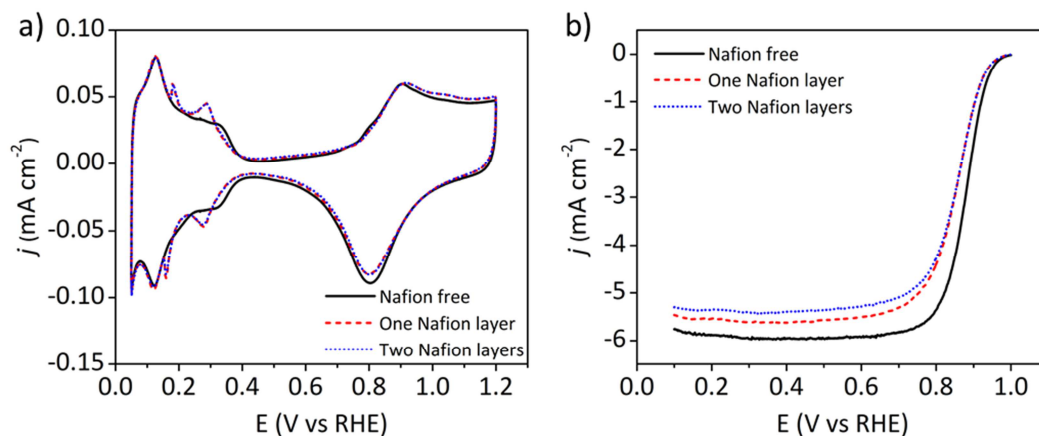


Figure 2. Comparisons of cyclic voltammograms for a polycrystalline Pt electrode with various amount of Nafion: Nafion free (black solid line), one Nafion layer (red dashed line) and two Nafion layer (blue dotted line) capped on the surface in a) an Ar-saturated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹, and b) an O₂-saturated 0.1 M HClO₄ solution at a scan rate of 10 mV s⁻¹, rotation speed = 1600 rpm.(9)

In order to evaluate the effect of Nafion ionomers on ORR kinetics in fuel cell electrodes, we conducted the thin-film RDE study using Pt/C. A certain amount of diluted Nafion solution was added on the dried catalyst film to make the I/C ratio reach 0.67 and 1.33. As shown in Figure 3a, the CV curves are nearly identical for the Pt/C samples with and without Nafion, which is totally different from that of polycrystalline Pt electrode (Figure 2a). As expected, the limiting current density in the mass transport control region slightly decreased upon adding Nafion due to larger resistance for O_2 transport (Figure 3b). However, the ORR polarization curves in the kinetic and mass transport mixed controlled region (0.8 - 1.0 V) showed no noticeable difference even with an I/C as high as 1.33. These results suggest that Nafion as a binder in typical ORR measurements does not affect the activity noticeably. Based on our CV and ORR curves of Pt/C in Figure 3, we may conclude that the coverage of Nafion ionomers on surfaces of Pt nanoparticles is low. One of possible reasons is due to the high specific area of carbon black ($\sim 800 \text{ m}^2 \text{ g}^{-1}$) as compared to Pt nanoparticles ($\sim 80 \text{ m}^2 \text{ g}^{-1}$).

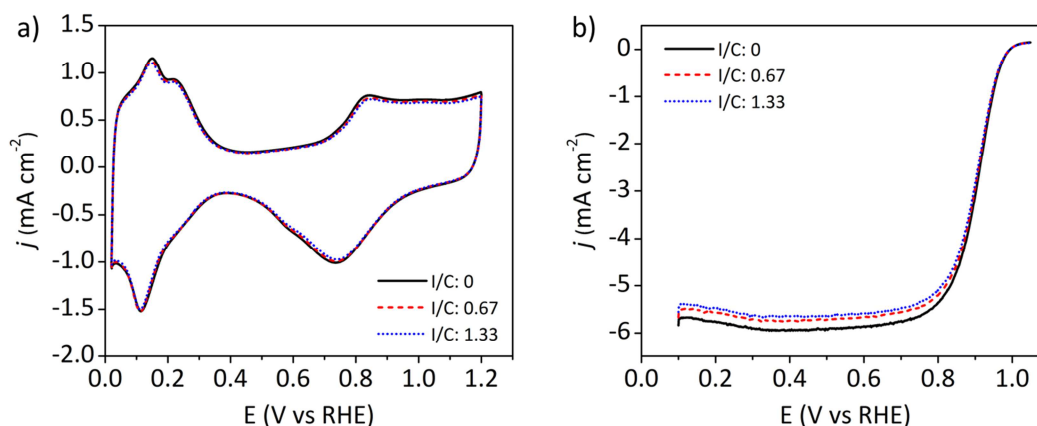


Figure 3. Comparisons of cyclic voltammograms for Pt/C with various I/C ratio: 0 (black solid line), 0.67 (red dashed line) and 1.33 (blue dotted line) supported on a glassy carbon electrode in a) an Ar-saturated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹, and b) an O₂-saturated 0.1 M HClO₄ solution at a scan rate of 10 mV s⁻¹, rotation speed = 1600 rpm.(9)

Citrate Impact

The effect of citrate on Pt/C was assessed. The addition of 0.1 M sodium citrate was found to significantly change both the CVs and ORR polarization curves. As illustrated in Figure 4a, immediately after transferring the pre-cleaned working electrode into the sodium citrate-contained NaOH solution, the potential was scanned from the double layer region (0.4 V) negatively to 0.02 V and then to 1.2 V. There was a small current wave between 0.5 and 0.7 V in comparison with the CV in 0.1 M NaOH (black dashed line). In order to uncover the origin of this faradaic current, CVs were recorded after holding at 0.4 V for 300 s (red line) and 600 s (blue line). Both curves showed a strong current peak centered at ~0.68 V that may be associated with oxidation of species adsorbed on the surface of Pt/C. As shown in Figure 4b, keeping the potential at the H adsorption/desorption (0.23 V) and double layer (0.4 V) region for 300 s led to similar CVs with an oxidation peak at 0.68 V. The suppression on H desorption peaks was much smaller if a higher potential (0.68 V) was applied, along with a small current wave rather than a strong faradaic peak at 0.68 V (Figure 4b, blue line). This phenomenon can be explained by the fact that the adsorbed species cannot be accumulated at 0.68 V as they are oxidized at this potential. Based on the above results, we hypothesize that a dissociation-adsorption mechanism of citrate occurs on Pt surfaces in the alkaline medium.

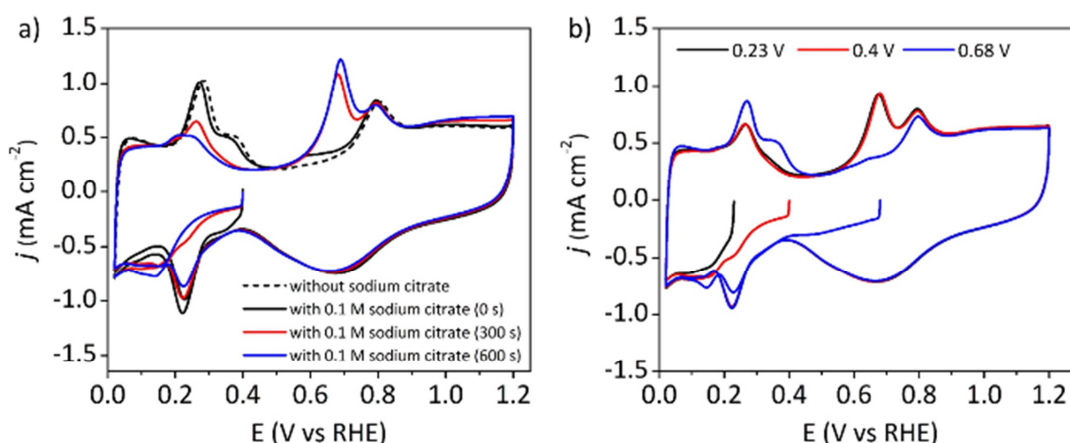


Figure 4. Comparisons of cyclic voltammograms for Pt/C supported on a glassy carbon electrode in a) Ar-saturated 0.1 M NaOH (black dashed line) and 0.1 M NaOH + 0.1 M sodium citrate solutions with initial potential kept at 0.4 V for 0 s (black line), 300 s (red line), and 600 s (blue line), b) an Ar-saturated 0.1 M NaOH + 0.1 M sodium citrate solution with initially keeping the potential at 0.23 V (black line), 0.4 V (red line), and 0.68 V (blue line) for 300 s, scan rate = 50 mV s^{-1} .(14)

The impact of citrate on ORR activity of Pt/C was evaluated in NaOH solutions. As shown in Figure 5, the presence of 0.033 M sodium citrate (to keep the same Na^+ concentration of 0.1 M as in other studies) in the NaOH solution led to a very small negative shift of 4 mV on the $E_{\text{half-wave}}$. This result indicates that the species adsorbed on the Pt/C do not affect the ORR activity. It is reasonable since they are oxidized at potentials lower than the mixed controlled region and will not affect the kinetics of ORR. By tripling the concentration of sodium citrate, the $E_{\text{half-wave}}$ shifted negatively by 20 mV along with a significant drop of the limiting current. This large activity drop could be caused by the much severer poison effect of Na^+ due to its quadrupled concentration.

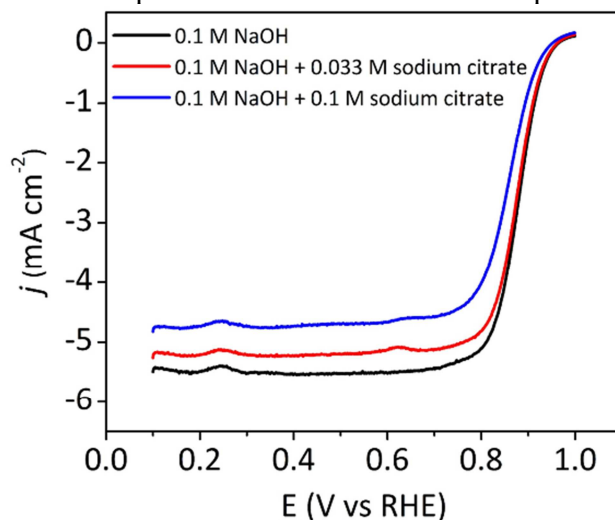


Figure 5. Comparisons of cyclic voltammograms for Pt/C supported on a glassy carbon electrode in O_2 -saturated 0.1 M NaOH solution (black line), 0.1 M NaOH + 0.033 M sodium citrate (red line), and 0.1 M NaOH + 0.1 M sodium citrate (blue line) solutions at a scan rate of 10 mV s^{-1} , rotation speed = 1600 rpm.(14)

The effect of citrate was also assessed on Pd/C. As shown in Figure 6, the addition of

0.1 M sodium citrate was found to significantly change both the CVs and ORR polarization curves. As shown in Figure 6a, the potential was scanned from the double layer region (0.39 V) negatively to 0.07 V and then to 1.2 V immediately after transferring the pre-cleaned working electrode into the sodium citrate-contained NaOH solution. The slight suppression on OH adsorption on Pd surfaces was observed between 0.4 and 0.7 V as compared with the CV in 0.1 M NaOH (black dashed line). In order to reveal the reasons for this phenomenon, CVs were recorded after holding the potential at 0.39 V for 300 s (red line) and 600 s (blue line). Both curves showed a strong current peak centered near 0.8 V that may be associated with oxidation of species adsorbed on the surface of Pd/C. As illustrated in Figure 6b, a weaker oxidation peak located at ~ 0.7 V was observed if the potential was initially kept at 0.2 V for 300 s, along with a slighter suppression on H adsorption/desorption and OH adsorption in comparison with the those obtained after keeping initial potential at 0.39 V, indicating the decomposition of citrate was preferred in the double layer region.

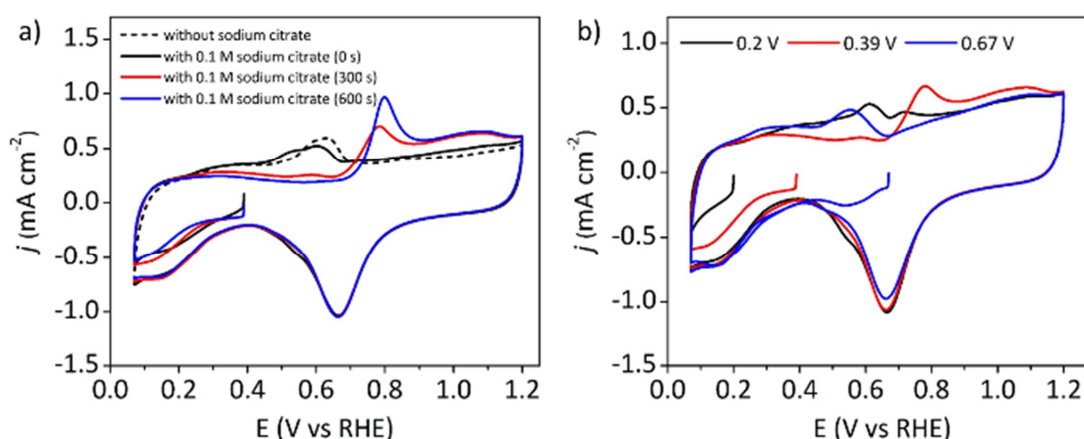


Figure 6. Comparisons of cyclic voltammograms for Pd/C supported on a glassy carbon electrode in a) Ar-saturated 0.1 M NaOH (black dashed line) and 0.1 M NaOH + 0.1 M sodium citrate solutions with initial potential kept at 0.39 V for 0 s (black line), 300 s (red line), and 600 s (blue line), b) an Ar-saturated 0.1 M NaOH + 0.1 M sodium citrate solution with initially keeping the potential at 0.2 V (black line), 0.39 V (red line), and 0.67 V (blue line) for 300 s, scan rate = 50 mV s^{-1} .(14)

ORR polarization curves of Pd/C were recorded in NaOH solutions with and without sodium citrate. As observed in Figure 7, the addition of 0.033 M sodium citrate in the NaOH solution would lead to a noticeable negative shift on $E_{\text{half-wave}}$ (14 mV, from 0.910 to 0.896 V), which was distinct to the negligible impact of citrate with the same concentration on Pt/C surfaces. It is worth noting that the oxidation of adsorbed species would not complete until ~ 0.915 V (Figure 7a), which was partially overlapped with the ORR mixed controlled region (higher than 0.86 V). Thus, it is reasonable to claim that the un-oxidized adsorbed species from citrate dissociation and their occupation on active sites were the reasons for the reduced ORR activity observed in RDE measurements.

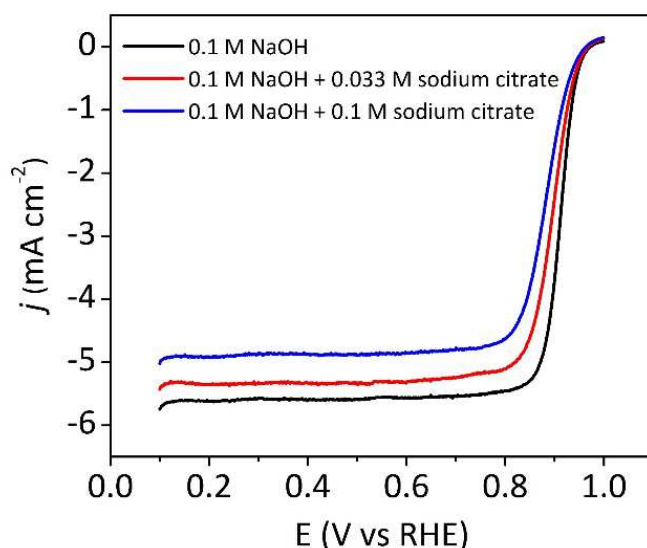


Figure 7. Comparisons of cyclic voltammograms for Pd/C supported on a glassy carbon electrode in O₂-saturated 0.1 M NaOH solution (black line), 0.1 M NaOH + 0.033 M sodium citrate (red line), and 0.1 M NaOH + 0.1 M sodium citrate (blue line) solutions at a scan rate of 10 mV s⁻¹, rotation speed = 1600 rpm.(14)

Conclusion

In this study, the specific adsorption of ClO₄⁻, Nafion ionomer, cations and citrate on Pt/C and Pd/C, and their effects on the ORR kinetics were studied. The main findings are summarized below. The specific adsorption of ClO₄⁻ was revisited on Pt/C, and the results showed that its adsorption strength might be too weak to have a discernable impact on ORR. In terms of Nafion, a severe loss on ORR activity of a bulk Pt disk electrode in an acidic electrolyte was observed when it was covered with a Nafion thin film. This was mainly due to the significant poisoning effect from the sulfonate group adsorbed on Pt surfaces. On the other hand, a careful study revealed a negligible effect of Nafion ionomer on ORR kinetics of Pt/C with an I/C ratio below 1.33. This result demonstrated that adding Nafion ionomer in catalyst ink in RDE experiment would not change the activity of Pt/C. In addition, it implied that the Nafion ionomer in the electrode of MEA will not negatively impact the ORR kinetics of Pt/C, but on oxygen transport in wet conditions.

Self-dissociation of citrate anion can occur on both Pt and Pd surfaces at the H adsorption/desorption and double-layer regions. The adsorbed species have a negligible effect on ORR activity on Pt/C as they are removed by oxidation before 0.75 V. In contrast, their oxidation on Pd/C surfaces is not complete until 0.91 V, which causes a lower ORR activity. The findings in this paper emphasized the importance of specific adsorption of ions and double-layer interfacial effects on the ORR activity.

Acknowledgment

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The Impact of Adsorbates on Metal Deposition Through The Curvature Enhanced Accelerator Coverage Mechanism... And Beyond

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Superconformal electrodeposition utilizing additives that adsorb on the deposit surface and either enhance or suppress metal deposition enabled the implementation of Cu damascene interconnects in microelectronics. The filling process is a consequence of the Curvature Enhanced Accelerator Coverage (CEAC) mechanism, which captures the interplay between adsorbate coverage and the metal deposition rate during area change that necessarily accompanies growth on nonplanar surfaces. CEAC-based models have successfully predicted superconformal deposition using a variety of different chemistries that yield void-free filling of fine features, as well as optically smooth, surfaces of metals such as Cu, Ag and Au. Herein a brief review of advances in the superconformal Au deposition will be detailed. Of particular interest are additives whose behavior is non-monotonic with adsorbate coverage that present new challenges for understanding as well as interesting opportunities for application.

Superconformal Feature Filling

Superconformal film growth by additive-based electrodeposition underlies the successful implementation of Cu in state-of-the-art multilevel interconnect metallization for the silicon based semiconductor industry (1,2). Subsequent exploration of superfilling in other systems have focused on coinage metals and an example of superconformal Au deposition yielding void-free filling in sub-micrometer trenches is shown in Figure 1. A key development was identification of depolarizing behavior of sub-monolayer quantities of heavy p-block metals on Au deposition from cyanide solutions reported by McIntyre and Peck (3). This finding stimulated numerous more detailed investigations into the phenomena of underpotential deposition including those by Professor Adzic, his colleagues and others (4,5,6). More recently the impact of heavy metal up processes on superconformal Au deposition from both cyanide and friendlier, sulfite electrolytes have been pursued. For certain heavy metals enhanced deposition toward the bottom of the feature, also known as “superfill”, results from the interplay of deposition accelerating adsorbates and area change on non-planar surfaces.

The Au deposits in Figure 1 reflect an initial period of conformal deposition followed by enhanced deposition at the bottom corners of the trench and then accelerating deposition from the trench bottom. Superconformal feature filling manifesting these characteristic signs has been demonstrated with the coinage metals Cu (1, 2), Ag (7, 8) and Au (9, 10). All utilize dilute additives in the electrolyte that are known to accelerate metal electrodeposition through adsorption on the surface of the growing deposit (2, 7-10) where

these “accelerators” all exhibit a surfactant nature, remaining on the surface through metal deposition.

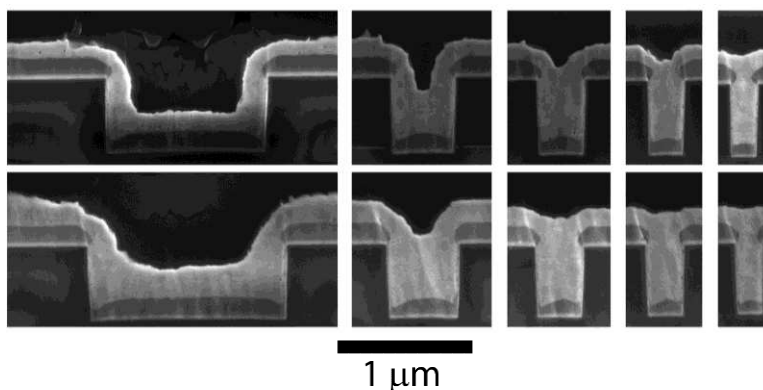


Figure 1. Filling of trenches down to $\approx 0.2 \mu\text{m}$ width at -1.2 V from a $\text{Na}_3\text{Au}(\text{SO}_3)_2$ - Na_2SO_3 electrolyte containing $5 \mu\text{mol/L}$ $\text{Pb}(\text{ClO}_4)_2$ accelerating additive. Deposition times are 3 min (Top) and 5 min (Bottom). Additional details can be found in Ref. 9.

Curvature Enhanced Accelerator Coverage

The physical basis for the observed filling evolution is captured in the Curvature Enhanced Accelerator Coverage (CEAC) mechanism. Models based on the CEAC mechanism quantify both the impact of the adsorbates on the metal deposition rate and the rate at which the local adsorbate coverage changes due to metal deposition. Most important in the latter expression is the evolution of adsorbate coverage imposed by mass conservation where the area of the deposit/electrolyte interface is changing during growth; this is captured by a term proportional to the local curvature of the interface multiplied by the metal deposition rate (i.e., current density), with additional terms representing adsorption from the electrolyte as well as consumption for non-ideal surfactant adsorbates. The parameters used in CEAC models of feature filling come from fitting electroanalytical measurements on planar rotating disk electrodes (RDE), particularly rising current transients in chronoamperometry and hysteresis in cyclic voltammetry, both due to positive feedback on the metal deposition rate with accelerator adsorption. The examples in Figure 2 capture the impact of adsorbing Pb accelerator on Au deposition from a sulfite based electrolyte.

Most CEAC models assume a simple linear dependence of the metal deposition rate on accelerator coverage. Simulations produced by such models, using only the kinetics derived from the RDE studies, generally capture the evolution of filling as shown for superconformal Au filling of trenches in Figure 3.

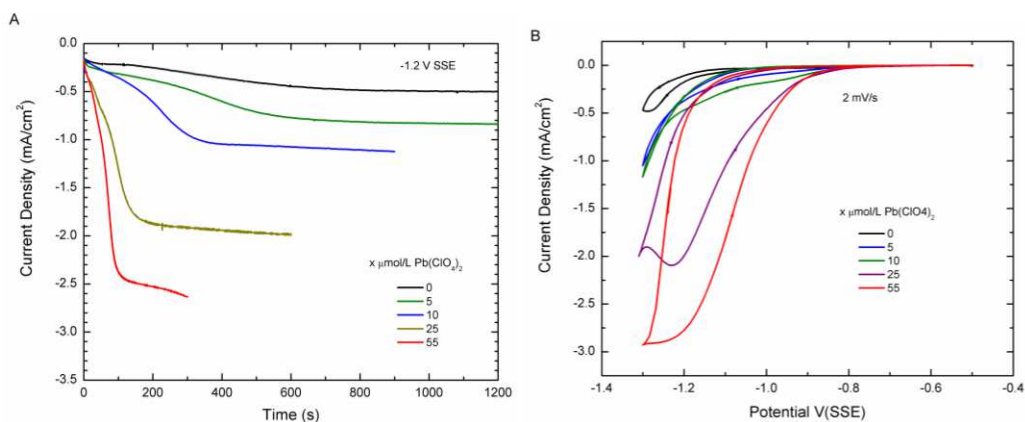


Figure 2. A) Chronoamperometric measurements showing the acceleration of Au deposition, with both faster rise and larger impact observed for increasing concentration of Pb accelerator. B) Cyclic voltammograms of gold deposition during potential cycling from -0.5 V to -1.3 V and back. The positive feedback hysteresis and maximum current density increase in magnitude with the Pb concentration. Potentials are relative to a mercury/mercurous sulfate/saturated potassium sulfate reference, SSE. (From Ref. 9).

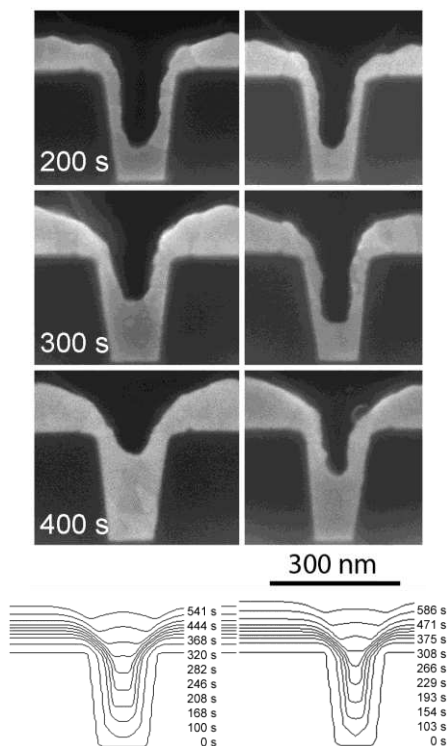


Figure 3. (Top) Superconformal Au deposition in trenches from a cyanide electrolyte after derivatizing the substrate surface in electrolyte containing 10 μmol/L Pb(NO₃)₂ accelerator for 60 s then depositing Au for the indicated deposition times in Pb-free electrolyte. All depositions were at -0.95 V relative to a mercury/mercury(I) chloride/saturated potassium chloride reference, SCE. (Bottom) Simulations of Au deposition in the trenches from a CEAC model assuming pre-adsorbed Pb coverage that is 0.15 of saturation value. Additional details can be found in Reference 10.

Non-Linear Behavior

It is known that not only the structure but also the impact of the adsorbates on the metal deposition reaction can change as a function of coverage. Thallium, in particular, is reported to accelerate Au deposition at low coverage but suppress it at higher coverage (11-15). A schematic of the velocity versus coverage dependence and the anticipated deposition morphology is shown in Figure 4 along with electrochemical measurements that capture the highly nonlinear response in both voltammetry and chronoamperometry of a Ti_2SO_4 containing electrolyte.

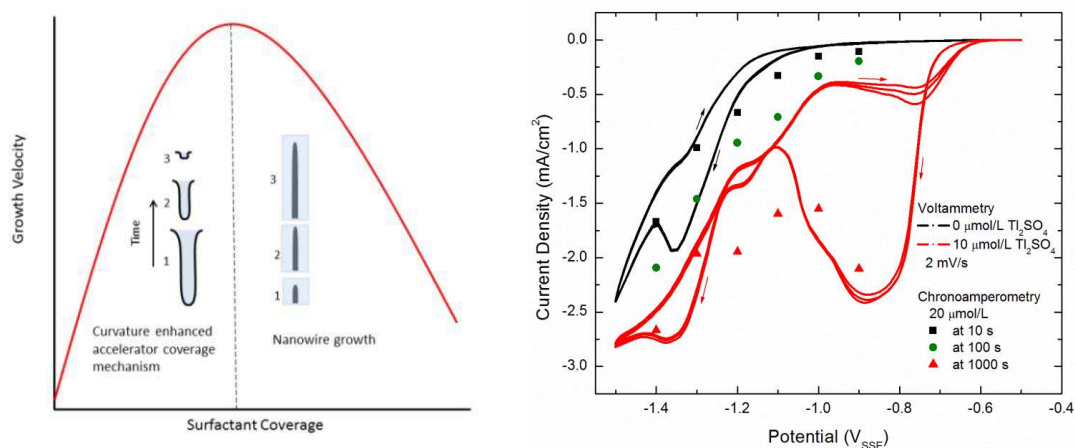


Figure 4. (Left) A schematic of the non-monotonic influence of Tl surfactant on the Au electrodeposition rate with associated deposition morphologies (from Reference 16). At low coverages smoothing by the CEAC mechanism enriches accelerating surfactant on concave surfaces, enhancing deposition at the bottoms of recessed surface features. At high coverages where the surfactant behaves as an inhibitor, area expansion on convex surface segments leads to dilution of the suppressing adsorbate and enhanced growth at the tips of asperities. (Right) Cyclic voltammetry in a sulfite electrolyte containing dilute Tl additive exhibits nonmonotonic behavior including negative differential resistance, also evident in chronoamperometry, resulting from the changing nature of Tl with surface coverage. (from Reference 16).

Figure 5 shows the wide range of behaviors that can be observed when the adsorbate exhibits the nonlinear behavior manifest in Figure 4. At the less negative potentials where lower saturation coverage is associated with accelerated deposition (-0.9 V), surface smoothing through the CEAC mechanism is observed. At the more negative potentials where higher saturation coverage is associated with negative differential resistance in the voltammetry (-1.0 V), growth of single crystal nanowires is observed.

The varied surfactant behaviors also give rise to different deposition morphologies within recessed features. These include the CEAC superfill and nanowire growth geometries already noted. Other growth morphologies are shown in Figure 6 for Au deposition in trenches. These include highly subconformal filling that manifests the enhanced metal ion depletion from the accelerated growth; the feature filling is analogous

to that obtained from additive-free electrolytes at high overpotentials but with extremely smooth surfaces rather than the dendritic instabilities inherent in large concentration gradients (17,18). A potentially more useful morphology is extreme bottom-up filling of dense, crystalline material that is entirely localized within the feature. It contrasts favorably with a bottom-up filling process using a polymeric suppressing additive where the Au deposits contain substantial nanoscale porosity (19).

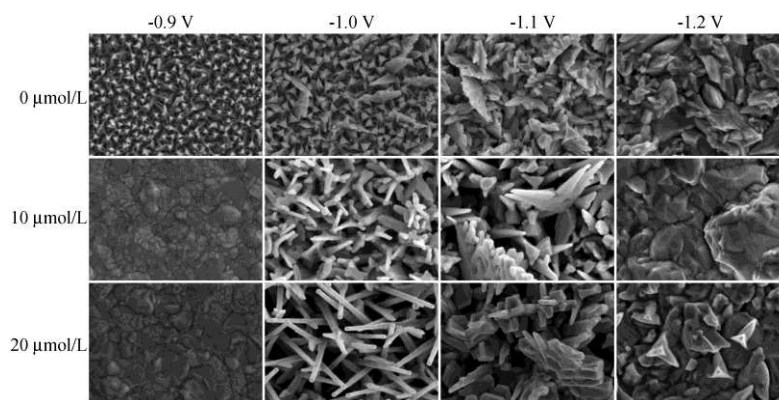


Figure 5. Au deposits from a sulfite electrolyte containing the indicated Tl_2SO_4 concentrations after 20 min deposition at the indicated potentials. All images are approximately 1 μm wide. Potentials are SSE. For more details see Reference 16.

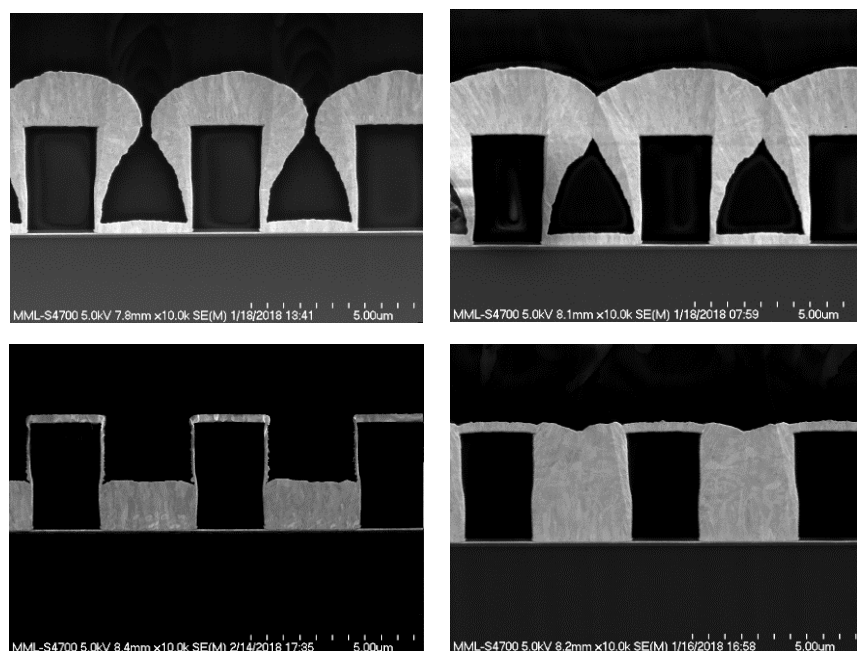


Figure 6. Gold deposition in trenches from a non-cyanide electrolyte: (Top) Smooth highly subconformal deposition and (Bottom) extreme bottom-up filling.

Conclusion

The role of surfactants and their impact on metal deposition remain a central topic in the practice and development of electrodeposition processes. A variety of behaviors has been observed, with new chemistries and applications continuing to be described and past discoveries still being translated into new understanding and critical technologies. Newer results promise to continue this trend.

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From Salt to Germanene: A Cookbook for Electrochemical Formation of 2D Materials (Inspired by R. Adžić)

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2D materials with honeycomb lattices are increasingly studied due to their unique electronic and mechanical properties. The typical preparation techniques, such as chemical vapor deposition and cleavage of bulk crystals, are either complicated or limited to only certain classes of materials. Here we discuss basic ordering principles in 2D monoatomic layers and show that electrochemical deposition can also result in 2D films with desired honeycomb structures. The principles are first studied on model ionic 2D layers prepared in ultrahigh vacuum. Two ordering possibilities are identified: a bilayer structure for covalently bonded films and a mixed monolayer structure for ionically bonded films. Typically, the most energetically favorable configuration in mixed layers is when ions with one polarity are closely surrounded by ions of the opposite polarity. This translates into a layer with honeycomb structure on substrates with p6/p3 symmetry. This phenomenon can be used to prepare germanene, a layer with such a structure.

Introduction

The re-discovery of graphene, until now the most studied 2D material, opened a large playground for scientists to study exotic properties of confined electrons (1). A few monolayers thick 2D sheets of insulating or semiconducting materials with various atomic compositions rapidly became a hot topic (2). Such sheets were shown to behave differently compared to their 3D counterparts, in large part due to the different electronic structure arising from the 2D nature of the material. They bear great promise for applications in electronics and optoelectronics, sensors, composite materials, photovoltaics, medicine, quantum dots, energy storage and cryptography. The most renowned 2D material is certainly graphene, but its analogs silicene, germanene, stanene and phosphorene have also drawn increased attention due to their potentially simpler incorporation in current semiconductor electronics (3).

There are several means of preparation for 2D materials: exfoliation or cleavage, chemical vapor deposition (CVD) and, as recently shown, also by underpotential deposition (UPD) (3-5). Because standard UPD of transition metals also effectively results in formation of 2D layers, it might therefore be possible to explain the recently observed electrochemical formation of germanene by principles discovered by R. Adžić

and coworkers regarding UPD growth (6). They suggested that depending on the nature of the bond within the binary 2D layer (ionic vs. covalent) one can perhaps predict the general 2D structure of the layer.

As an example, hexagonal structures with various stoichiometries were found when halides were coadsorbed with Tl on an Au(111) electrode in an aqueous environment (6-8). The layers were either mixed monolayers or bilayers, depending on the size of the halogen atoms. The observed mixed monolayer or "coplanar" layers (Fig. 1 left) were rationalized in terms of 2D ionic crystals with moderate substrate influence, where both halogen and Tl atoms were partially charged.

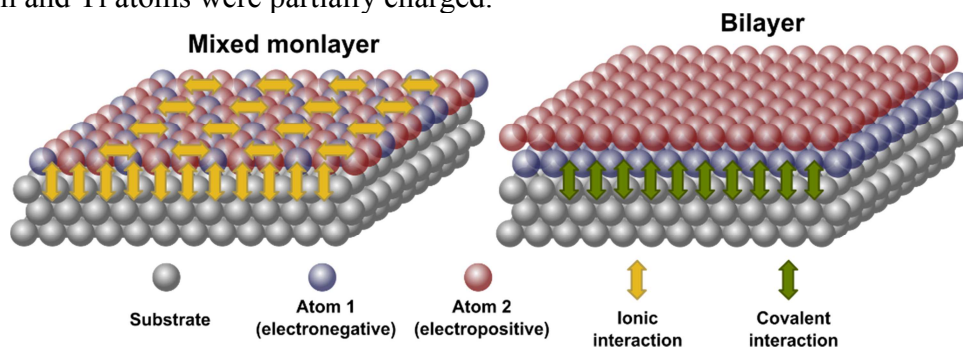


Figure 1. The mixed monolayer and bilayer structures found for bimetallic layers deposited on (111) surfaces. The observations were rationalized by the nature of the bonding within the system: ionic bonding results in a mixed monolayer while covalent bonding results in a bilayer.

The authors proposed that 1:1, 1:2 and 1:3 stoichiometries are the most favorable for 2D binary ionic layers because they maximize the interactions between adjacent oppositely-charged ions. The coplanar structure was also found by Labayen and Harrington when Tl and I were electrodeposited on a Pt(111) surface (9). The experimental findings of Cs and I coadsorption on an Au(110) surface performed by Wang et al. showed similar behavior: Cs and I ions formed a coplanar structure with a quasi-square symmetry (10). In the studies of AgI layers electrodeposited on Pt(111), Labayen and Harrington rationalized the structure of the adlayer in terms of covalent bonding within the layer (11-12). They suggested that the covalent characteristic of an Ag-I bond is responsible for an AgI bulk-like bilayer surface structure. The studies mentioned above suggest that the structure of binary layers has either a bilayer or planar character depending on the bonding type. For surfaces where the bond between the adsorbates is covalent, the predicted structure is a bilayer. For layers where bonds between adsorbates are predominantly ionic, the predicted structure is a mixed monolayer.

Results and discussion

To further test the proposed hypothesis, we prepared binary layers from highly electropositive cesium and electronegative iodine or oxygen deposited on Pt(111) (13,14). According to the previous observations, the resulting ionically bonded layers are expected to have a mixed monolayer structure. These layers were prepared in UHV conditions (10^{-10} mbar base pressure) in order to minimize the influence of the surrounding electrolyte and to better control the preparation process. The use of alkali metal and halogen is necessary to assure that the resulting layer will be as ionic as

possible because the previous work typically used binary systems consisting of transition metal and halogens, where the ionicity of the bonding is less guaranteed due to the smaller difference in electronegativity.

The first step in the preparation process is the deposition of Cs on Pt(111) from a getter material (SAES getters). The typical work function (WF) response, together with the Low Energy Electron Diffraction (LEED) patterns and real space structures, is shown in Fig. 2 (15).

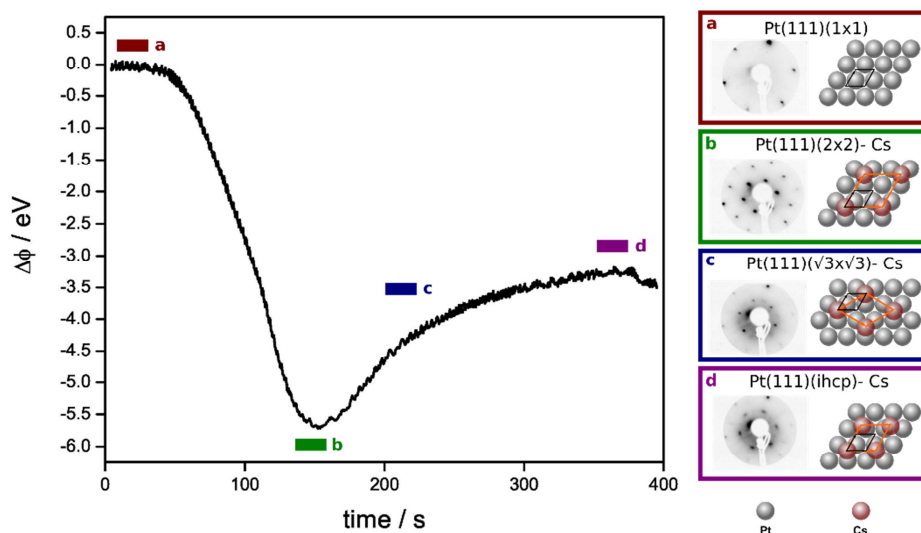


Figure 2. The work function (WF) response upon Cs adsorption on Pt(111) in UHV conditions. The WF first drops significantly to the minimum corresponding to the (2×2) LEED pattern. Upon further dosing the WF increases and the LEED pattern changes to (√3×√3)-R30°. The maximum Cs coverage corresponds to an incommensurate hexagonal close packed (ihcp) structure. The real space structures are shown on the right side together with the LEED patterns.

First, the WF drops significantly by -5.5 eV when compared to the bare Pt surface. At the minimum of the WF we observe Pt(111)(2×2)-Cs (Cs coverage $\theta_{\text{Cs}}=0.25$) structure which then evolves through Pt(111)(√3×√3)-R30°-Cs ($\theta_{\text{Cs}}=0.33$) to the Cs saturated surface. At saturation the surface is covered by a hexagonal close packed incommensurate Cs layer (Pt(111)(ihcp)-Cs) with the work function change about -3.5 eV compared to the initial bare Pt surface, and Cs coverage of 0.41 as determined by Auger Electron Spectroscopy (AES).

To prepare the CsI mixed layer we further dosed iodine on Cs saturated (Pt(111)(ihcp)-Cs) surface from a Ag₄RbI₅ solid state electrochemical cell (Fig.3) (13,16).

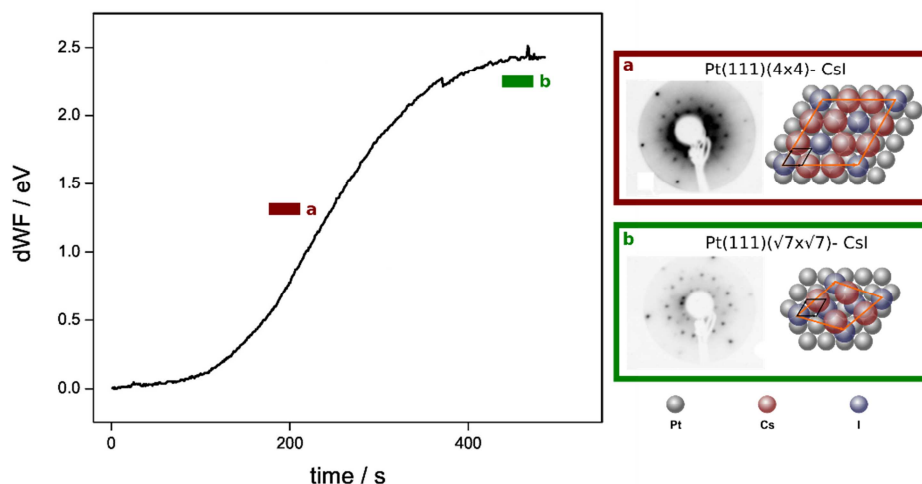


Figure 3. The work function (WF) response upon I dosing Cs saturated on Pt(111)(ihcp)-Cs in UHV conditions. The WF steadily rises by 1.5 eV from the initial value. The LEED pattern changes through (4×4) to ($\sqrt{7}\times\sqrt{7}$)- $R19.1^\circ$ at the Cs and I saturated surface. The real space structures are shown on the right side together with the LEED patterns.

Incorporation of I into the Cs layer causes the WF to increase due to the introduction of charge of opposite polarity into the structure. After reaching the desired WF change corresponding to a certain CsI coverage, the surface was briefly annealed to 350 K to enhance the layer ordering. The LEED pattern changes from Pt(111)(ihcp)-Cs present at the beginning of the I dose to a Pt(111)(4×4)-Cs,I pattern which corresponds to a WF change of about 1 eV. After further I dosing the pattern changes to Pt(111)($\sqrt{7}\times\sqrt{7}$)- $R19.1^\circ$ -Cs,I. The coverages of then ordered layers were determined by Auger Electron Spectroscopy (AES) as $\theta_{\text{Cs}}=0.35\pm0.11$, $\theta_{\text{I}}=0.28\pm0.07$ for Pt(111)(4×4)-Cs,I and $\theta_{\text{Cs}}=0.33\pm0.07$, $\theta_{\text{I}}=0.35\pm0.06$ for Pt(111)($\sqrt{7}\times\sqrt{7}$)- $R19.1^\circ$ -Cs,I (13). Given the high packing density of the Pt(111)($\sqrt{7}\times\sqrt{7}$)- $R19.1^\circ$ -Cs,I structure, it is likely that this layer is a bilayer where the I atoms are in contact with the Pt substrate and the Cs atoms are located on top of the stack as schematically depicted on the right side of Figure 1.

More interesting for further discussion is the Pt(111)(4×4)-Cs,I layer where the packing allows accommodation of all atoms in one monolayer, forming the mixed monolayer structure. However, more than one packing order is possible for a structure with hexagonal symmetry (13). The possibilities are shown in Figure 4.

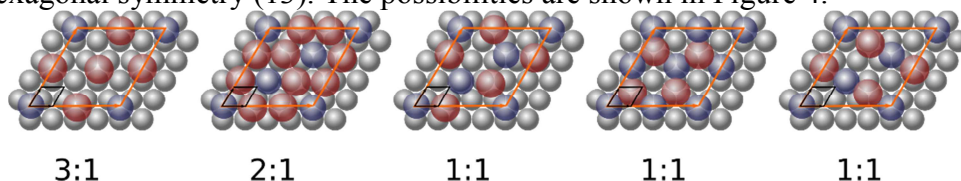


Figure 4. Possible Pt(111)(4×4)-Cs,I structures of various Cs:I stoichiometries for mixed CsI monolayers.

Based on the symmetry and AES measured coverages, we concluded that the most probable atomic arrangement of the Pt(111)(4×4)-Cs,I structure is the one depicted second from the left in Figure 4 (7,13). In this arrangement the Cs:I ratio is 2:1 and each I atom is surrounded by the maximum number of Cs counterions. According to the LEED

and thermal desorption measurements, the surface is not only covered by this structure, but a significant area is also covered by high iodine coverage structures (13).

The fact that the ionic layers organize into very defined arrangements is not a surprise, as suggested by standard electrostatic calculations taking into the account the image charges in the metal substrate (7,13). These calculations show that, depending on the electrostatic charge of each atom and on the distance from the surface, only a few surface stoichiometries are favorable, namely Cs_2I and CsI where the overall electrostatic energy is minimized.

To check the universality of these observations, we prepared layers consisting of Cs and oxygen. For such layers we also expect high ionicity of the bonding given the large electronegativity difference between Cs and oxygen. The structures were prepared by oxidation of the fully saturated $\text{Pt}(111)(\text{ihcp})\text{-Cs}$ structure at 5×10^{-8} mbar of oxygen pressure. Such layers initially show no obvious order, but a clear $\text{Pt}(111)(4 \times 4)\text{-Cs}_2\text{O}$ LEED pattern appeared after annealing to 650 K (14). Similar to the CsI case and after taking into the consideration the stoichiometry of the surface layer measured by AES, the surface can be the best described by the structure where the anions (oxygen) are surrounded by the maximum number of cations (cesium) in a closely packed arrangement (Figure 5).

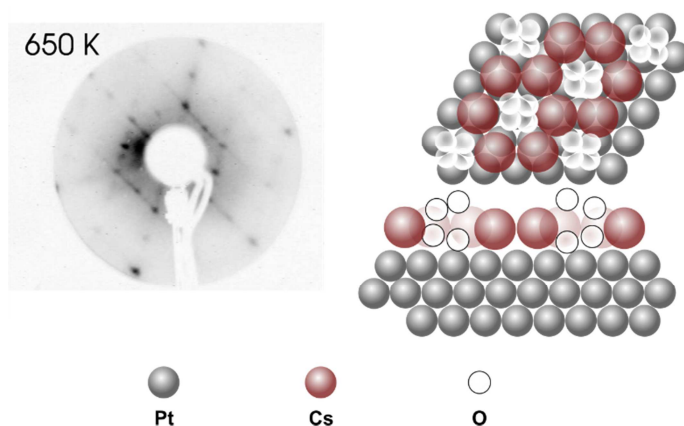


Figure 5. The LEED pattern and the proposed structure for the $\text{Pt}(111)(4 \times 4)\text{-Cs}_2\text{O}$ prepared by exposing the $\text{Pt}(111)(\text{ihcp})\text{-Cs}$ structure to 5×10^{-8} mbar oxygen pressure and annealing to 650 K.

Such honeycomb arrangements are not only specific to the above-mentioned coadsorption systems prepared in UHV conditions. The (4×4) LEED patterns and mixed layer structures were also observed for CsI layers prepared by electrochemical deposition on $\text{Au}(111)$ (17), and KO deposits on $\text{Pt}(111)$ prepared in UHV (18). Even though here we consider only the (111) surface orientation of a f.c.c. crystal lattice, the same principles have been proposed to govern the coadsorption for other symmetries. The same general behavior was also observed for Cs and I coadsorption on $\text{Au}(110)$ electrodes in electrochemical conditions (19-20). At low potentials, the mixed $\text{Au}(110)(2 \times 4)\text{-Cs}_2\text{I}$ structure was observed and the model favored by Wang et al. has a planar, mixed layer with 1:1 stoichiometry and atomic spacing almost identical to that in the bulk CsI crystal (20). In this case the ions of one polarity are also surrounded by maximum numbers of counterions in the four-fold symmetry arrangement. Given the above, it seems that there is now a significant body of knowledge justifying the

hypothesis made by Wang et al. and Drnec and Harrington regarding the nature of the bonding and structure of 2D layers. The honeycomb arrangement observed for the (111) surfaces is interesting as it is the same, for one of the ionic species, as the arrangement of graphene and other materials with sp^2 or mixed sp^2 - sp^3 hybridization. Such materials hold much promise given the unique properties leading to interesting electronic, optical and mechanical behavior. The examples of such materials are graphene, silicene, germanene and stanene (1,21-23).

This raises a question if the universality of the structure-bonding relationship for ionic layer cannot be translated into the preparation of advanced 2D materials with honeycomb lattices. According to the hypothesis it should be possible to imprint the honeycomb structure during the deposition of arbitrary atomic species on the six-fold symmetry substrate. However, two basic conditions need to be satisfied: i) the interaction of the deposited film with the metallic substrate is relatively weak or at least non-directional (ionic or van der Waals bonding) and ii) the deposition proceeds from the environment where the deposited atoms are present in an ionic state together with ions of opposite polarity. The electrochemical environment is almost an ideal deposition medium as the depositing material is normally surrounded by the counterions in the ion-conducting electrolyte. In the double layer region there is typically enough mobility that the ions can organize in the precursor state, as in the case of $[PdCl_4]^{2-}$ complexes on Au(111) prior to the Pd deposition (24). Such an organized precursor state, together with the driving electric field from induced image charges on the metallic surface, can serve as a template for further deposition. This process can facilitate formation of certain structures, in this case the honeycomb structure, as depicted in Figure 6.

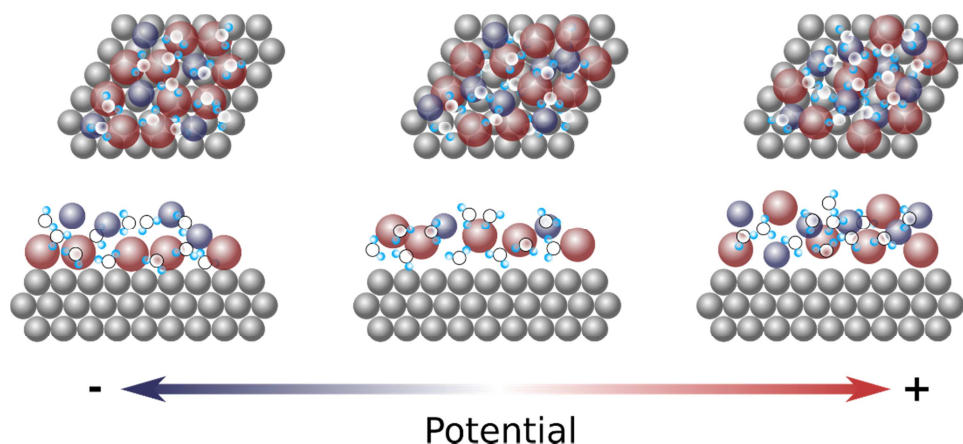


Figure 6. Hypothesis: The deposition of the honeycomb structure proceeds from the precursor state formed in the double layer at the potentials higher than the deposition potential. Firstly, the ions in double layer are disordered (right) at potentials higher than the deposition potential. Upon sweeping the potential negatively towards the deposition potential, the ions organize in the ordered precursor state (middle). Finally, the positive ionic species deposit on the substrate from the ordered precursor state (left).

Above the deposition potential (right scheme in Figure 6) the double layer (DL) consists of a disordered mix of ions of opposite polarity and water molecules. As the potential decreases to the UPD potential, cations move closer to the surface, possibly interacting with the substrate through ionic and van der Waals interactions. This, together

with the presence of the anions, forces the cations to assemble in the DL into the favorable structure, which in the case of $p3/p6$ symmetry of the substrate is the honeycomb (Figure 6 middle). Upon further potential decrease, the cations specifically adsorb on the surface from the precursor state (Figure 6 left). If the adsorbed atoms interact with the substrate ionically or this bond is weak, e.g., van der Waals, then the adsorbed layer keeps its structure. If there is a strong covalent bonding, then the structure reorganizes to the typical UPD closely packed layer (6).

Following this hypothesis, we tried to deposit germanium on Au(111) substrate in order to form germanene, the analog for graphene with the honeycomb lattice (4-5). This structure cannot be formed by exfoliation as there is no Ge analog to graphite, where 2D sheets are held together by the van der Waals forces. The last monolayer of the Au(111) substrate has $p6$ symmetry, as for Pt(111), but it has a large herringbone reconstruction. The lattice parameter is such that it matches the atomic distances of the theoretically calculated germanene honeycomb lattice, therefore it is ideal for germanene formation. Even though various groups have tried to deposit germanene in the UHV environment in the past, only in recent years there has been success (25-31).

We found that it is possible to form germanene from aqueous electrolyte by finely tuning the deposition conditions (4). In the case of Au(111) at pH 4.5, the reconstruction is first lifted by incorporation of some of the Ge atoms into the substrate, forming a surface alloy. This alloy releases the surface stress and the unreconstructed (111) surface is formed, which then acts as a better template for the deposition of the germanene. The substrate effects seem to be dependent on the deposition conditions and pH because at pH 9 the germanene also forms on the reconstructed Au(111) surface (5). A specific potential control procedure needs to be applied to form the germanene 2D layer (Figure 7). Such deposited germanene shows many defects. However, fine tuning of the deposition conditions helps to form less defective layers. Deposition at other conditions results in less well ordered 2D deposits and surface alloys. According to the hypothesis this is not surprising as fine potential control is likely required in order to form the ordered precursor state.

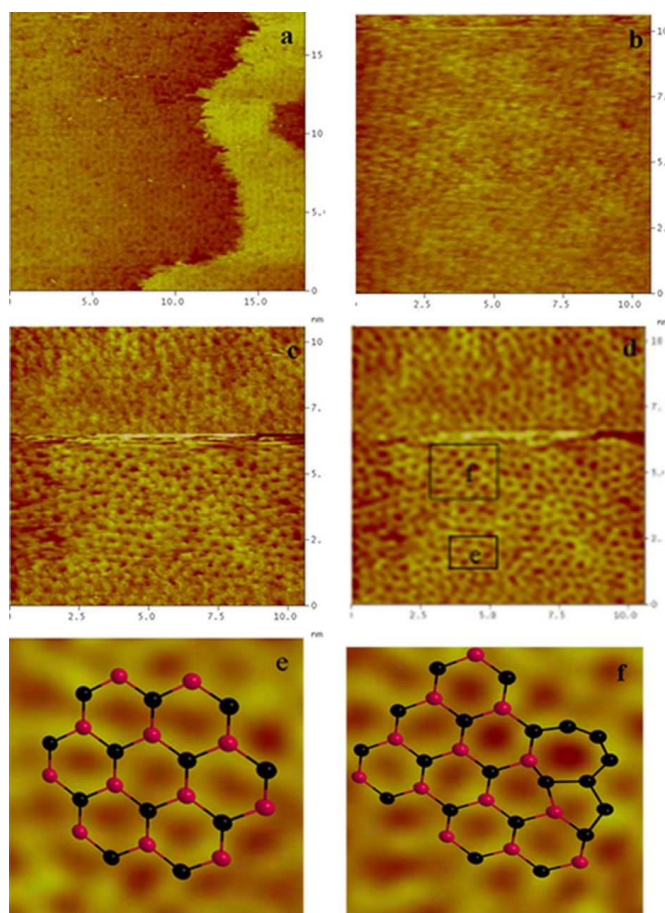


Figure 7. a-f (left to right) are STM images of Au(111) in 1 mM GeO_2 and 0.1 M KClO_4 (pH 4.2) after the potential was scanned to -1.4 V and then to -900 mV vs. Ag/AgCl . a) shows a strip of germanene on a layer of germanene. b) shows a honeycomb structure, with 0.44 ± 0.02 nm between the holes. c) shows nearly atomically resolved germanene. The boxes indicate where figures e and f were taken. e) Superposition of honeycomb structure and a FFT-filtered STM image of a germanene domain. f) Superposition of a germanene model, including 5- and 7-membered rings at a domain wall, on a FFT-filtered germanene STM image. Reproduced with permission from *J. Electrochem. Soc.*, **164** (2017), D469-D477. Copyright 2017, The Electrochemical Society.

At pH 9 a buffer solution can be used and the process can be better controlled due to the shift of the hydrogen evolution reaction to lower potentials and better control of the surface pH. Here germanene growth on both reconstructed and unreconstructed surfaces was observed, but the growth was accelerated on the unreconstructed part of the surface. This is again presumably due to the better templating effects for the deposition. Stepping out of the ideal growth conditions results in less well ordered germanene, as in the pH 4.5 case. This is expected from the hypothesis, where the right conditions need to be found to preassemble the monolayer in the precursors state.

Conclusions

Above we have shown that the nature of the bonding and the symmetry of the substrate determine the structure of (electro)deposited atomically thin bimetallic layers. In the case of a substrate with the hexagonal symmetry, ionically bonded layers form a honeycomb planar structure where ions of one polarity are surrounded by maximum ions of opposite polarity. This behavior can be explored in preparation of 2D materials with honeycomb structures, such as germanene, in an aqueous environment, where the deposited atomic species exist in an ionic form surrounded by counterions. Given the above observations, it is perhaps feasible to expect that the same phenomena will direct the deposition of other exotic 2D materials which are non-directionally bonded to the substrate. For example, silicon has been shown to deposit from ionic liquids at various conditions on the Au(111) surface (32). Given that silicene is a stable allotrope of silicon, it is not unreasonable to expect silicene formation on one of the transition metals, e.g., Au(111), in electrochemical conditions. The same might be expected for carbon deposition from CH₄ or CO, where by finely tuning the conditions, it might be possible to prepare graphene at room temperature. Such an approach might be also used to prepare as-yet-unknown 2D materials.

Acknowledgments

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Recent Progress in the Understanding of the Electrocatalysis of the CO-Tolerant Hydrogen Oxidation Reaction in Polymer Electrolyte Fuel Cells

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Recent combined experimental and theoretical efforts have led to progress in the understanding of hydrogen oxidation and oxygen reduction reactions in fuel cells. The hydrogen anode in the polymer electrolyte fuel cell needs to be tolerant of CO concentrations in the tens of ppm in the reformed natural gas fuel. We have found that various Pt-M (M = Fe, Co, Ni, Ru) nanoparticulate alloys have significantly greater tolerance than pure Pt, and also, the area-specific hydrogen oxidation activity is higher. We have been able to explain the CO tolerance and catalytic activity with a novel metal-to-metal hydrogen spillover mechanism that is based on density functional theory calculations. The latter have also been supported by in situ spectroscopic measurements, both X-ray absorption and infrared reflection-absorption.

Introduction

The recent history of electrocatalysis has involved significant efforts by a number of groups to make use of rational design concepts based on fundamental understanding. In the area of platinum-based catalysts, one of the key approaches in increasing activity and decreasing platinum loading has been the use of alloys containing first row transition metals, as pioneered in early work at UTC (1). Watanabe et al. were among the first to realize that the alloying metal easily dissolves in hot acid, leaving an extremely thin surface layer that is nearly pure platinum (2). Later, this type of surface, consisting of only one or two atomic layers, was termed a platinum “skin” (3) and was concluded to have modified electronic properties depending upon the underlying alloy (4, 5). The logical extension of this concept was to envisage a single monolayer of Pt on a pure non-precious metal substrate, as pioneered by Adzic and his group. This impressive body of work has been recently reviewed by Shao et al. (6). At the University of Yamanashi (UY), we have also continued to conduct pioneering work in electrocatalysis (7-9). In particular, we have sought to understand the relationships between surface structure, electronic properties and catalytic activity for the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR) on platinum and several of its alloys, making use of advanced spectroscopic and structural characterization techniques, as well as density functional theory (DFT). In this paper, we will briefly summarize some of our recent results in the area of the HOR.

Results and Discussion

For nearly thirty years, it has been realized that platinum-based reformat-fed fuel cell anodes could be made to be more CO-tolerant by alloying platinum with a less noble transition metal such as cobalt in order to decrease the CO adsorption strength, as discussed by Ross (10). The concept of the CO-tolerant HOR began to be developed at UY nearly twenty years ago in a series of papers that introduced a “detoxification” mechanism, in which CO was observed to have increased mobility and decreased coverage on the Pt “skin” surface of the alloy (11-13). The normally electron-rich Pt surface’s electronic properties were considered to be modified by the presence of the electron-poor alloying element below the surface. This early insight has been confirmed in an X-ray photoelectron spectroscopic (XPS) study of Wakisaka et al. (14) and in a more recent series of papers of Shi et al. (15-17), the most recent one employing *in situ* X-ray absorption spectroscopic (XAS) measurements. Also, Ogihara et al. added further confirmation in their *in situ* Fourier-transform infrared (FTIR) study (18).

Various arguments have been advanced to explain the bonding, including the so-called Blyholder model (19) and the d-band center model (20). The scheme proposed by Watanabe et al. (12, 13) was related to the former model, which involves weakening of back-donation. In our recent work, we have carried out detailed DFT studies, which have also confirmed the basic concept of CO tolerance (15-17). Even though some details differ from those in earlier studies, the overall picture remains the same. In simple terms, there are fewer d-band electrons available for the bonding, so the adsorption of CO becomes weaker.

We have made use of stepped surfaces that consist of (111) terraces and (110) steps, with the top surface always being pure Pt (Fig. 1). The terraces are effectively three atomic rows wide, since there is no bonding to the row at the bottom of the step. This somewhat narrow step is consistent with the curvature of the catalyst nanoparticles in the nanometer range, but the adsorption still resembles that on wider terraces. The adsorption of the important species such as H and CO is typically stronger by ca. 1 eV at the top of the step, in comparison with that on the terrace. Also, the adsorption of CO is typically ca. 1.0 eV stronger than that of H on a given site, which accounts for the fact that CO so easily poisons the surface.

The most active surface of Pt for the HOR in acid has been shown to be the (110) surface by Markovic et al. (21). This fact was explained by theoretical work of Ishikawa and coworkers (22), who presented DFT calculations detailing the spontaneous dissociation of the H₂ molecule at the tops of ridges, with the rate-determining step (rds) being the subsequent oxidative desorption of H to produce hydrated protons. The (110) step on the (221) surface provides a type of site that is geometrically similar to the ridges on the (110) surface itself, so therefore, we have assumed that these steps are the active sites, even on catalyst nanoparticles. The mechanism proposed is as follows (Fig. 2):





At all of the alloy (221) surfaces studied, the adsorption of H_2 at the (110) step is spontaneous, so the so-called Tafel step cannot be the rate-determining step (rds). The H_2 molecule cannot adsorb easily on the (111) terraces, because the adsorption is weaker than that of water. Only at the step can H_2 adsorption compete with that of water. The adsorption of CO is thus particularly important at the step edges, where the bonding is very strong for pure Pt, so the presence of the alloying element is necessary to weaken the adsorption.

Even though the principal emphasis in previous work has always been on the CO tolerance, we found experimentally that the HOR itself is also somewhat higher in activity on the Pt alloy surfaces, with the activity increasing in the order $\text{Pt} < \text{Pt-Ru} < \text{Pt-Ni} < \text{Pt-Co} < \text{Pt-Fe}$ (16). Initially, we expected that this would be due to a similar ordering of adsorption strengths of H at the corresponding steps. However, interestingly, we found that the DFT-calculated adsorption strengths for H at the step differed only slightly for Pt-Fe, Pt-Co and Pt-Ni.

$\text{Pt}_{\text{xAL}}\text{PtCo}(221)$ side views

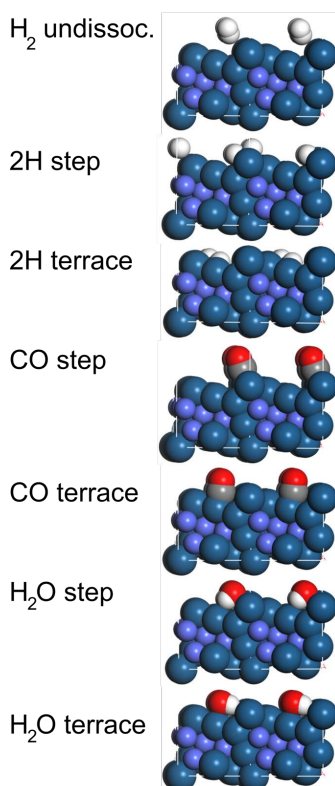


Figure 1. Side-view atomic models of the $\text{Pt}_{\text{xAL}}\text{-PtCo}(221)$ surface, showing non-dissociative H_2 adsorption, spontaneously dissociated 2H at the (110) step, 2H after diffusion to the (111) terraces, CO adsorbed at the step and on the terrace, and H_2O adsorbed at the step and on the terrace.

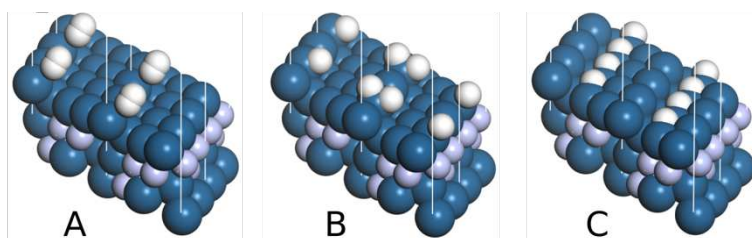


Figure 2. Oblique view of atomic models of the $\text{Pt}_{x\text{AL}}\text{-PtCo}(221)$ surface, showing (A) non-dissociative H_2 adsorption, (B) spontaneously dissociated 2H at the (110) step, and (C) 2H after diffusion to the (111) terraces.

Instead, the H adsorption strengths differed much more clearly on the terraces. This is the reason that we were forced to consider the possibility that adsorbed H must diffuse to the terraces first before undergoing oxidative desorption. This process can be considered a specific type of metal-metal spillover. Since the adsorption strength is larger at the step, it appears that the process is endothermic, but the energetics can depend on the coverages and potential, which have not been considered in detail thus far.

Recent *in situ* XAS measurements for Pt and Pt-Co nanoparticles have led to further insights into the structural and electronic characteristics occurring under electrochemical conditions (17). The extended X-ray absorption fine structure (EXAFS) measurements have led to the conclusion that the Pt-Co lattice structure is significantly more rigid and undergoes much smaller structural changes during the adsorption of either H or CO, in comparison with pure Pt. Another factor contributing to the structural stability is simply that the adsorption is weaker and produces less stress.

The *in situ* X-ray near-edge spectra for the Pt-Co (not shown) indicate that adsorption of either H or CO has a negligible effect on the density of states (DOS) at the Fermi level (FL). Indeed, this is supported by the DFT calculations. The latter have also led to a deeper understanding of the adsorptive bonding of CO to the Pt skin surface. Figure 3 shows DOS plots of the CO-covered surfaces for Pt and Pt-Co.

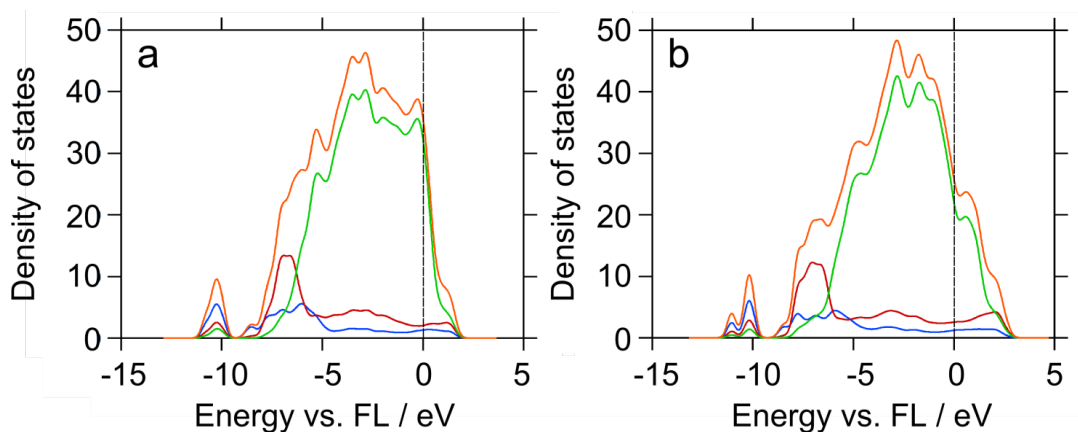


Figure 3. Density of states for (a) $\text{Pt}(221)\text{-}4\text{CO}$ and (b) $\text{Pt}_{1\text{AL}}\text{-PtCo}(221)\text{-}4\text{CO}$; s-projected DOS (blue), p-projected DOS (red), d-projected DOS (green), total DOS (orange).

As reported by others, the DOS at the FL is much lower for the case of the Pt-Co alloy. However, this is not the most important factor in the bonding. Instead, the plots indicate that the bonding of CO to the surface involves p-like orbitals located at ca. -7.5 eV, and the effectiveness of the bonding appears to reflect the overlap between CO p-orbitals and Pt d-states, which is greater in the case of pure Pt (Fig. 3a). This type of bonding is consistent with that proposed for CO on Ni(111) by Pettersson and Nilsson (23).

Conclusions

The recent combined experimental and theoretical work has led to deeper insights into the reasons for the enhanced CO tolerance and HOR activity of alloys such as Pt-Co and Pt-Fe. Specifically, we conclude that the oxidative desorption of H from terrace sites is an important rate-determining step. This will have to be supported by further, more detailed work, including the calculation of activation barriers. With these efforts, we hope to begin to lay a foundation for further improvements in the activity.

Acknowledgments

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Chapter 2

Core-shell

Non-Noble Metal Cored Pt-Skin Catalyst and Its Highly Enhanced Stability in Oxygen Reduction Reaction By Controlling the Nitriding Level For the Core

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In this study, we introduce non-precious metals as core material for core-shell type electrocatalysts. The Pt-skin catalyst using cobalt, transition metal, as a core was nitrided to improve the stability of the electrocatalyst. Nitriding levels were systematically controlled by the adjusting of ammonia gas pressure (1, 40, 80 bar) during the heat treatment process. We obtained catalysts in which the Pt-skin structure was clearly maintained even under various preparation conditions and the average particle size of the active metal was uniformly distributed in the range of 3 to 4 nm. CoN@Pt/C catalysts have high mass activity over 0.44 mA/mg_{PGM} @ 0.9 V (vs. RHE). The most important point is not only the initial activity but also the much-improved durability. In addition, unlike the other electrocatalysts, in the accelerated stress test protocol, the change in the electrochemical surface area (ECSA) is extremely small and the ORR (oxygen reduction reaction) activity is maintained. Through the control of the nitridation level of the transition metal core, the possibility of producing a low cost, high-performance core-shell electrocatalyst was confirmed.

Introduction

Cost reduction is a key barrier for the commercialization of polymer electrolyte fuel cells (PEFCs), and the adaption of core-shell type electrocatalyst is expected to play a major role(1,2). The core-shell electrocatalysts have shown outstanding performance in terms of catalytic activity as well as durability(2,3). Pd or PdM alloy have been representative model as a core for the core-shell electrocatalyst considering the durability as well as activity. However, there is still a request for Pt-skin type electrocatalyst which does not contain expensive noble metal as a core material. Therefore, low-cost and abundant transition-metals are getting attention as candidates for core materials, but their instability is main obstacle for using them as a core material.

Adzic et al. recently reported on the Pt-skin catalysts with nitride cores.(4-6). The existence of N nearby the Pt lowers the diffusion energy of Pt atoms for filling the defect sites thus preventing the dissolution of active metals into the electrolyte. They claimed that the concentration of N in the core is crucial to the durability of the catalysts. In those papers, they prepared the transition metal nitride core and Pt-skin electrocatalyst by two approaches as below. The first method is an electrodeposition of Pt on the top of transition metal nitride core(5). The other method is the thermal segregation of PtM alloy for the Pt-skin formation and the nitriding of core simultaneously(4,6). However, the former has insufficient productivity for practical use and the less uniform coating of Pt-skin may be expected. In the latter case, precise temperature control may be necessary for

getting well segregated Pt-skin layer and nitride cores at the same time. In both cases, there were no comments on the controlling the concentration of N in the cores. On the other hand, we conducted nitriding process to the as-prepared core-shell catalyst (Co@Pt/C) by a sonochemical method. By using this approach, we could control the nitriding temperature for the cores in separately regardless of Pt segregation temperatures. Moreover, the control of N concentration in the cores was achieved by changing the nitriding pressure under the ammonia environment.

In this study, we, therefore, synthesized carbon supported cobalt nitride cores and Pt-skin electrocatalyst (denoted as CoN@Pt/C_xbar, $x = 1, 40, 80$) by a sequential process composed with ultrasound-assisted polyol method and ammonia heat treatment(7). In addition, our process enables the gram scale production without the particle agglomeration and phase segregation. More importantly, we experimentally demonstrated that the durability of core-shell electrocatalyst is much improved with the nitriding level of transition metal core. The details of physicochemical characterization of samples will be discussed herein.

Experimental

Preparation of electrocatalyst

For the preparation of core-shell electrocatalysts, one-pot process via sonochemical approach was used. We put 0.520 g of Pt(acac)₂, 0.333 g of Co(acac)₂ and 0.675 g of Vulcan XC-72 into N₂ purged ethylene glycol (EG). Thereafter, the precursor dispersion is irradiated by using a horn-type sonicator (Sonic & Materials, VCX 750 model, Tip diameter: 13 mm, solid probe). After sonochemical reaction for 3 h, the black slurry was filtered through the membrane filter (0.4 μm of pore size). During the filtration, the sample was washed with an excess of ethanol and D.I. water to remove the residue of EG. Finally, the sample was dried at 70 $^{\circ}\text{C}$ in the vacuum oven. The sample obtained from above process was denoted as Co@Pt/C. For the nitriding of the sample, as-prepared Co@Pt/C sample powder was placed in the alumina furnace. And, the sample was annealed in our home-made tubular furnace at 510 $^{\circ}\text{C}$ for 2 h. During the annealing, the pressure of the NH₃ gas was adjusted from 1 bar to 80 bar for the control of nitriding level in the Co core. The final samples were denoted as CoN@Pt/C_xbar ($x = 1, 40$ and 80 bar).

Electrochemical measurement

Catalyst ink was prepared following steps. First, 5 mg of sample powder was put in 2 mL of solution mixed of D.I. water and isopropyl alcohol (IPA) ($v/v = 1:9$). Thereafter, the 5 μL of Nafion solution (D521, DuPontTM) was added in the dispersion and sonicated until homogenous catalyst ink is formed. And then, 8 μL of catalyst ink was pipetted on the glassy carbon electrode ($d = 5\text{ mm}$, area: 0.196 cm^2) and dried at room temperature and ambient atmosphere. The catalyst loadings of electrodes were adjusted as 20 $\mu\text{g}_{\text{Pt}}\text{ cm}^{-2}$.

Electrochemical analysis was carried out with typical three-electrode systems coupled with rotating electrode disk (RDE). The Pt wire and hydrogen reference electrode (Gaskatel GmbH, Germany) was used as the counter and reference electrode, respectively. The catalyst coated RDE electrode was used as working electrode. The cyclic voltammograms (CVs) of the sample were recorded with a scan rate of 20 mV s^{-1} from

0.03 V to 1.1 V (vs. RHE) in N_2 -saturated 0.1 M $HClO_4$. The linear sweep voltammograms (LSVs) for ORR were measured with a scan rate of 10 mV s^{-1} and 1600 rpm in the potential range from 0.00 V to 1.1 V (vs. RHE) in O_2 -saturated 0.1 M $HClO_4$. All LSV curves of samples were corrected by the IR-compensation and the removal of background capacitance current. The accelerated stress test (AST) of the sample was conducted by the 10k cycles repeating of chronoamperometry at 0.6 V for 3 s and 0.95 V for 3 s.

Characterizations

The crystalline structure of samples was investigated by X-ray diffractometer (XRD, Rigaku DMAX-2500, $Cu\text{ }K\alpha$, $\lambda = 1.5406\text{ \AA}$). The composition and Pt loading of sample were determined by the Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Thermo Scientific Co./iCAP 6300 Duo). Microscopic study was conducted with the field emission transmission electron microscopy (FM-TEM, FEI, Talos F200X, 200 kV) and Cs-corrected FE-TEM (JEOL, JEM-ARM200F, 200 kV).

Results and Discussion

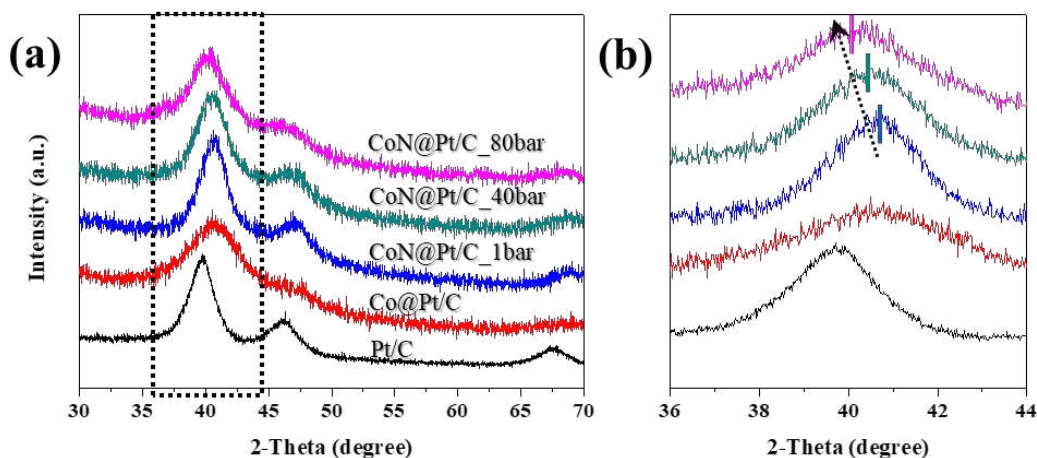


Figure 1. (a) X-ray diffraction (XRD) patterns of samples and (b) enlarged Pt(111) peak corresponding to the black dotted box.

Figure 1 showed the XRD patterns of samples along with Pt/C. As shown in Figure 1, all samples showed the typical face-centered cubic (FCC) structure corresponding to Pt (JCPDS, No. 87-0646)(8). In the full range, other distinguish peaks were not observed, indicating no any phase segregation in the samples. We also observed that (111) peak position of Co@Pt/C is shifted to the high angle compared with that of Pt/C. It indicates that Co atoms with relatively smaller atomic size were incorporated into the Pt lattice, causing the compressive strain(8). The crystallite size of samples calculated by using Scherrer's equation was 1.7 nm for Co@Pt/C and 2.4-3.4 nm for CoN@Pt/C_xbar samples. Because of the amorphous nature and small crystallite size of cobalt nitride core, the distinct peak corresponding to it couldn't be observed. The direct evidence on the nitriding of Co core was not confirmed from XRD analysis, but we found that the N content in all samples is systematically increased with the increase of NH_3 pressure from the elemental analysis on C, H, N, S and O (Table 1). We also found that the nitriding

level of Co core affects the full width half maximum (FWHM) and (111) peak position of the nitridized samples. As shown in Figure 1(b), FWHM is increased and (111) peak position is gradually shifted to low angle as the increase of nitriding level. It is reported that cobalt nitrides have various crystal structures depending on the nitriding level (e.g. Co_4N (cubic), Co_3N (hexagonal) and Co_2N (orthorhombic))(9). In addition, it is well-known that the microstrain induces the XRD peak broadening(10). Therefore, we understood that the difference in the nitriding level may lead the change of crystal structure in the Co core, causing the different lattice mismatch between Pt-skin and cobalt nitride core. It can be indirect evidence on the nitriding of Co core. The structural information of samples was summarized in Table 1.

TABLE I. Structural information and N contents of samples

Sample	Crystallite size	Lattice constant (nm)	Pt-Pt distance (nm)	N content (wt%)
Pt/C (JM)	3.4	0.3930	0.2780	-
Co@Pt/C	1.7	0.3837	0.2713	-
CoN@Pt/C_1bar	3.4	0.3843	0.2717	0.15
CoN@Pt/C_40bar	2.9	0.3856	0.2726	0.60
CoN@Pt/C_80bar	2.4	0.3880	0.2743	0.99

Figure 2 showed the low magnified TEM images and particle size histograms of samples. As shown in Figure 2, all samples have well-dispersed and uniform size of NPs on the carbon support. The particle sizes of samples were 2.9 nm for Co@Pt/C and 3.7-4.2 nm for CoN@Pt/C samples calculated by averaging of 250 NPs. During the nitriding annealing, the particle size slightly increased but, the dispersion and uniformity of NPs were maintained compared with that of Co@Pt/C. For the relatively big discrepancy in the NP sizes between XRD and TEM analysis, we interpreted that XRD peak broadening by the microstrain within NP may lead an difference of particle size calculation

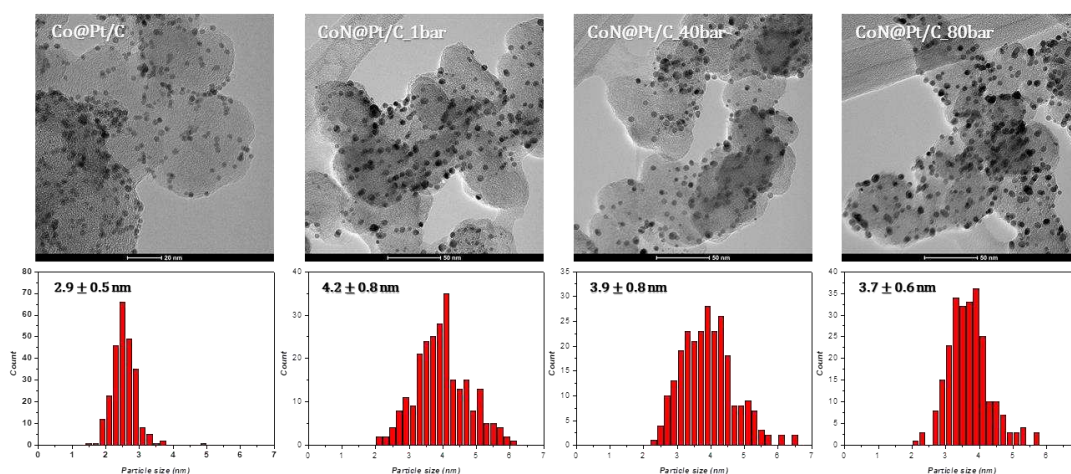


Figure 2. Transmission electron microscopy (TEM) images and particle size histograms of samples.

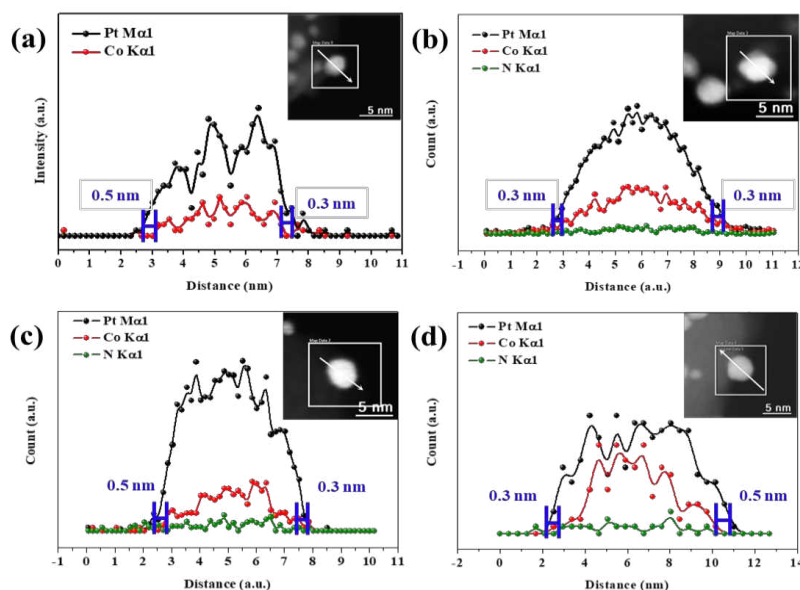


Figure 3. STEM-EDS line profiles of (a) Co@Pt/C, (b) CoN@Pt/C_1bar, (c) CoN@Pt/C_40bar and (d) CoN@Pt/C_80bar. Each inset shows correspond to the HAADF image.

To investigate the structures of NPs, the STEM-EDS profiles of samples were obtained by using a Cs-corrected TEM. As shown in Figure 3, Pt $M\alpha$, Co $K\alpha$, and N $K\alpha$ signals were detected by a scanning with an electron beam (0.8 Å). In the all STEM-EDS line profiles, the red line for Co $K\alpha$ exists at the core part and black line for Pt $M\alpha$ is detected in the full range. In addition, the calculated gap (indicated blue line) for Pt-skin were 0.3-0.5 nm and it is corresponding to 1-2 Pt monolayer considering the diameter of Pt atom (0.3 nm)(8). The presence of N atom within NP is observed (indicated green line in Figure (b-d)) and we also confirmed that the intensity of N $K\alpha$ gradually increases with N content increase. Based on the microscopy analysis, we found that our samples have clear Pt-skin and Co core with varied nitriding levels.

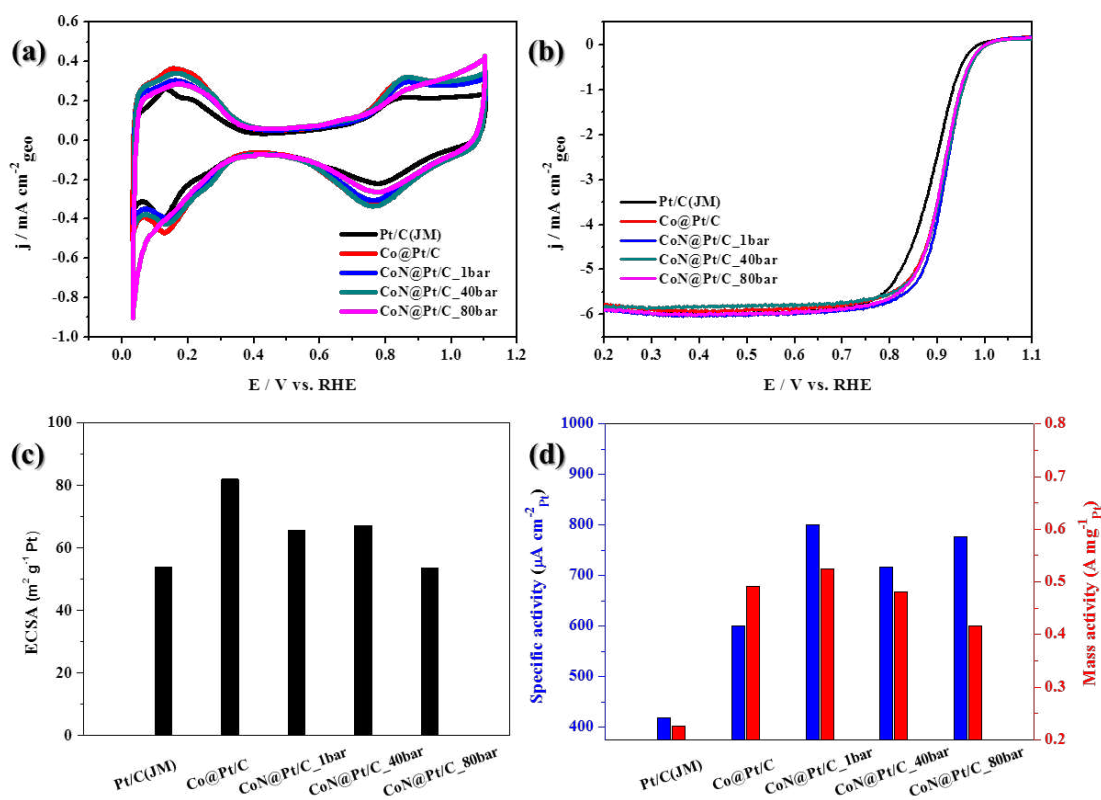


Figure 4. Electrochemical analysis of samples in 0.1 M HClO₄ (a) cyclic voltammograms (CVs), (b) linear sweep voltammograms (LSVs), (c) electrochemical surface area (ECSA) and (d) specific and mass activity at 0.9 V.

Electrochemical studies of samples were conducted with RDE measurement in 0.1 M HClO₄. The cyclic voltammograms (CVs) of the sample showed the typical hydrogen ad/desorption and oxygen species redox peaks (Figure 4(a)). The ECSA of samples were calculated from hydrogen desorption charge (assuming the reference value of $210 \mu\text{C cm}^{-2}$ for polycrystalline Pt)(8). All core-shell catalysts prepared in this study showed relatively larger ECSA compared to the commercial Pt/C. It's also an evidence that our samples contain core-shell structure resulting in higher Pt utilization. The ORR performance of samples was compared with Pt/C by linear sweep voltammograms (LSVs) in O₂-saturated 0.1 M HClO₄. As shown in Figure 4(b), Co@Pt/C sample showed higher onset potential and half-wave potential ($E_{1/2}$) compared with those of Pt/C. In addition, we found that the nitriding of the core for the samples increased the specific activity at 0.9 V by 1.2-1.3 times whereas the mass activity of samples did not change much even after the nitriding treatments. The mass activity of samples at 0.9 V were 0.49, 0.53, 0.48 and 0.42 A mg⁻¹ Pt for Co@Pt/C, CoN@Pt/C_1bar, CoN@Pt/C_40bar and CoN@Pt/C_80bar, respectively. Compared with a mass activity of Pt/C(JM) (0.23 A mg⁻¹ Pt), the calculated mass activity of samples is ~ 2 times higher (0.42-0.53 A mg⁻¹ Pt). Based on the mass activity, the order of ORR performance is CoN@Pt/C_1bar > Co@Pt/C > CoN@Pt/C_40bar > CoN@Pt/C_80bar > Pt/C(JM).

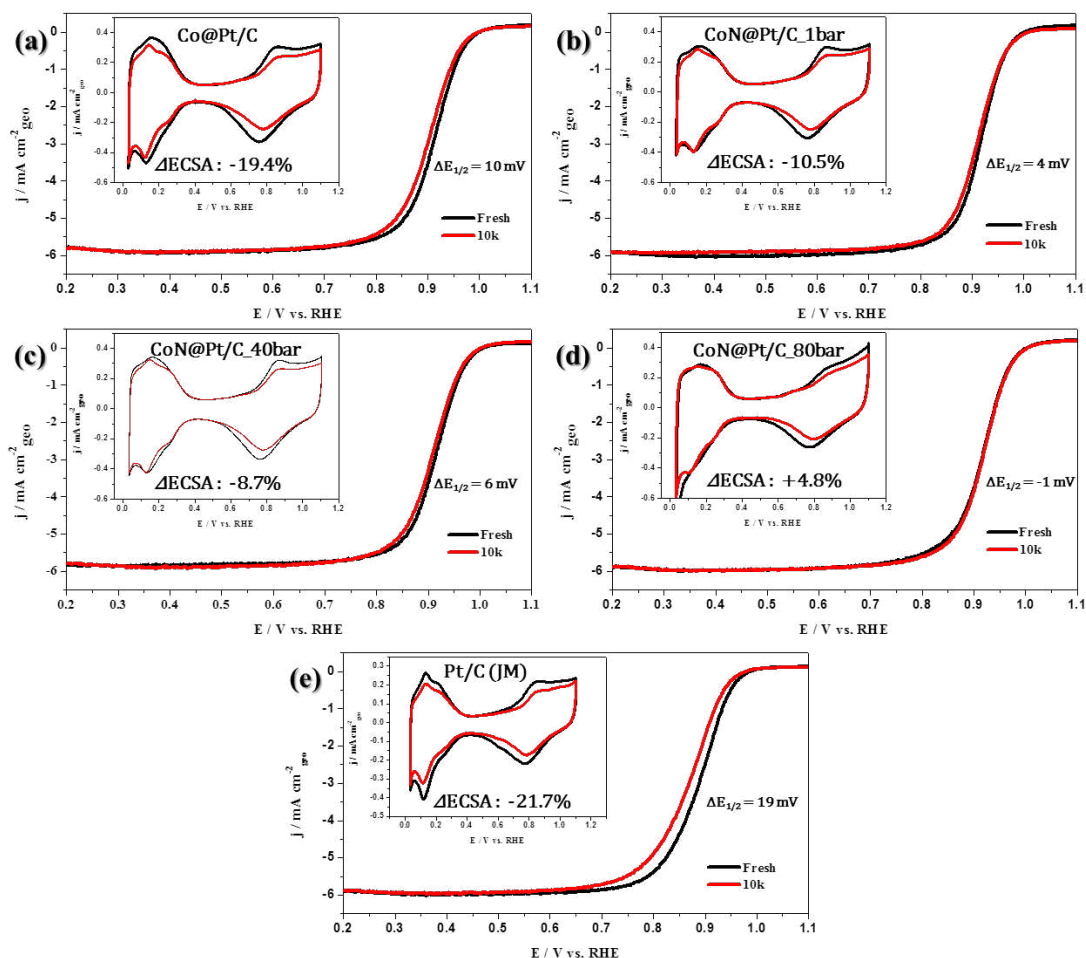


Figure 5. LSV curves of samples before and after accelerated stress test (AST) 10k in O_2 -saturated 0.1 M HClO_4 . Inset showed the CVs before and after AST 10k.

The durability of samples was investigated by using DOE's AST protocol. We evaluated the durability of samples based on the changes in ECSA and the $\text{E}_{1/2}$. As shown in Figure 5, ECSA loss of samples was 19.4% for Co@Pt/C which is very similar to that of Pt/C (21.7%). Interestingly, we found that ECSA increased for the highest N concentrated core-shell catalyst. In addition, the $\Delta\text{E}_{1/2}$ of CoN@Pt/C samples is much decreased compared to Co@Pt/C. It indicated that the N concentration is directly proportion to the durability within three CoN@Pt/C samples. Adzic et al. reported that the N atom in the nickel nitride core induces the migration of inner Pt atoms into defect site on the surface of NP and the higher N concentration leads easier diffusion of Pt atoms(4). Our result can be a direct proof for the hypothesis of the Adzic's.

Conclusion

Non-noble metal cored Pt-skin electrocatalyst were synthesized. By controlling the N concentration for the cobalt core of the core-shell catalyst prepared through the sonochemical method, the durability as well as the activity increased to a great extent. The N level could be controlled via alternating the pressure of ammonia during thermal treatment. Electrochemical analysis reveals that samples with elevated nitriding level show much little changes in ECSA and ORR, indicating the improved durability which is comparable to the noble-metal-cored electrocatalysts. Based on our result, it's confirmed that low-cost transition metals can be used as core material via controlling the nitriding level for the commercial-ready electrocatalyst of PEFCs.

Acknowledgments

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Enhanced Oxygen Reduction Reaction Activity on Pt-Monolayer-Shell PdIr/Ni-core Catalysts

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Platinum monolayer oxygen reduction reaction catalysts present promising way of reducing the Pt content without sacrificing its fuel cell performance. Here, we present a facile way of preparing Pt monolayer shell PdIr-based core catalysts, which showed much higher activity for oxygen reduction reaction than that of TTK 46.6% Pt/C catalyst. Among tested samples, PtMLPd2Ir/Ni/C performs the best with Pt and Platinum Group Metal mass activity around 9 and 0.25 times higher of that of TTK 46.6% Pt/C. In addition, accelerated aging test indicates its excellent durability.

Introduction

Proton exchange membrane fuel cell (PEMFC) is promising power source for automobiles and other mobile applications of all sizes, because of its compactness, low temperature operation conditions, high energy generation efficiency and negligible impacts on the environment¹⁻³. However, among many technical difficulties and challenges, the most significant one is low reaction rate towards oxygen reduction reaction (ORR)^{4, 5} on the cathode, even on Pt - the best ORR catalyst, requiring high Pt loading and thus making PEMFC costly^{6, 7} for widespread commercial application. An effective way of reducing Pt content is by designing a core-shell-structured catalyst where core is made of less expensive but corrosion stable noble metals or alloys while the shell is made of Pt monolayer (PtML). In addition, the catalytic properties of the Pt monolayer catalysts can be tuned through its interaction with the substrate core⁸.

Pd, a Pt-group metal (PGM), has similar lattice constants and chemical reactivity as Pt. Pd and its alloys nanoparticles have been proved to be suitable substrates for Pt monolayer ORR catalysts⁸ because of preventing the corrosion of Pt by sacrificing Pd^{9, 10} and their beneficial influence on Pt monolayer ORR activity^{8, 9, 11}. Alloying Pd with Ir enhances the durability of the Pd core due to the high standard redox potential of Ir ($\text{Ir}^{3+}/\text{Ir} = 1.16\text{V}$). In addition, the ORR activity of Pt_{ML} on PdIr alloy and structured nanoparticles increases due to significant decrease of the d-band center caused by contraction of Pt lattice imposed by the substrate¹²⁻¹⁴.

To make this catalyst commercially viable, in this work we utilized Ni as a sub-core of PdIr nanoparticles to lower the Pd and Ir content in the core. The Ni was chosen due to its similar electronic properties with Pd and Ir and its ability of alloying with them^{12, 15-17}. Pt monolayer on PdIr/Ni core catalysts with different Pd and Ir contents were prepared. Their ORR activities were examined and compared to the ORR activity of Pt monolayer on PdIr core. Additionally, their durability was tested by accelerated protocol consisting of 30,000 potential cycles between 0.6V and 1.0V (RHE).

Experimental

Materials and chemicals

The Vulcan XC72 carbon black was purchased from Cabot. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Pd}(\text{NO}_3)_2$, K_2IrCl_6 , and citric acid were purchased from Sigma-Aldrich without further purification. Ar (99.999%), O_2 (99%), and H_2 (99%) gases were purchased from Praxair. All aqueous solutions and suspensions used in this study were prepared using Millipore ultrapure ($18\text{M}\Omega$) water.

Preparation of PdIr/Ni/C and PdIr/C

The carbon supported PdIr-alloy shell/Ni core nanoparticles (PdIr/Ni/C) were synthesized through a facile two-step reduction/displacement method. In the first step, carbon-supported Ni nanoparticles were prepared by mixing 0.2mmol $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 2mmol citric acid, and 30mg Vulcan VX-72C Carbon black in 20ml water. 0.05M KOH aqueous solution was used to adjust the pH to 8~9. The mixture was purged with Ar, cooled in ice bath and sonicated for 10min before adding 20ml 0.1M NaBH_4 (reducing agent) solution. After sonicating for 2h, the Ni^{2+} ions were completely reduced to form carbon-supported Ni particles (Ni/C) and the excess of NaBH_4 was decomposed. In the second step, mixture of 0.05M $\text{Pd}(\text{NO}_3)_2$ and 0.05M K_2IrCl_6 solutions with desired atomic ratio was added to galvanically displace the surface layers of Ni nanoparticles and form Ni-core PdIr-shell structured nanoparticles (denoted as Pd2Ir/Ni/C and PdIr2/Ni/C). The Pd2Ir/C nanoparticles were synthesized by mixing carbon black, citric acid, and the appropriate atomic ratio of Pd^{2+} and Ir^{4+} precursors. This mixture was purged with Ar and sonicated in ice bath. Then Pd^{2+} and Ir^{4+} ions were reduced with excessive amount of NaBH_4 . The final PGM metal loadings for PdIr2/Ni/C, Pd2Ir/Ni/C, and Pd2Ir/C are 30 wt.%, 36 wt.%, and 40 wt.%, respectively.

Preparation of electrodes with PtML ORR electrocatalysts

A PtML ORR electrocatalyst was prepared through applying underpotential deposition methodology described elsewhere⁸⁻¹⁰. First, glassy carbon rotating disk electrode (RDE) was coated with thin film of PdIr/Ni/C (PdIr/C) nanoparticles by placing 10 μL of ink which was prepared by dispersing 2mg of PdIr/Ni/C (PdIr/C) in 2mL of water : iso-propanol = 3:1 mixture with 0.05 vol.% Nafion[®] (perfluorinated resin, equivalent weight 1000, Aldrich) and drying in air. Then, electrode was immersed into de-aerated solution containing 50mM CuSO_4 and 50mM H_2SO_4 and Cu monolayer was deposited on the PdIr/Ni (PdIr) through under potential deposition (UPD)¹⁴. After that, electrode was immersed in de-aerated Pt solution (1mM K_2PtCl_4 + 50mM H_2SO_4) for few minutes to completely displace the Cu monolayer with Pt. Finally, the electrode with PtML catalysts was rinsed with water. The overall synthesis process is schematically shown in Fig. 1.

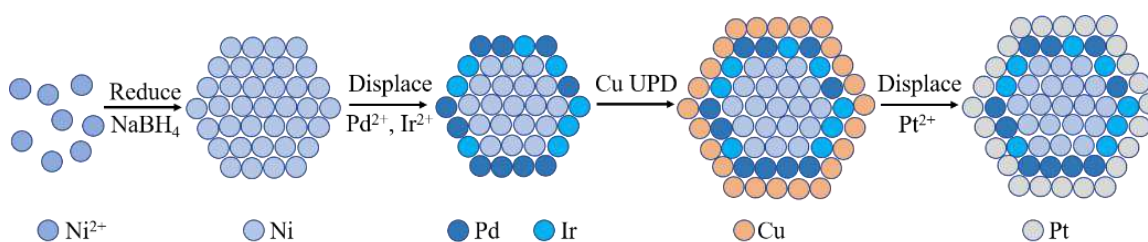


Figure 1. Schematic procedure of synthesizing PtML catalyst on Ni-core/PdIr-shell nanoparticles.

Physical characterization

Scanning Electron Microscopy (SEM) Hitachi S-3400N equipped with an Ametek Apollo X EDAX was used to determine the relative atomic and weight percentage of each element in the catalysts. This was used to calculate the PGM mass activity.

For the transmission electron microscopy (TEM) measurements, the JEOL TEM-1400 equipped with a LaB6 electron source with a maximum accelerating voltage of 120KeV and JEOL TEM 2100F equipped with a Schottky field-emission gun and an energy dispersive x-ray spectrometer for chemical analysis were used at Center for Functional Nanomaterials at Brookhaven National Laboratory. The samples for TEM were prepared by dispersing 1 mg carbon supported nanoparticles in 10 mL an ethanol : water = 4:1 mixture (by volume). Then 3 μL of this dispersion was deposited on a carbon covered copper grid (EMS, Hatfield, PA). All TEM images were recorded with a slow-scan CCD camera.

X-ray diffraction measurement of the PdIr/Ni/C nanoparticles were carried out on Rigaku Miniflex II using Cu $K\alpha$ radiation with a wavelength of 1.5406 Å. The diffraction patterns were collected from 30° to 75° at a scanning rate of 1° per minute with a step size of 0.02°.

Electrochemical characterization

The electrochemical setup consisted of a computer-controlled BioLogic potentiostat (VSP) and Pine Instruments Company RDE setup with a rotating disk electrode made of 5mm diameter glassy carbon electrode (GCE). A typical three-electrode electrochemical cell was used to carry out the electrochemical measurements, in which a catalyst-covered GCE is used as working electrode, a Pt-flag as counter electrode, and an Ag/AgCl, connected via salt bridge, as a reference electrode. All the potentials presented in this work are quoted versus a reversible hydrogen electrode (RHE). The cyclic voltammetry was obtained in Ar-saturated 0.1M HClO_4 at a scanning rate of 20mV/s in the potential range of 0.05 to 1.1V vs. RHE, while the polarization curves for ORR were recorded in O_2 -saturated 0.1M HClO_4 at a scanning rate of 10mV/s and rotating speed of 1600rpm in potential range of 0.1-1.1V vs. RHE. Accelerated durability tests (ADT) were carried out under air atmosphere (naturally oxygenated solution) for 30,000 cycles at scanning rate of 50mV/s between 0.6V and 1.0V.

Results and discussion

Physical characterization

TEM images (Fig.2 (a)-(c)) and size distribution (Fig.2 (d)-(f)) of as-prepared Ni-core/PdIr-shell and PdIr nanoparticles were obtained to better understand the influence of the core on the catalytic performance of the PtML ORR electrocatalysts. Generally, the particles are round in shape with an average size of 5.1 nm for PdIr₂/Ni/C, 4.4nm for Pd₂Ir/Ni/C, and 2.5nm for PdIr₂/C nanoparticles. High resolution TEM images of these nanoparticles were also obtained (Fig. 3).

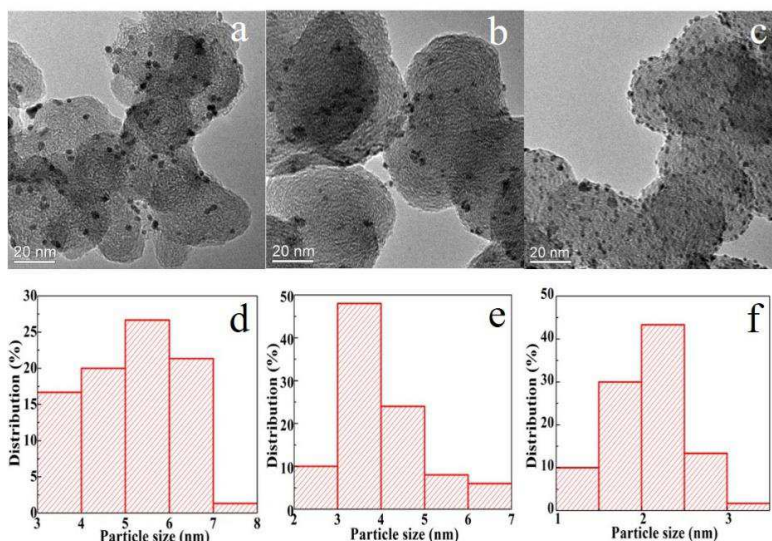


Figure 2. TEM image and size distribution of PdIr₂/Ni/C (a, d), Pd₂Ir/Ni/C (b, e) and PdIr₂/C (c, f) nanoparticles.

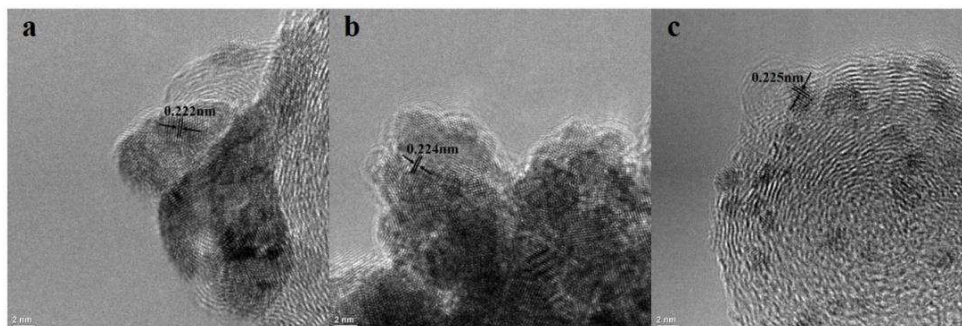


Figure 3. High resolution TEM images of as-prepared (a) PdIr₂/Ni/C, (b) Pd₂Ir/Ni/C, and (c) PdIr₂/C nanoparticles.

Since Ni has smaller atomic radius than Pd and Ir, the Ni sub-core helps reducing the interplanar spacing of the PdIr-shells as evidenced from Fig. 3. The interplanar spacing of the PdIr₂/Ni/C, Pd₂Ir/Ni/C and PdIr₂/C nanoparticles were measured to be 0.222nm, 0.224nm and 0.225nm, respectively, which are all smaller than that of Pt (111) plane (0.227nm), indicating the ability of the core to induce favorable compressive strain on the Pt monolayer catalyst to enhance its ORR activity^{10, 18}.

XRD pattern for Pd₂Ir/Ni/C nanoparticles was shown in Fig. 4. Diffraction peaks for pure Pd and pure Ir were not observed. However, there is a diffraction peak at 40.82° positioned between pure Pd (40.42°) and pure Ir (40.99°) indicating existence of PdIr alloy. Ni diffraction peaks were also observed and slightly shifted to the lower angles comparing with pure Ni. This results from small compression of Ni core due to their

small sizes, which was calculated to be ~ 5 nm from Scherrer Equation and was in good accordance with the sizes of Pd₂Ir/Ni/C nanoparticles observed in TEM (Fig. 2(b)).

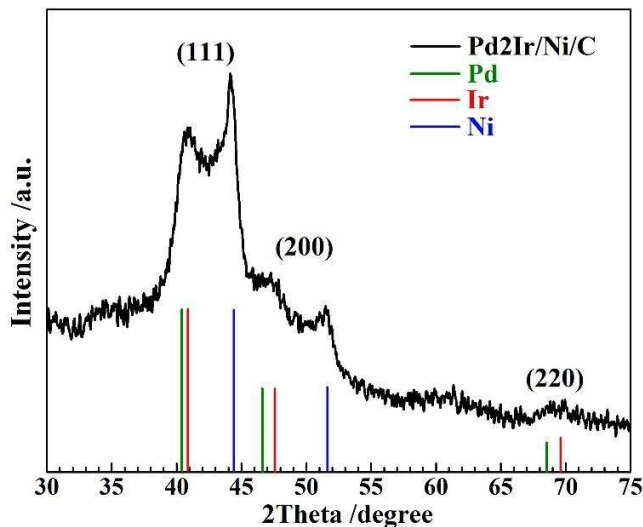


Figure 4. XRD pattern of Pd₂Ir/Ni/C nanoparticles. The colored lines represent the standard (hkl) reflection lines of Pd, Ir, and Ni.

Electrochemical characterization PdIr/Ni/C and PdIr/C

Fig. 5 shows the cyclic voltammetry of the as-prepared PdIr-based nanoparticles. Since no anodic/cathodic currents that can be ascribed to the oxidation/dissolution of Ni were observed indicates the inaccessibility of Ni core to the electrolyte solution thus demonstrating the protection of the Ni core by the PdIr shell. The presence of both Pd and Ir on the surface of the as-prepared PdIr-based nanoparticles is evident from their behavior in the H-upd region. The characteristic behavior of both Ir/C and Pd/C can be noticed with relative contribution of Pd and Ir depending on Pd/Ir ratio¹⁴. Since positions of characteristic features of Pd and Ir are not changed, suggests that their behavior in the H-upd region is independent of each other. However, surface oxidation of PdIr-based catalysts occurs in potential region between the Ir/C and Pd/C indicating interaction between Pd and Ir atoms.

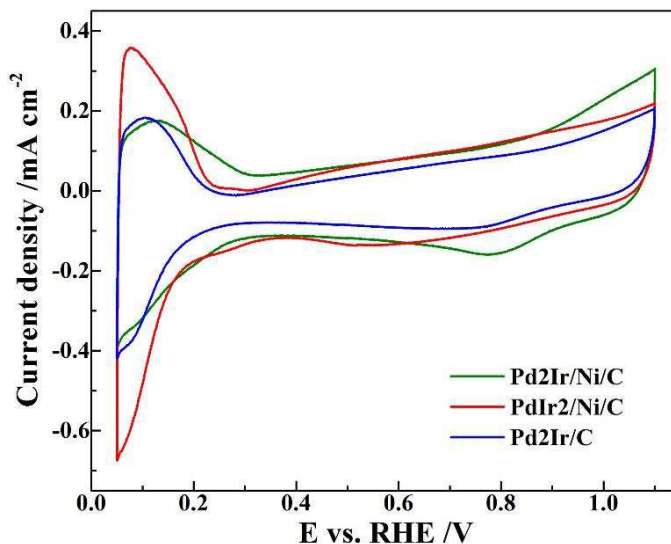


Figure 5. Cyclic voltammetry of the as-prepared Pd₂Ir/Ni/C (green line), PdIr₂/Ni/C (red line) and Pd₂Ir/C (blue line) nanocatalysts.

Electrochemical characterization PtML ORR electrocatalysts

Fig.6 shows the CVs of Pt monolayer on PdIr-based cores catalysts and Pt/C for comparison. Similarity of the CVs of the tested samples with the one for Pt/C in H-upd region indicates that the cores are covered with PtML. PtML deposited on PdIr-based cores is under compression, as indicated by TEM experiments, since Pd, Ir, and Ni have smaller atomic radius compared to the one of Pt. Based on DFT calculations^{8,9,11}, d-band center of such compressed PtML will shift down compared to Pt/C and as a result Pt-OH interaction will weaken. This can be observed in CVs of Pt monolayer on PdIr-based cores samples where oxidation of PtML is postponed compared to Pt/C as evidenced by positive shift of Pt-OH reduction peak.

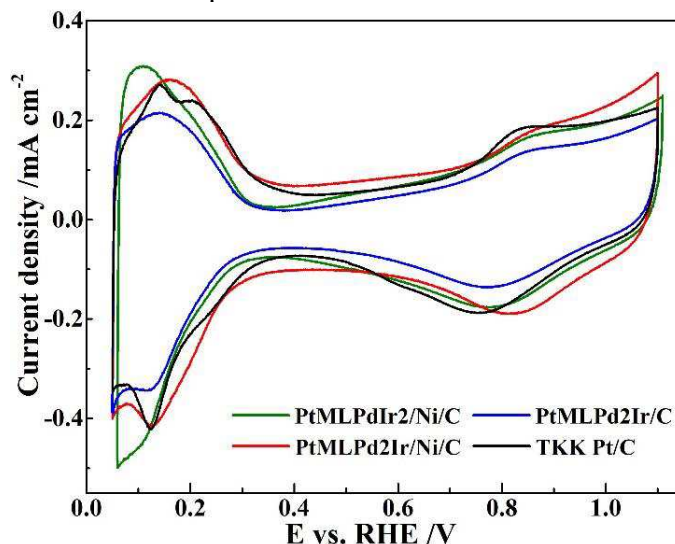


Figure 6. Cyclic voltammetry of PtMLPdIr2/Ni/C (green), PtMLPd2Ir/Ni/C (red), PtMLPd2Ir/C (blue), and TKK Pt/C (black) catalysts in Ar-saturated 0.1M HClO₄ solution.

ORR Study

Rotating disk electrode technique was used to examine ORR catalytic activities of studied catalysts. Fig.7 shows the polarization curves for ORR on the Pt monolayer covered PdIr-based nanoparticles and commercial TKK Pt/C catalysts for comparison. It can be noticed that values for half-wave and onset potentials of examined samples are quite close, Fig. 7 inset. However, since onset and half-wave potentials are only indicators of ORR activity but not true measures of it, trends in the ORR activity were analyzed by comparing Pt and PGM mass activities obtained at 0.9 V, Fig. 8. The Pt mass activity decreases in the following sequence: PtML/Pd2Ir/Ni/C > PtML/Pd2Ir/C > PtML/PdIr2/Ni/C > Pt/C, while the PGM mass activity decreases in the following sequence: PtML/Pd2Ir/Ni/C > Pt/C > PtML/Pd2Ir/C > PtML/PdIr2/Ni/C. DFT calculations and experimental results showed that slightly compressed PtML catalyst has better ORR activity than bulk Pt^{8,9,11} due to reduced interaction between Pt and oxygen containing species. However, relation between an increase in compression of PtML and an increase in Pt Mass activity of studied samples is not linear but volcano-type with PtMLPd2Ir/Ni/C at the top. This indicated that there is an optimal value of PtML compression since volcano-type behavior is a result of two opposing trends: O/OH hydrogenation activity and O-O bond scission activity.

The relationship between PGM mass activities of PtML on PdIr-based cores catalysts remains volcano-type, however, the Pt/C moves in to the second place among PGM mass activities. This is a consequence of the difference between Pt and PGM mass activities and that kinetic currents for PtML covered PdIr-based catalysts is not large enough to compensate for the additional mass of Pd and Ir used in PGM mass activities.

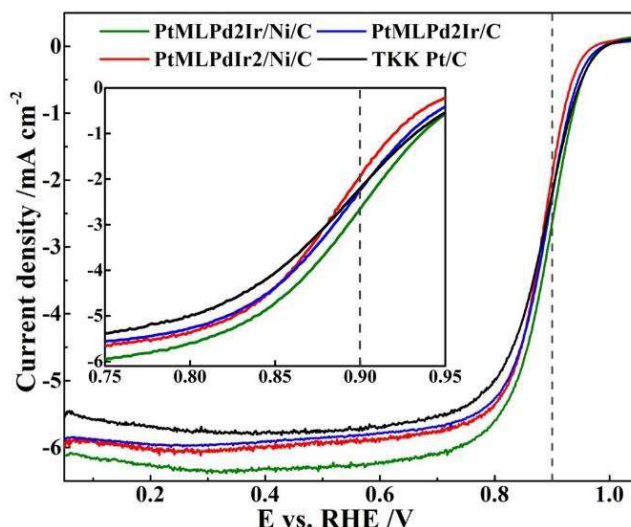


Figure 7. Polarization curves for the PdIr-based nanoparticles with Pt monolayer and commercial TKK Pt/C catalyst obtained in O₂-saturated 0.1M HClO₄ solutions in a range of 0.1-1.1V vs. RHE at a scanning rate of 10mV/s before (a) and after (b) 30,000 cycles.

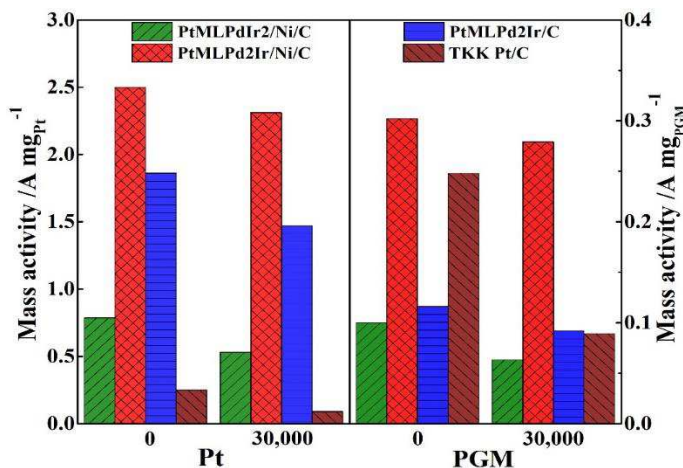


Figure 8. Pt and PGM mass activities of PtML on PdIr-based cores and commercial TKK Pt/C catalysts.

Accelerated Durability Test

Durability of the PtML on PdIr-based cores and Pt/C catalysts was examined by potential cycling between 0.6V and 1.0V for 30,000 cycles in 0.1M HClO₄ at a scan rate of 50mV/s. Fig.9 shows the CVs of studied catalysts before (blue) and after (red) durability test. It can be noticed that electrochemical surface area of all catalysts is reduced, but that reduction is smaller for PtML on PdIr-based core samples compared to Pt/C. This is reflected in better retention of Pt and PGM mass activities of PtML on PdIr-based core samples compared to Pt/C, Fig. 8. Relative loss in PGM activities presented in Table I show that PtMLPd2Ir/Ni/C lost 7.6% compared to 64.4% for Pt/C.

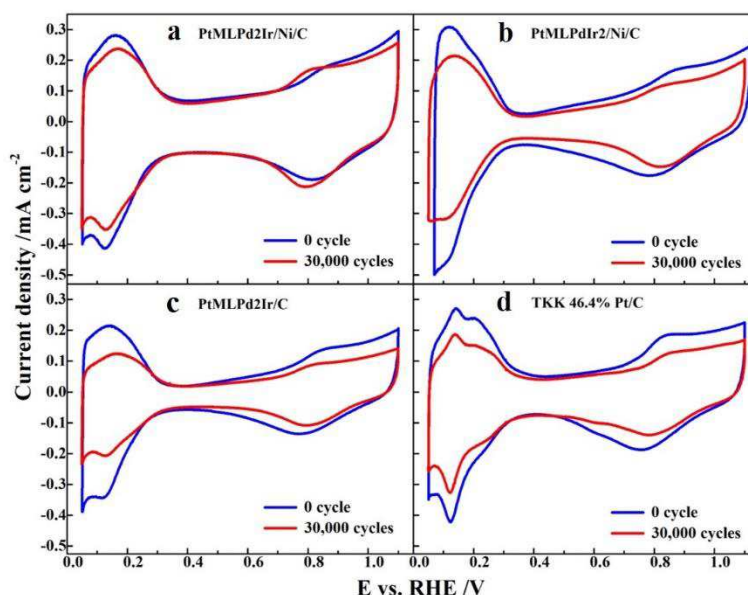


Figure 9. Cyclic voltammetry of (a) PtMLPd2Ir/Ni/C, (b) PtMLPdIr2/Ni/C, (c) PtMLPd2Ir/C, and (d) TKK 46.6% Pt/C nanocatalysts before (blue) and after (red) 30,000 cycles.

TABLE I. PGM mass activities of PtML on PdIr-based and TKK Pt/C catalysts before and after ADT cycling.

Cycle(s)	PtMLPd2Ir/Ni/C	PtMLPd2Ir/C	PtMLPdIr2/Ni/C	TKK 46.6% Pt
0	0.303	0.116	0.100	0.25
30,000	0.280	0.092	0.063	0.089
Loss (%)	7.6	20.7	37	64.4

Conclusions

This work describes an easy two-step reduction/displacement method to synthesize PdIr nanoparticles with Ni as sub-cores as substrates for PtML ORR electrocatalysts. All the PtML on PdIr-based cores catalysts showed higher Pt mass activity than that of TKK 46.6% Pt/C due to the contraction of PtML. They also showed better durability compared to Pt/C. Among these catalysts, the PtMLPd2Ir/Ni/C catalyst showed the best Pt and PGM mass activity of 2.5 and 0.303 A/mg respectively. After durability test, it lost 7.6% of initial PGM mass activity compared to 64.4% for Pt/C. This indicates that PtMLPd2Ir/Ni/C catalyst is a potential candidate for cathodic catalyst in PEMFCs.

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Highly Dispersed Carbon Supported PdNiMo Core with Pt Monolayer Shell Electrocatalysts for Oxygen Reduction Reaction

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Abstract

The development of low-cost, durable, and high-performance materials that could substitute for the current platinum-based electrocatalysts would accelerate the commercialization of polymer electrolyte membrane fuel cells as an alternative power source. We report herein a new fabrication approach of carbon-supported platinum monolayer (ML) on ternary palladium-nickel-molybdenum core electrocatalysts (Pt_{ML}/PdNiMo/C) by a sonochemical method using ionic liquid (IL) as a dispersion medium. The sonolysis technique can control the size and distribution of the ternary-metal nanoparticles on different carbon supports without addition of any external reducing agents, surfactants or capping agents. Depositing Pt MLs using under-potential deposition method on the ternary PdNiMo nanoparticle cores could enhance activity and durability of the cathode during the oxygen reduction reaction of the fuel cell. Herein, we show that the described sonolysis method produces more reliable and cost-effective electrocatalysts that outperforms a commercial Pt-based catalyst.

Introduction

It is widely known that electrochemical energy conversion and storage systems such as fuel cells, electrolyzers and supercapacitors can serve as viable paths to energy sustainability. However, the low performance and high cost of most of these systems remain a major obstacle for their full commercialization. The performance of these systems depends largely on the properties of the materials used in the electrode, which is one of the most vital components (1). In proton exchange membrane fuel cells (PEMFCs) that use hydrogen as a fuel, platinum (Pt) has been the dominant choice for both the cathode and the anode, but the high cost and content of Pt particularly at the cathode resulting in sluggish oxygen reduction reaction (ORR) and poor stability, are some of the challenges facing its commercial viability (2). Therefore, the most recent research effort is focused on reducing the Pt content through synthesis of Pt-based alloys and Pt core-shell electrocatalysts.

Several techniques to fabricate electrocatalysts and their support materials for fuel cell applications have been developed. Most of these techniques have inherent limitations such as high costs, severe synthesis conditions involving high vacuum and high temperature, long durations, and safety issues. The synthesis of metal/bimetal nanoparticles (NPs) on carbon supports have been widely studied; several synthetic methods have emerged, such as chemical reduction (2-7), electrochemical reduction (4, 8), photochemical reduction (4), microwave (1, 8), gas-phase sputtering (8), and physical vapor deposition (4, 8). In most chemical methods, the use of some reducing agents or solvents makes the process unacceptable due to the associated environmental problems for mass production. Most other methods are either too expensive or have other mass production issues.

Recently, a sonochemical technique, which utilizes a cavitation phenomenon induced by irradiation of high-intensity ultrasound, has been paid attention as a facile method to synthesize various forms of NPs. Suslick *et al.* synthesized monometallic and bimetallic nanoparticles by high intensity ultrasound at low temperatures (9). The bimetallic NPs in which they have synthesized have various forms including solid solution, core-shell, and segregated two-phase structures. However, the stability of the bimetallic nanomaterials seemed unsatisfactory. Mizukoshi *et al.* (10) reported the preparation of Au@Pd core-shell NPs by sonochemical reduction, simultaneously applied in an aqueous solution containing Au^{3+} and Pd^{2+} ions, and the thickness of a Pd shell and the size of Au core may depend on the ratio of added concentration of the ions.

As for ternary NP synthesis, the formation of solid solution alloys were not guaranteed due to many factors such as different reaction kinetics and surface free energies of the metals that contribute to the final product formation. When an immiscible mixture of metals is used, alloy formation is unlikely, and the formation of core-shell, fused cluster, and NPs depend on the reaction kinetics and surface interactions with the surrounding medium (10). Other researchers such as Manthiram *et al.* (11) and Yoon *et al.* (12) prepared PdMo electrocatalysts for the methanol oxidation reaction and the oxygen reduction reaction in fuel cells, respectively. The synthesis methods used were either thermal decomposition of palladium acetylacetonate and molybdenum hexacarbonyl precursors at very high temperatures or by hydrothermal decomposition in different pH. In these studies, the high temperature used during synthesis resulted in large sized nanoparticles and moderate stability of the final products in alkaline media, but highly unstable in acidic media of PEMFC. Furthermore, since one of the primary functions of electrodes is to convert ionic conductivity into electrical conductivity; electrode

materials should have intrinsic properties. Ionic liquids use in synthesis has achieved that objective as presented by Dupont and coworkers (3, 13) in their studies on synthesis of transition metal nanoparticle catalysts in which they generated small size nanoparticles, with narrow size distribution and different shapes.

Janiack (8) provided a comprehensive review on the synthesis and stabilization of metal nanoparticles, while Kraynov and Muller (4) investigated the stabilization mechanism through modeling. None of these studies pointed out that produced electrocatalysts with good stability for electrochemical applications, used mild or green solvents. Recently, we described sonochemical synthesis of metal alloy nanoparticles in different solvents as electrocatalysts with improved catalytic activity (14). In the study, we observed that ionic liquid and solvents used have significant influence on the size, shape and dispersion of synthesized nanoparticles. Based on our previous work, we developed ternary PdNiMo alloy nanoparticles to provide a stable core support for Pt monolayer electrocatalysts.

2. Experimental

2.1. Materials

Molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$), palladium acetylacetonate ($\text{Pd}(\text{acac})_2$), bis(1,5-cyclooctadiene)nickel ($\text{Ni}(\text{COD})_2$), benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$) were purchased from Sigma Aldrich, while an ionic liquid (IL), tributyl-methyl phosphonium bis(trifluoromethylsulfonyl)imide (TBPh Tf_2N) was purchased from Iolitec Inc.

2.2. Sonochemical synthesis of PdNiMo nanoparticles on IL functionalized carbon.

60 mg of Vulcan XC72R carbon was mixed with 15 ml of TBPh Tf_2N , and the mixture was ground using a motor for 20 min to form a black paste. The paste was centrifuged twice at

9000 rpm for 30 min to separate the carbon from IL. The resulting paste was washed thoroughly with a 1:1 ratio of acetonitrile and deionized (DI) water before drying in a vacuum oven at 40°C for 2 days. The recovered IL was recycled twice in subsequent paste preparation. The IL functionalized carbon (236 mg) was placed in 70 ml of ethanol / DI water (1:1) solvent. Previous studies have shown that addition of benzoic acid acts as a modulator to promote the formation of defects that can enhance the reactivity of materials (15, 16). Therefore, 1 g of benzoic acid was added to the solution to promote the yield and Ni deposition. The slurry was purged with N₂ gas for 20 min, and Pd(acac)₂, Ni(COD)₂, and Mo(CO)₆ precursors were added to the slurry. The total metal loading was 30 wt-%. The solution was purged again with N₂ gas for 10 min before sonolysis. The sonochemical treatments were carried out using an ultrasonic liquid processor Misonix 3000 with variable power up to 200 W at a fixed frequency of 20 kHz. The sonolysis processes were monitored through carbon monoxide (CO) gas evolution, and the power of 81W was on average required at 40 °C for 0.5 h to achieve full decomposition of the metal precursors. The collected gas during sonolysis was analyzed using Gow-Mac 580 gas chromatograph fitted with a molecular sieve column under helium flow. We noted that inert nitrogen gas, carbon monoxide from carbonyls and some from the IL, contributed to the observed gases from analysis.

The product was separated by centrifugation, washed two times with acetone and deionized water, and dried in a vacuum oven at 40 °C for 24 h. The carbon-supported PdNiMo NPs were then annealed at 200 °C in a 5% H₂/Ar gas for 3 h.

2.3. Electrochemical measurements

Electrochemical measurements were carried out with a Biologic potentiostat and a three-electrode cell. The PdNiMo/C electrocatalyst was dispersed in a water/isopropyl alcohol mixed solution by sonication to give a content of 1 mg/ml. A catalyst ink/dispersion was dropped on a

glassy carbon rotating disk (RDE) electrode as the working electrode. The electrode was then covered by a small amount of a Nafion solution (5 μL of 4 $\mu\text{g}/10 \mu\text{L}$) and dried in air. We deposited Pt monolayer on the prepared PdNiMo/C surfaces using the galvanic displacement of Cu layer formed by Cu under-potential deposition (UPD) (17). A Pt wire was used as a counter electrode, and Ag/AgCl/KCl (3M) electrode with double junction as a reference electrode. All potentials presented are quoted versus a reversible hydrogen electrode (RHE). Cyclic voltammograms (CVs) were recorded between 0.0 to 1.1V with a scanning rate of 20 mV s^{-1} in an Ar-saturated 0.1 M HClO_4 solution. ORR polarization curves were recorded using the RDE in O_2 -saturated 0.1 M HClO_4 electrolyte at rotation rates from 400 to 2500 rpm at a sweep rate of 10 mV s^{-1} . Stability tests for the electrocatalysts were conducted in air-saturated 0.1 M HClO_4 , with a potential range between 0.6 and 1.0 V at a sweep rate of 50 mV s^{-1} at room temperature for 8,000 cycles. A commercial E-TEK Pt/C catalyst with a particle size of 3.2 nm was used for comparison.

2.4 Characterization

The Hitachi aberration-corrected scanning transmission electron microscope (STEM), equipped with a high resolution Gatan Enfina electron energy loss spectrometer (EELS) at the Center for Functional Nanomaterial (CFN), Brookhaven National Laboratory (BNL), was used to characterize the PdNiMo/C electrocatalysts. The STEM imaging and EELS data were collected using 1.3 Å electron probe with a probe current of 50 pA. The STEM convergence and collection angles were 28 mrad and 114 - 600 mrad respectively. The contrast of the images directly related with atomic number (Z-contrast), while the EELS energy of resolution was about 0.4 eV as estimated from the half width of zero loss peaks.

Ex situ XRD experiments were performed at the XPD beamline at NSLS-II. The XRD spectra were recorded using a 2D detector (Perkin Elmer XRD 1621 N ES) at 12.4 keV and subsequently processed using standard data processing software. The dark current and the diffraction pattern were collected over 40 seconds (10 exposures at 4 s each) and the diffraction pattern was recorded over 400 seconds (100 exposures at 4 s per exposure). The wavelength of X-ray used was 0.18351 Å.

X-ray absorption spectroscopy (XAS) measurements were undertaken at the BL 2-2 beamline at the Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator Laboratory. The *ex situ* measurements were carried out at the Pd K edge (24350 eV), Mo K edge (20000 eV) and Ni K edge (8333 eV) at room temperature. The XAS data were acquired in both the transmission and fluorescence modes. The data acquired were processed and analyzed by Athena and Artemis software (18).

3. Results and discussion

3.1 Morphology and Structure

Figure 1 shows the high angle annular dark field (HAADF) HRTEM images of the PdNiMo/C nanoparticles, which are almost spherical with a mean particles size of 4.1 nm. As shown in Figure 1a, most of the nanoparticles were between 2.5 nm and 6 nm in size. The IL introduces a large number of active sites on the carbon surfaces for the initiation and growth of nanoparticles (19). The physical interactions of the IL with surfaces of carbon not only serve as dispersion and functionalization agents but also allow the metal precursors to interact electrostatically with the IL ions (*i.e.* TBPh Tf₂N anions) that need to bond to the surfaces of the carbon material (20). Thus, it is considered that the IL used for the functionalization of carbon

provides ideal templates for the deposition and dispersion of PdNiMo nanoparticles. The composition of the PdNiMo nanoparticles was identified by energy dispersive X-ray (EDX) measurements. The Pd, Ni and Mo contents were 19 wt-%, 7 wt-% and 4 wt-% respectively. We note that the composition of prepared PdNiMo nanoparticles can be controlled by changing the ratio of concentrations of the precursors.

A comparison of the EELS intensities (Figure 1d) for the Pd M-edge, Ni L-edge and Mo L-edge on a PdNiMo nanoparticle was obtained by moving the electron probe along the line indicated in Figure 1c (we note on the arbitrary scales of the y axis). The intensities of both Mo and Ni are the highest around $x=3.8$ nm and become lower toward to both edge of the nanoparticle, while the intensity of Pd shows a more uniform distribution over the particle compared with other two elements.

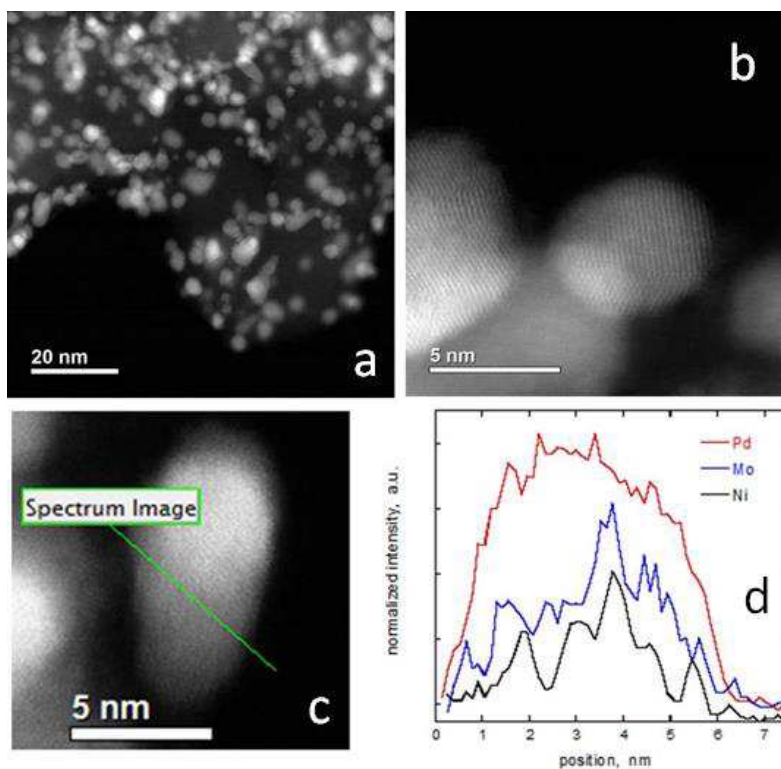


Figure 1. (a, b) HAADF-STEM images of PdNiMo nanoparticles. (d) EELS line-scan profiles of Pd M edge, Mo L edge, and Ni L edge scanned along the line as indicated in (c) HAADF-STEM image of a single nanoparticle.

The synchrotron XRD pattern of the PdNiMo /C catalysts is shown in Figure 2. The average particles diameter calculated from the Pd(1 0 0) peak using the Scherrer equation was 4.4 nm, which is in line with the result from HAADF-STEM observation. No clear individual peaks for Ni and Mo were observed on the XRD pattern. As discussed below, Ni and Mo are present as a form of oxides.

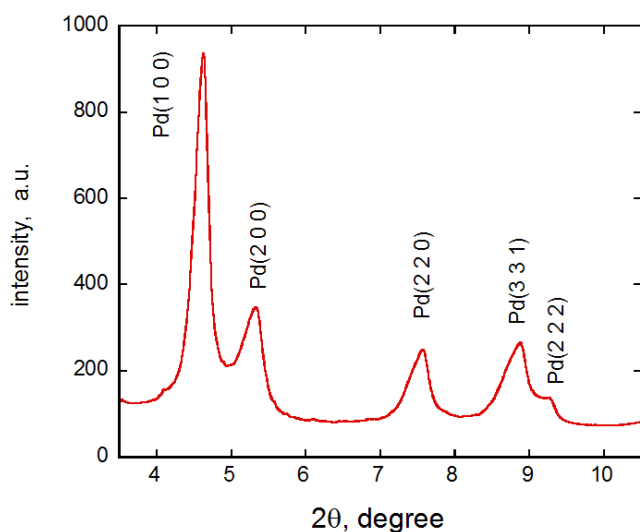


Figure 2. Synchrotron XRD pattern of PdNiMo/C. Wavelength: 0.1825 Å.

Figure 3 shows *ex situ* X-ray absorption near-edge structure (XANES) and the Fourier transformed (FT) extended X-ray absorption fine structure (EXAFS) spectra of the Pd K edge (24350 eV) (a, b), the Ni K edge (8331 eV) (c, d), and the Mo K edge (20000 eV) (e, f) from PdNiMo/C, together with their reference foils and oxides. Fig. 3a shows a slight difference between the Pd K edge XANES spectra from PdNiMo/C and a Pd foil. The intensity of the first peak of PdNiMo/C is a little lower than that of the foil, and thus the difference is not due to

oxidation of Pd in PdNiMo/C, but is caused by a change in the *d*-band electronic state in Pd due to the presence of Ni and/or Mo atoms (21). The FT EXAFS spectrum of Pd K edge from PdNiMo/C (Fig. 3b) is also dissimilar to that of the foil. In addition, in the spectrum in *k*-space from PdNiMo/C (Fig. S2), the phase in oscillation is slightly shifted compared with that from the foil (at $4 < k < 13 \text{ \AA}^{-1}$); these two spectra represent alloying of Pd with Ni and/or Mo to some degree. The Ni K edge XANES spectrum from PdNiMo/C (Fig. 3c) shows a strong white line signal at 8350 eV, which indicates the formation of Ni oxide in the PdNiMo nanoparticles. The FT EXAFS spectrum of Ni K edge from PdNiMo/C (Fig. 3d) is similar to that of NiO. The XANES spectrum of Mo K edge from PdNiMo/C (Fig. 3e) is different from that of Mo foil. It shows a distinctive pre-edge peak, and a similar pre-peak is also seen in the spectrum of ammonium molybdate ((NH₄)₂MoO₄). Such a pre-peak is known to be the characteristic Mo(VI) species as a result of the dipole forbidden $1s \rightarrow 4d$ transitions (22), thus the oxidation state of Mo in PdNiMo/C could be 6. We note that similar XANES spectra of Ni and Mo K edges have been observed in NiMo nanoparticles synthesized by annealing in H₂ at 400 °C in our previous study (23). We interpreted that the NiMo nanoparticles could have oxidized promptly after the annealing step. The annealing temperature for this study was 200°C in a 5% H₂/Ar gas, and it is also likely that Mo and Ni oxides were spontaneously formed while stored in air after the synthesis.

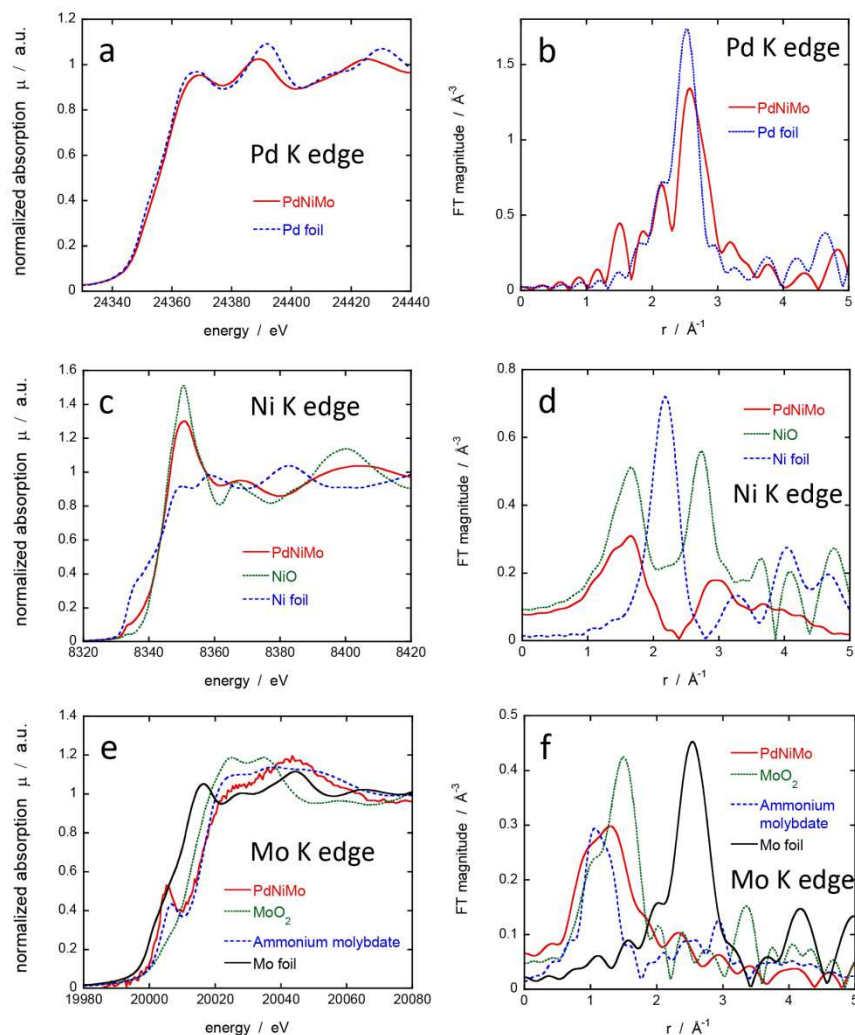


Figure 3. *Ex situ* XANES and the Fourier transformed (FT) EXAFS spectra of (a, b) the Pd K edge (24351 eV), (c, d) the Ni K edge (8331 eV), and (e, f) the Mo K edge (20000 eV) from PdNiMo/C, together with their reference foils and oxides.

We suggest a plausible mechanism for the formation of PdNiMo nanoparticles based on the decomposition reaction kinetics data and surface interactions with the surrounding medium during sonolysis. In the presence of Tf_2N IL-functionalized carbon, it is possible that the Tf_2N anion on carbon intervenes in the $\text{Ni}(0)$ formation through interaction with the COD ligands, leading to the spontaneous decomposition of $\text{Ni}(\text{COD})_2$ on carbon surfaces (24). Owing to the interaction between Tf_2N anion and COD ligands, $\text{Ni}(\text{COD})_2$ may decompose more rapidly than

the deposition of Mo and Pd precursors. Then, the decomposition of Mo(CO)_6 through dissociation of carbonyl ligand and the reduction of Pd(acac)_2 by sonochemically generated hydrogen radicals (25) occur preferentially on the surface of nickel nuclei that have already been formed.

3.2. Electrochemical ORR activity and stability

Platinum monolayers were deposited on the surfaces of PdNiMo/C nanoparticles by replacing underpotentially deposited copper monolayers. The cyclic voltammetry (CV) curves were generated for $\text{Pt}_{\text{ML}}/\text{PdNiMo}/\text{C}$ and commercial Pt/C (E-TEK 10 wt-% Pt on Vulcan X72R) catalysts (Figure 4). The Pt loading for $\text{Pt}_{\text{ML}}/\text{PdNiMo}/\text{C}$ and Pt/C catalyst based on the geometric electrode area of 0.196 cm^2 were $3.2 \text{ }\mu\text{g}/\text{cm}^2$ and $7.7 \text{ }\mu\text{g}/\text{cm}^2$, respectively. The oxide adsorption/desorption potentials observed from $\text{Pt}_{\text{ML}}/\text{PdNiMo}/\text{C}$ shifted more positively (ca. 40 mV) in comparison with those from Pt/C, indicating a remarkable effect of the substrate on Pt atoms on the surfaces. Figure 4b shows a comparison of polarization curves for the ORR on $\text{Pt}_{\text{ML}}/\text{PdNiMo}/\text{C}$ and commercial Pt/C electrocatalysts in oxygen-saturated 0.1 M HClO_4 at a rotation rate of 1600 rpm. It is clearly seen that the ORR activity of Pt/PdNiMo/C is much higher than that of Pt/C in spite of the lower Pt loading. The ORR curves of the $\text{Pt}_{\text{ML}}/\text{PdNiMo}/\text{C}$ electrocatalyst at different rotation speeds (400 to 2500 rpm) in a 0.1 M HClO_4 solution purged by O_2 are shown in supplementary material (Figure S3). Using the same data, the Koutecky-Levich plot, *i.e.*, the inverse current ($1/I$) plotted as a function of inverse of square root of the rotation rate ($\omega^{1/2}$), is presented in Figure S3. The linearity and parallelism of these plots indicate a first-order kinetics with respect to molecular oxygen (26). The kinetic currents for ORR can be determined from the intercepts of the $1/I$ axis at $\omega^{1/2} = 0$. The Pt specific and mass activities of the $\text{Pt}_{\text{ML}}/\text{PdNiMo}/\text{C}$ electrocatalyst at 0.9 V were determined to be $0.55 \text{ mA}/\text{cm}^2$ and

1.14 A/mg_{Pt}, which are approximately 2.3 and 5.7 times higher than those of the commercial Pt/C electrocatalyst (0.24 mA/cm² and 0.2 A/mg_{Pt}). Its total platinum group metal (PGM) (Pt+Pd) mass activity is 0.21 A/mg_{PGM}, and the electrochemical surface area (ECSA) is 188 m²/g_{Pt}. The enhancement in activity observed for the Pt_{ML}/PdNiMo/C catalyst can be explained in terms of electronic modifications of Pt surface atoms induced by strain, ligand and segregation effects in ternary PdNiMo surfaces (27). Even though the PGM mass activity of Pt_{ML}/PdNiMo/C is lower than that of the other Pt_{ML} on ternary nanoparticle core catalyst such as Pt_{ML}/AuPdNi/C (0.53 A/mg_{PGM}) which was developed and reported earlier by our group (28), the stability and lower cost due to the absence of gold in the nanostructure of the present system is favorable.

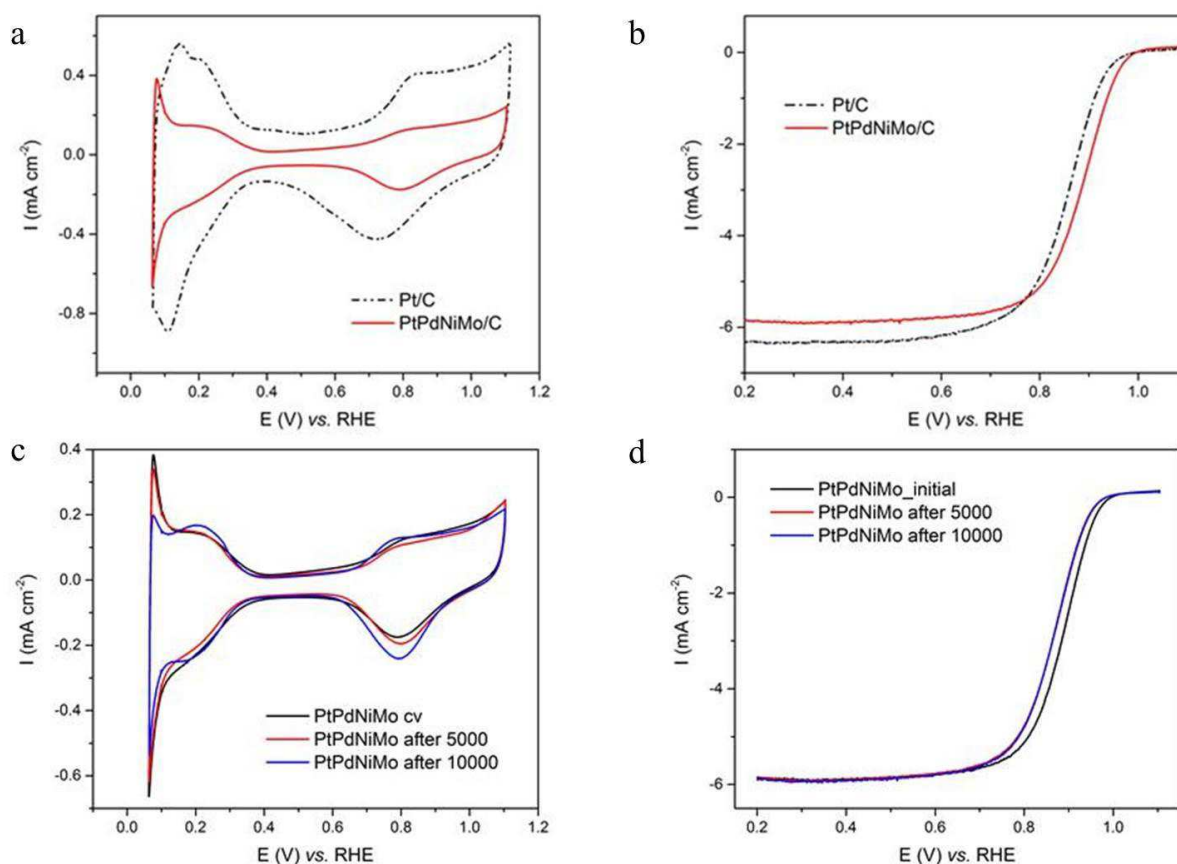


Figure 4. (a) A comparison of CV in Ar-saturated and (b) ORR Polarization curves at 1600 rpm in oxygen-saturated 0.1 M HClO₄ on thin-film electrodes for Pt/C and Pt_{ML}/PdNiMo/C respectively. (c, d) CV and ORR of Pt_{ML}/PdNiMo/C electrocatalyst after potential cycling test.

Another important criterion in electrocatalysts design for fuel cells is the long-term stability. The accelerated stability tests for Pt_{ML}/PdNiMo/C were carried out by applying triangular sweeps between 0.6 V and 1.0V with a scan rate of 50 mV/s in an air-saturated 0.1M HClO₄ solution at room temperature. The initial half-wave potential ($E_{1/2}$) of PdNiMo/C was 888 mV and reduced to 869 mV after 10,000 cycles. The ORR polarization curve showed only a decrease of 19 mV after cycling for 10,000 cycles, while the CVs exhibited nearly no loss in the hydrogen adsorption/desorption peaks (Figure 4c), and the results exhibited higher durability than commercially available Pt/C (29, 30), demonstrating that using this ternary nanostructured substrate as a core for Pt MLs also produces highly stable electrocatalysts.

Membrane electrode assembly (MEA) tests of the Pt ML on Pd core electrocatalyst (Pt_{ML}/Pd/C) demonstrated long-term stability (21, 31), and the EXAFS analysis showed that the Pt ML structure was almost retained after 60,000 potential cycles in MEA tests (31). Pd is a slightly more reactive metal than Pt with a lower standard electrochemical potential (U_{Pd}^0 : 0.92 V), and thus Pd dissolution occurs at slightly lower potentials than Pt (U_{Pt}^0 : 1.19 V). Owing to an exposure to fluctuating fuel-cell voltage, the Pd may be oxidized to Pd²⁺ and diffuse through any imperfection (puncture) in a Pt ML. The preferential Pd oxidation presumably prevents the oxidation of Pt MLs and exerts a certain degree of cathodic protection on Pt MLs. If Pd oxidation/dissolution is effectively inhibited, the overall durability of the Pt ML catalyst will be further improved. We have previously demonstrated that adding a small amount of Au atoms (approximately 10 at-%) to Pd and forming highly uniform nanoparticle cores make corrosion-

resistant PdAu nanoparticle cores, resulting in synthesizing the highly tolerant Pt ML electrocatalyst (21).

In the present study, we found that the addition of MoNi to Pd nanoparticles also retards Pd oxidation. Figures 5a and b show the *in situ* XANES and FT-EXAFS spectra of Pd K edge of the PdNiMo/C nanoparticles at different potentials (0.41 – 1.11 V), respectively. Both the XANES and FT-EXAFS of Pd K edge change only slightly with increasing potentials, which is different from those observed for a commercial Pd/C (Figure 5c) (21). In Figure 5c, the peak around 1.6 Å reflects the formation of Pd oxide on the Pd/C. Clearly, the oxidation of Pd of PdNiMo/C is significantly hampered and metallic Pd remained up to 1.11 V. We consider that the enhanced stability of Pd may be derived from the electronic effect of the alloying element Mo (rather than Ni), and the observation is supported by recent findings that addition of Mo to Pd inhibits Pd-O formation on the PdMo alloy nanoparticles (11, 12). The stable PdNiMo cores impart improved durability of Pt MLs, as reported in an earlier study of the Pt_{ML}/AuPd/C catalyst (21). The marked feature of the present study is that the highly stable Pt_{ML}/Pd-based-core catalyst has been developed by a sonochemical method, without the inclusion of an expensive element such as gold.

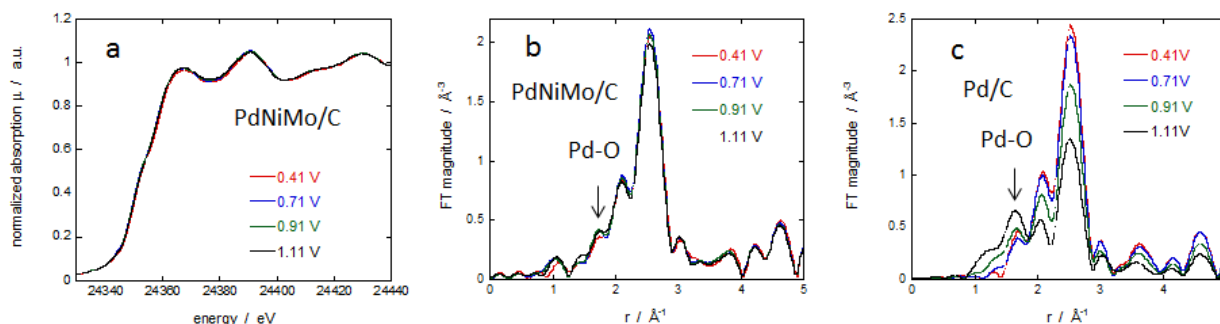


Figure 5. . *In situ* XANES (a) and FT-EXAFS (b) spectra of Pd K edge from PdNiMo/C in 1 M HClO₄ at different potentials. (c) *In situ* FT-EXAFS spectra of Pd K edge from a commercial

Pd/C catalyst in 1 M HClO₄ at different potentials from Ref (21).

Conclusions

In this work, we synthesized Pt monolayer on ternary PdNiMo nanostructure core (Pt_{ML}/PdNiMo/C) electrocatalysts for the ORR by a sonochemical method. We used ionic liquid as a medium for functionalization and stabilizer of nanoparticles in an ethanol/water solvent, without the need of extra stabilizing molecules or organic solvents. The Pt specific and mass activities of the Pt_{ML}/PdNiMo/C electrocatalyst at 0.9 V are determined to be 0.55 mA/cm² and 1.14 A/mg_{Pt}, respectively, which are higher than those of a commercial Pt/C catalyst. The *in situ* XAS characterization studies by XAS show that the PdNiMo/C nanoparticles are very stable under potential up to 1.11 V, a value indicative of high tolerance of a Pt ML catalyst. The sonochemical synthesis also offers a less costly technique of making metal nanoparticles, thus making the process suitable for mass production.

Acknowledgements

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Supplementary Information

Synthesis of Palladium-Nickel-Molybdenum (PdNiMo/C) nanoparticles.

We present the synthesis of carbon-supported palladium nickel molybdenum (PdNiMo/C) nanoparticles prepared by sonochemical decomposition of palladium acetylacetonate ($\text{Pd}(\text{acac})_2$), bis(1,5-cyclooctadiene)nickel(0) organometallic precursor ($\text{Ni}(\text{COD})_2$), and molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$) dispersed on activated carbon with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imid (Etmim Tf_2N) and tributylmethylphosphonium bis(trifluoromethylsulfonyl)imid (TBPh Tf_2N) ionic liquids (ILs). The phosphonium based IL was chosen for this study because it has one of the least coordinating anions and water- and air-sensitive ILs.

Our goal is to synthesize small and stable PdNiMo alloy core electrocatalysts by reducing three different metal precursors at lower temperature, reduced time, and without any external reducing agent, while saving energy in the process. One of the major challenges is to determine the nature of the Ni metal precursor that is suitable for the sonolysis of small size nanoparticles, catalytic activity and stability of the final product for electrochemical application. The ILs containing Tf_2N were chosen due to their high electrochemical window and stability.

Sonochemical synthesis method

All experiments were carried out using MISONIX S3000 ultrasonic liquid processor with microprocessor controlled auto tuning and temperature control with power output of 100W at a fixed frequency of 20 KHz. All manipulations were carried out in a well-ventilated fume hood. A general procedure was developed for the synthesis described herein. The reaction vessel was a

borosilicate glass four-neck flask, with walls tapered inward toward bottom that allowed for maximum solution makeup to the middle of the flask for adequate immersion of the sonication probe. A series of O-rings and standard greased ground-glass joints ensured tight seals to maintain rigorous exclusion of air or gas leakage from the flask during sonication. Any gas evolved during sonolysis was collected and analyzed. The flask was immersed in water bath and held at a constant temperature within the bath (16-18°C (± 1)). Prior to sonication, the solvent/IL mixture was thoroughly degassed with N₂ gas followed by the addition of metal precursor. The hydroxyl ions from water formed during sonolysis and the acetate ions from Pd(acac)₂ serves as reducing agents, while the IL serves as a stabilizer. The nanoparticles were synthesized at low temperatures of 40 °C within 30 min.

Metal precursors of Pd(acac)₂, Mo(CO)₆, and Ni(COD)₂ were stirred under N₂ in an ethanol/water mixture solvent. After a few mins of sonication the solution turned from pale yellow to green and later the black solution was obtained. Therefore, spontaneous decomposition of the metal precursors occurred without the addition of any reducing agent. In Tf₂N ILs, it is possible that the Tf₂N anion intervenes in the Ni(0) nanoparticle formation through interaction with the COD ligands leading to the spontaneous decomposition of Ni(COD)₂. Therefore, Ni(COD)₂ and Mo(CO)₆ dissolved in ethanol/water, undergo sonochemical decomposition, and no external reducing agent is needed since both precursors are already in (0) oxidation state

The slurry was centrifuged three times at 9,500 rpm for 30 min and the upper ethanol solvent layer was decanted to separate the product. The remaining black solid was washed twice with acetone and deionized water (3×10 ml) to remove the residual IL. The collected solid was dried in vacuum and then stored in a gas-tight vial purged with argon to avoid any sample oxidation.

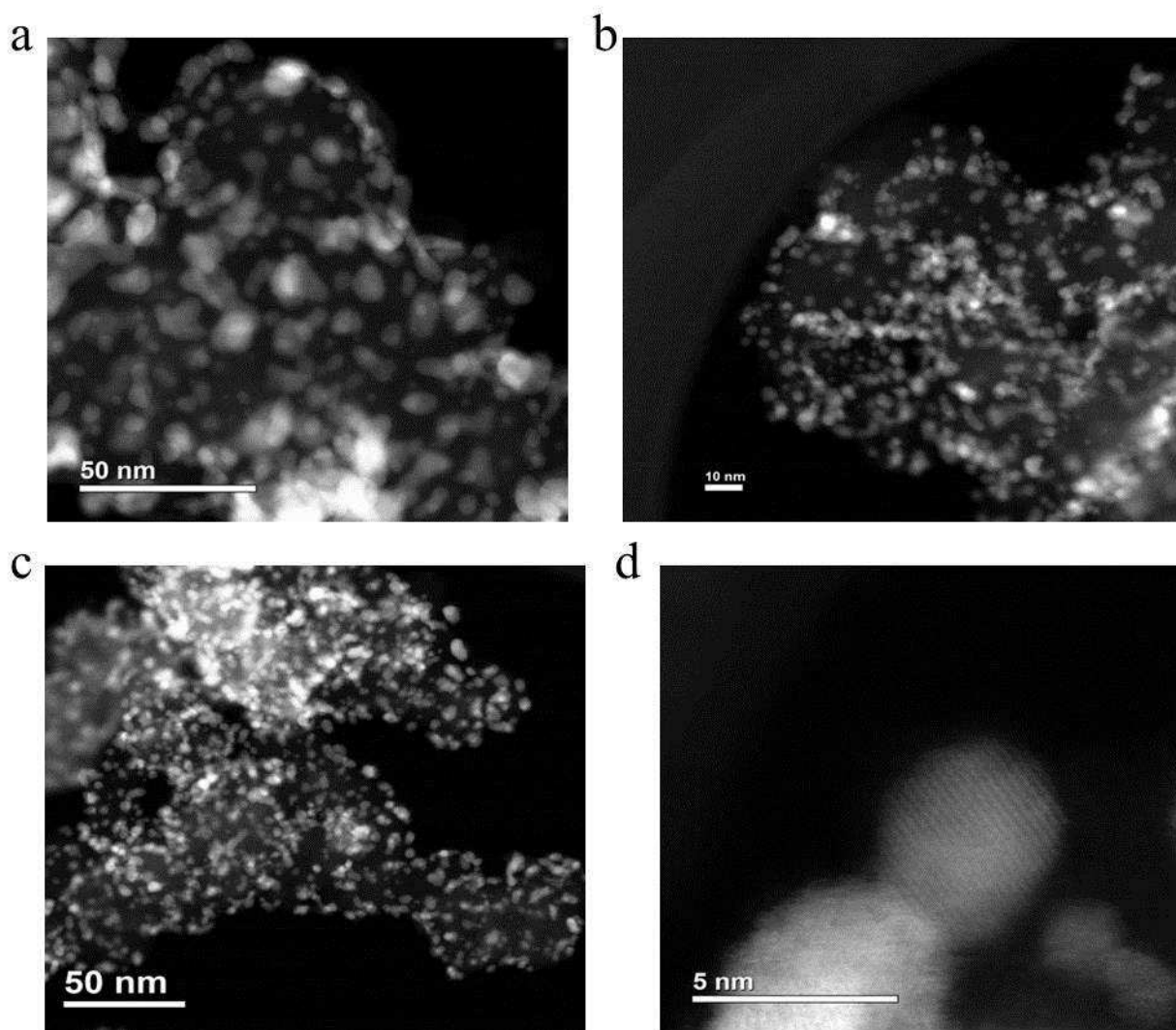


Figure S1. (a, b) HRTEM images of PdNiMo/C nanoparticles with the presence of IL. (c, d) HRTEM images of the same sample after acetone and deionized water wash.

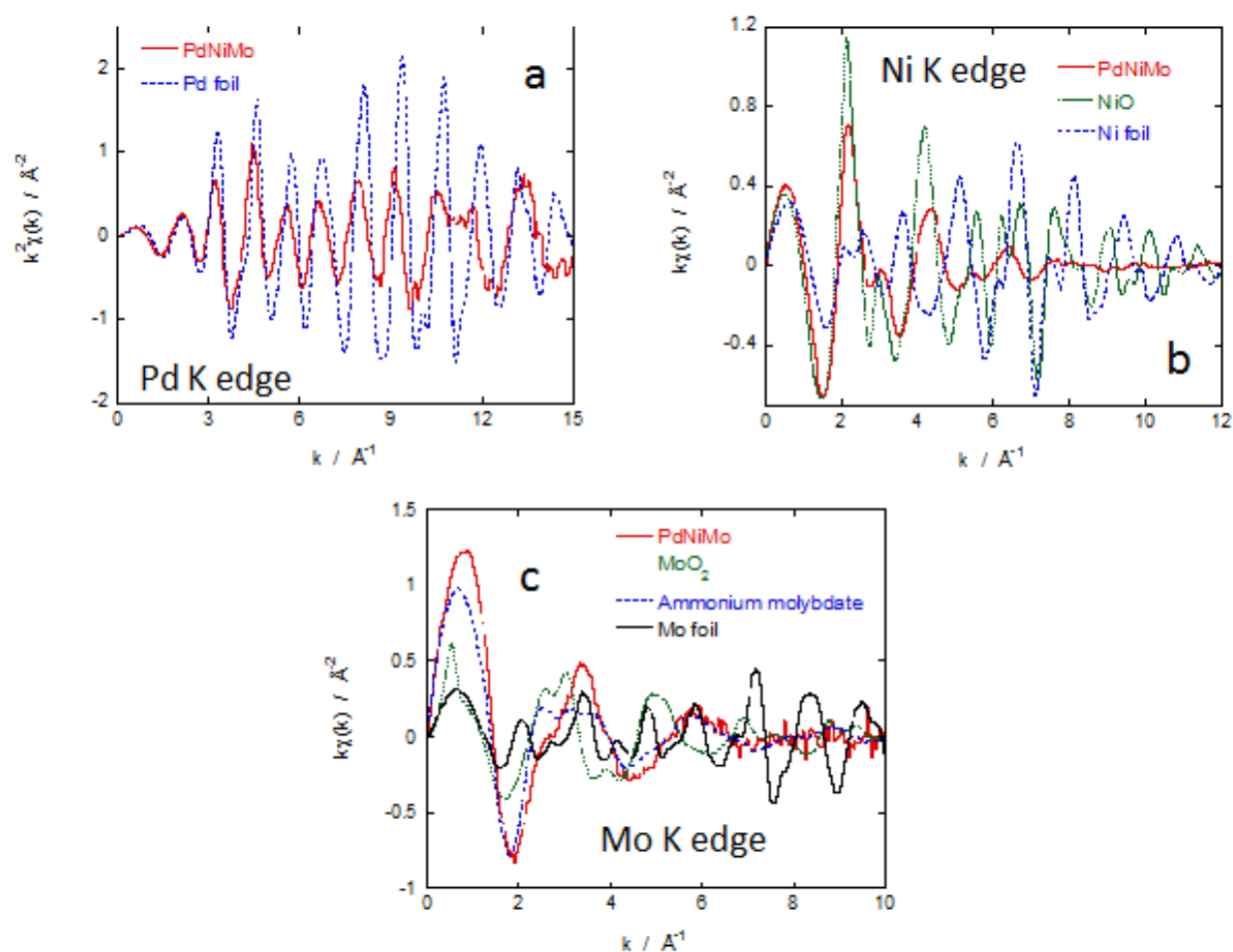


Figure S2. EXAFS in k-space of (a) the Pd K edge (24351 eV), (b) the Ni K edge (8331 eV), and (c) the Mo K edge (20000 eV) from PdMoNi/C catalyst, together with their reference foils and oxides.

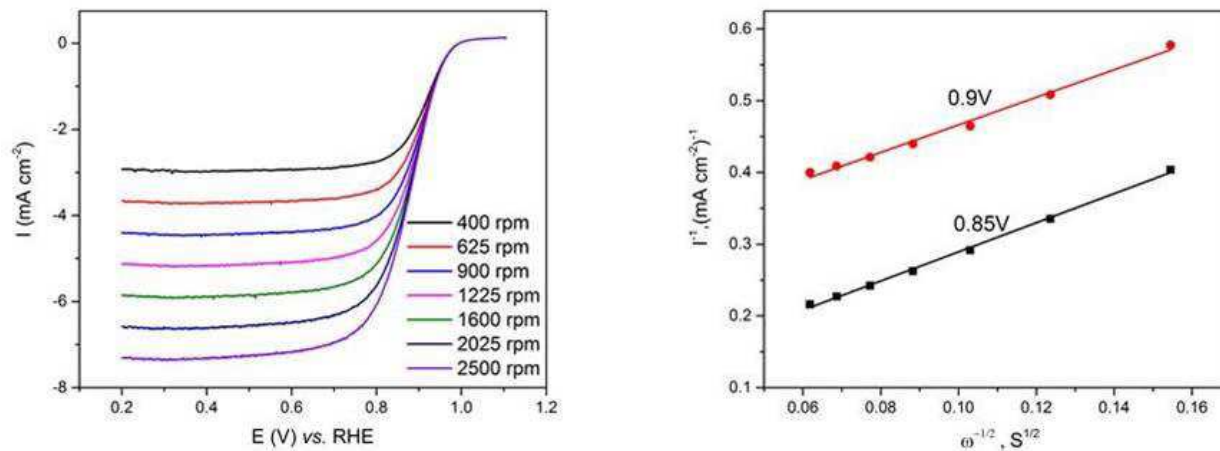


Figure S3. ORR curves on the $\text{Pt}_{\text{ML}}/\text{PdNiMo}/\text{C}$ electrocatalyst at different rotation speeds (400 to 2500 rpm) in 0.1 M HClO_4 along with its Koutecky-Levich plot at 0.9 and 0.85V.

Chapter 3

Oxygen Reduction Reaction

Oxygen Reduction on Gold Nanocrystal Surfaces in Alkaline Electrolyte: Evidence for Surface Proton Transfer Effects

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Four-electron oxygen reduction reaction (4e-ORR) pathway, as a key high-performance reaction pathway in energy conversion, has been sought after in numerous investigations on metal surfaces over the last decades. Although the surfaces of the most noble metals, including platinum and palladium, demonstrate the full-potential-range 4e-ORR, this is not the case, for gold (Au) surfaces. The 4e-ORR is only operative on Au surfaces with {100} sub-facets, e.g. Au(100), in alkaline solution, however restricted to a certain potential region at low overpotentials, while reverting to a 2e-ORR at high overpotentials. This ORR on Au(100) has been a long-standing puzzle of electrocatalysis. Hereby we review the ORR studies on Au, along with the studies of water effects on Au catalysts, and present our electrochemical results with monofacet Au nanocrystals. Combining with theoretical calculations, we demonstrate that surface proton transfer from co-adsorbed water plays the key role in determining the ORR mechanism on Au surfaces in base.

Introduction

Structure-activity correlations describe important properties of catalysts and electrocatalysts. Thus, controlling surface atomic structure is critical for our understanding of catalysts' behaviors and obtaining their high performance. Much progress has been made in establishing such correlations based on model bulk single-crystal surfaces. In oxygen reduction reaction (ORR), a complete four-electron (4e) ORR is preferred since it provides two-times more efficient energy conversion compared to the partial two-electron (2e) ORR (1). The ORR on a majority of noble metals (Figure 1a), such as platinum (Pt) and palladium (Pd), involves the 4e-ORR pathway regardless of their surface atomic structures (2, 3). On these noble metal surfaces which exhibit strong and dissociative interaction with the dioxygen (O₂) reactant, the 4e-ORR activity is controlled by desorption of reaction intermediates that allows releasing the occupied

active sites (4). However, on bulk gold (Au) surfaces, the ORR in alkaline electrolyte is highly sensitive to the surface structure because of the weak interaction between Au surfaces with O_2 (5-7). A partial 2e ORR proceeds on the most facets including Au(111), whereas the complete 4e-ORR only occurs on Au surfaces with {100} sub-facets in alkaline electrolyte in an about 200 mV wide potential window. The strong structural sensitivity for the ORR on Au surfaces remained elusive for long period. In this work we generated monofacet Au nanocrystals (8) and tested their ORR performance in alkaline electrolyte (9). In addition, density functional theory (DFT) calculations were carried out to gain insights on the ORR mechanism on Au. Our results reveal the key role of co-adsorbed water for the 4e-ORR on Au surfaces in alkaline media.

Review of Oxygen Reduction on Au Single Crystals in Alkaline Electrolytes

Before the structural effect on the electrocatalytic activity was universally recognized, early studies of oxygen reduction on polycrystalline Au electrodes (10-12) were not conclusive about the reaction mechanisms, because the results were partially dependent on the fraction of {100} sub-facets on the polycrystalline Au electrode surface. The extensive studies of structural effects in electrocatalysis, including hydrogen adsorption (13-15), underpotential deposition (UPD) (16) and oxidation of organic compounds (17-19), open up a new dimension in electrochemical research and help bring about the structure-activity correlations. Since then, surprising structural effects on the ORR have been found on Au surfaces, and the studies were pioneered by Adzic and colleagues (20, 21). In strong acidic solutions ($pH < 3$), a partial 2e ORR occurs on all the investigated Au single-crystal surfaces (3, 22-24). In contrast, in alkaline solutions, the ORR pathway has exhibited a strong structural sensitivity on Au surfaces (25, 26), reviewed in details as follows.

ORR in Base on the Majority of Au Surfaces Including Au(111)

A 2e reduction of O_2 to hydroperoxide ions (HO_2^-) in alkaline solution occurs on the most investigated Au single-crystal surfaces, including the low-index Au(111) and Au(110) surfaces (21), high-index surfaces with a large fraction of Au{111} sub-facets (25, 27). The ORR on the majority of Au surfaces proceeds via a 2e-only pathway, and the further reduction of HO_2^- is not operative (Figure 1a).

It's noteworthy that at very high overpotentials, because of the increased electron energy in the metal, a 4e-ORR is universally operative at the majority of surfaces including Au(111) and Au(100) (25, 26), with the surface diffusion of HO_2^- as the rate determining step (27). However, this potential region, which is close to 0 V versus the reversible hydrogen electrode (RHE), is out of electrochemists' interest owing to its difficulty in practical applications, and therefore is not discussed furthermore in this work.

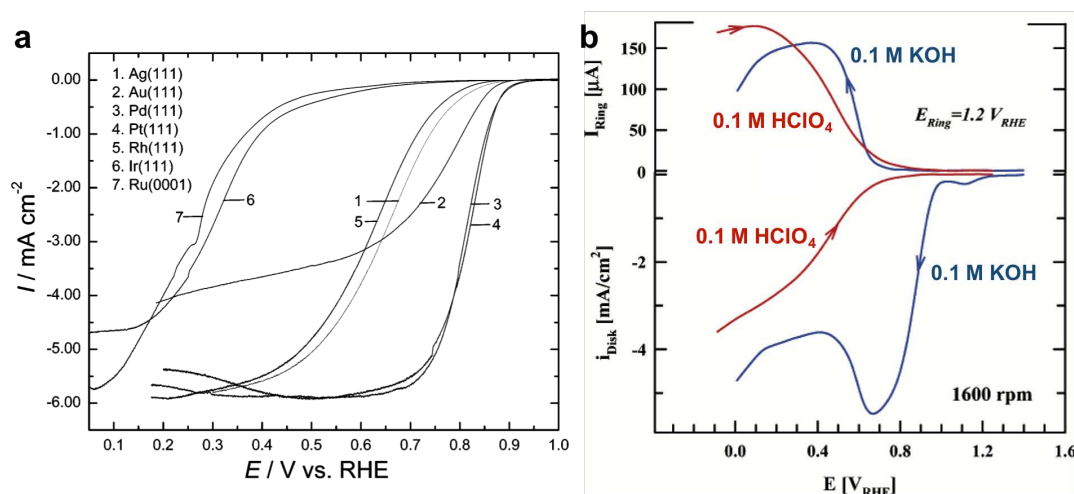


Figure 1. (a) ORR polarization curves measured using a rotating-disk-electrode (RDE) on different metal single crystals in O₂-saturated 0.1 M NaOH at 1600 rpm and 5 mV s⁻¹. Reprinted with permission from reference (2). Copyright (2007) American Chemical Society. (b) Oxygen reduction (bottom part) and peroxide oxidation (upper part) currents on Au(100) electrode in O₂-saturated 0.1 M KOH (dark blue) and 0.1 M HClO₄ (red) at 1600 rpm and 50 mV s⁻¹. Adapted with permission from reference (28). Copyright (2004) American Chemical Society.

ORR in Base on Au(100) and Au Surfaces with {100} Sub-facets

Au(100) surface was considered to be the most active catalyst for the ORR in alkaline solution, even more active than Pt (1), because of its high onset potential. In alkaline solution, Au(100) surface catalyzes a complete 4e reduction of O₂ to hydroxide ions (OH⁻) in a limited potential region, beyond which the 2e ORR takes over (20, 28, 29), as shown in Figure 1b. On the high-index Au(910) and Au(11,1,1) surfaces (30) with long (100) terraces, i. e., a large fraction of {100} sub-facet, the 4e-ORR is similarly operative within a limited potential region. The activity of Au(100) surface also exhibits a dependency on the electrolyte pH (23, 31). In strong acidic solutions (pH < 3), it catalyzes an incomplete 2e ORR. However, in the electrolytes with a pH > 3.5, it starts to catalyze a 4e-ORR within a certain potential window, and the fraction of 4e-ORR increases with the increasing pH.

The Effect of Hydroxyl (OH)

Electrochemical studies in 1990s (25) suggested that the 4e-ORR on Au(100) in alkaline solution might be correlated with hydroxyl (OH⁻) chemisorption at the Au(100) surface site with the four-fold symmetry, because of the overlapping of the limited 4e-ORR potential region of polarization curve with the current peak of cyclic voltammogram in deaerated electrolyte. A later study (32) carried out the *in situ* surface enhanced Raman scattering (SERS) measurements to investigate the ORR mechanism on polycrystalline Au in alkaline electrolyte, and found a SERS peak at 820 cm⁻¹, whose intensity decreased at the potential close to the 4e-to-2e switching potential on Au(100). This peak was at that time tentatively suggested to be a AuO-H bending mode. However, it still remains ambiguous how the adsorbed OH can promote the 4e-ORR in base (31, 33, 34).

Review of Oxygen Reduction on Au Nano-objects in Alkaline Electrolytes

ORR on Shape-Controlled Au Nanocrystals

Preparing perfect single-crystalline surfaces via conventional mechanical techniques, such as cutting and polishing, still remains comparatively challenging, since even minimal miscut may result in wide divergence of surface structure. Shape-controllable syntheses of metallic nanocrystals provide an alternative strategy for the fabrication of atomically tailored surface. In recent years, nano-objects with a wide range of compositions, sizes and shapes have been achieved through various synthetic processes (35-38), which would help uncover the effect of surface structure in this size regime (39-41) on catalytic activity.

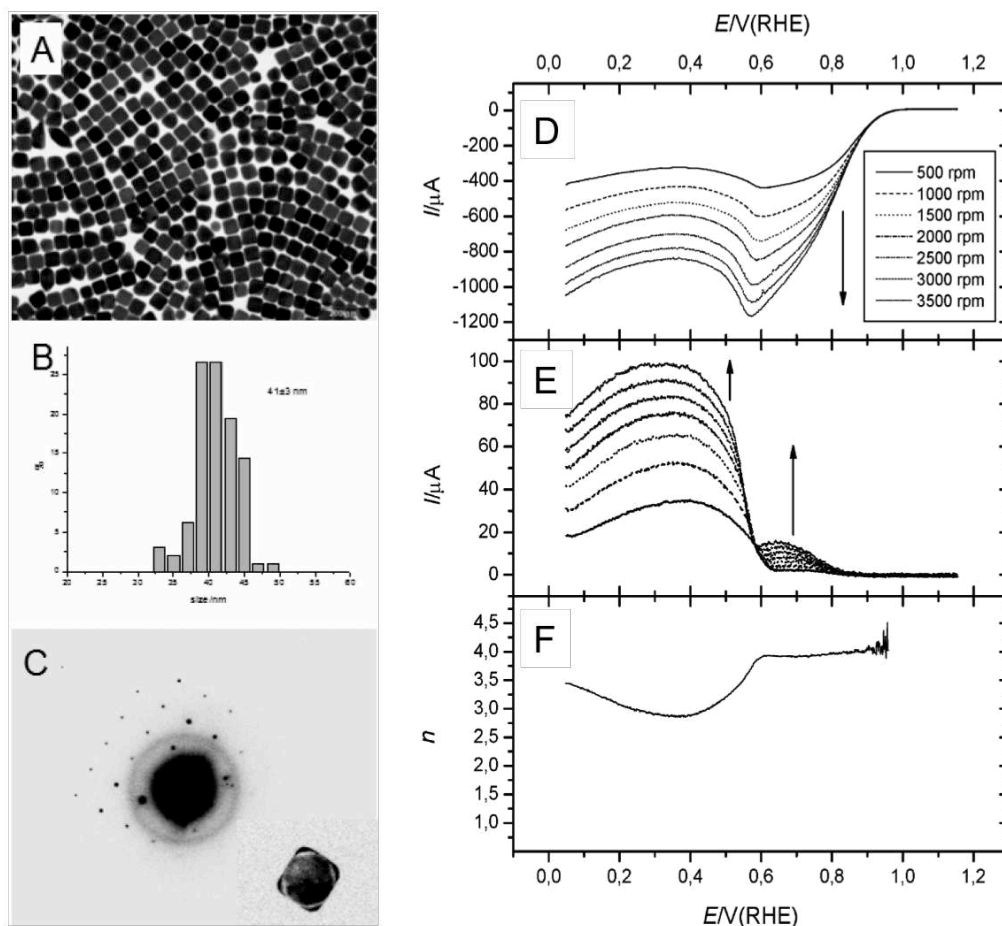


Figure 2. (A) Representative transmission electron microscopy (TEM) image of the Au cubic nanoparticles. (B) Size distribution of the Au nanoparticles. (C) SAED pattern of a single cubic nanoparticle (inset). (D) Disk currents and (E) ring currents of the ORR curves for cubic Au nanoparticles in O_2 -saturated 0.1 M NaOH, ring currents recorded at 1 V (versus RHE). (F) Apparent number of electrons involved in the oxygen reduction reaction. Adapted with permission from reference (42). Copyright (2007) American Chemical Society.

Solla-Gullon and colleagues (42) synthesized Au cubic nanoparticles (yield ~85%, size 41 ± 3 nm) and tested them for the ORR in alkaline solution (Figure 2). The selected

area electron diffraction (SAED) pattern carried out on single cubic Au particles (Figure 2C) demonstrates that these particles are mainly composed of $\{100\}$ -orientated single-crystalline facets, though the Pb UPD measurement shows that the particles' surfaces consist of wide $\{100\}$ domains with the presence of $\{110\}$ and $\{111\}$ sites. The ORR on such Au nanocubes (Figure 2D-F) is similar to that on Au(100) single-crystal surface, with the characteristic 4e-to-2e switch around 0.6 V (versus RHE).

Kanan and colleagues (43) synthesized Au cubes, Au dodecahedra and Au octahedra, and tested their ORR activities in alkaline solution. The ORR on Au cubes is close to that on Au(100) single-crystal surface, while the electron transfer number for the ORR on Au dodecahedra and Au octahedra is around 3 which could be contributed from the fraction of further HO_2^- reduction to OH^- on the particles' corners and edges. The "oxide-derived" Au is prepared by electrochemically reducing a gold oxide precursor (44) and exhibits a high 4e-ORR activity, but the mechanistic origin has not been investigated. The ORR has also been studied on other Au nano-objects without specifically exposed facets, including spherical Au nanoparticles (45-48) and Au nanorods (49).

The Prohibiting Effects of Surface Impurities

Albeit that such bottom-up synthetic approaches have yielded various monodisperse and well-shaped metallic nanocrystals, nevertheless, other surface-related concerns are brought up, such as the elimination of the stabilizers and/or capping agents used during synthesis which require extra cleaning processes (50-52), in addition to the possible surface structure infidelity after too much post-treatment (53, 54). Impurities, like surfactants, have detrimental effects by obstructing the reactants' adsorption to the catalysts' surface, which accordingly hinders the catalytic activities (55). Therefore, clean and well-ordered surfaces are essential for revealing their true catalytic behaviors.

Review of the Effect of Water on Au Catalysts

Water Adsorption on Au

There is growing appreciation for the role of water beyond a solvation medium. The electronic and configurational structures of water become central to understanding water-mediated interactions (56-62), for example, the electrochemical reactions at the electrode-electrolyte interface (63, 64).

Historically Au surface has been argued to be hydrophilic (65-68) or hydrophobic (69, 70). Interestingly, surface contamination could easily affect the hydrophilicity of clean Au surfaces, and less than a monolayer of carbonaceous contaminant could render the Au surface hydrophobic (66). The similar phenomenon has been observed on clean and contaminated graphene (71).

Water adsorption has been studied both experimentally and theoretically on Au(111) (65, 67, 68, 72-85), Au(100) (67, 77, 85-88), Au(110) (76, 89, 90), Au(211) (77, 91), Au(310) (92), Au(321) (93), Au(511) (86, 88), and Au(11,1,1) (86). Huzayyin and colleagues (76) studied the water monomer adsorption on Au(111) and Au(110) under electric field using DFT. They found that both translation and rotation of water monomers on Au surfaces are nonlinear and asymmetric in response to the electric field. Due to the stronger adsorption of water monomers on Au(110) than that on Au(111), water monomers on Au(110) tend to respond less to the applied electric field and display smaller translation and rotation than those on Au(111), as shown in Figure 3. Salmeron

and colleagues (63) used X-ray absorption spectroscopy (XAS) and first principles calculations to investigate the structure of interfacial water on gold surface under applied potential. They found that under open circuit and at positive potentials, the interfacial water has different structures compared to bulk water; while at negative potentials, the interfacial water structure is like that of bulk water.

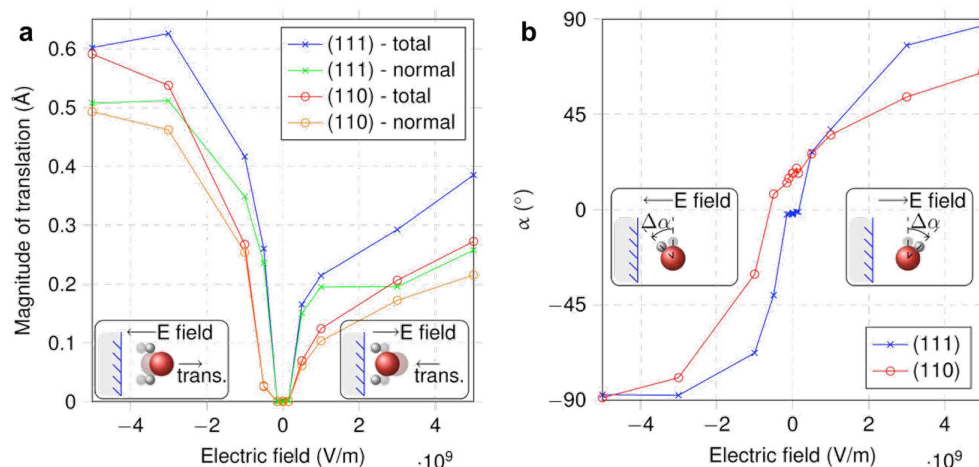


Figure 3. (a) Total/normal translation of water monomer with respect to external electric field. A magnitude of translation is used for normal translation for comparison, but normal translation represents the water molecule moving closer to (away from) the surface when the applied electric field is positive (negative) as depicted in the right-bottom (left-bottom) illustration within. (b) Binding angle of water monomer demonstrating its rotation, with respect to applied normal electric field. Adapted with permission from reference (76). Copyright (2014) American Chemical Society.

The Effect of Water on ORR

As discussed in previous paragraphs, it still remains puzzling how the adsorbed OH can promote the 4e-ORR on Au(100) in base. Here, we propose to account for the influence of specifically co-adsorbed water on the 4e-ORR on Au in alkaline solution. Since H₂O is the proton source for the ORR in basic electrolyte, the co-adsorbed H₂O may act as the proton donor and contribute to the 4e-ORR. In recent years, increasing attention has been paid to the effect of water on the ORR (94-99).

Markovic and colleagues (95) carried out the ORR experiments on Au(100) and Au(111) in ultra-dry organic electrolytes with controlled water content. They found that the ORR becomes highly structural sensitive with the water content being as low as 2000 ppm (Figure 4), and proposed that the observed structural sensitivity on Au for the ORR could be mainly resulted from the promoting effect of water and the water-controlled formation of protonated intermediates.

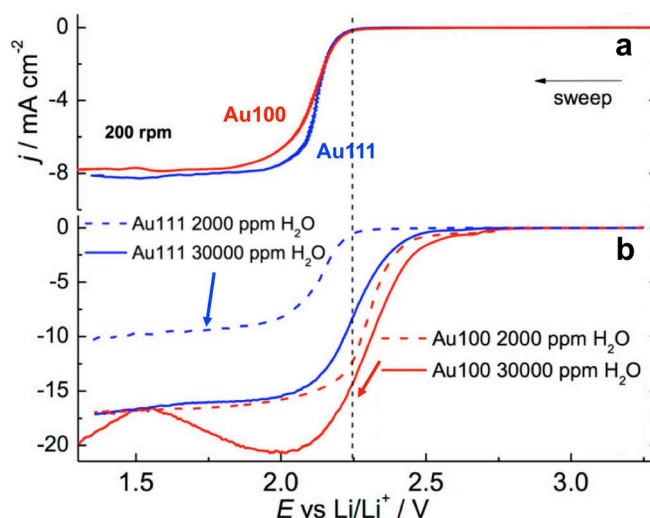


Figure 4. (a) RDE experiment on Au(100) and Au(111) in O_2 -saturated dry DME and 0.3 M TBAPF_6 (<1 ppm of H_2O), at 200 rpm; (b) RDE results in the same electrolyte as in (a) but containing 2000 and 30000 ppm of water, at 200 rpm and 100 mV s^{-1} . Adapted with permission from reference (95) (<http://pubs.acs.org/doi/10.1021/acscatal.5b01779>). Copyright (2015) American Chemical Society. Further permissions related to the material excerpted should be directed to the ACS.

Koper and colleagues (96) performed DFT simulations to model the ORR on Au(100) and Au(111), and presented a general reaction pathway diagram. They also carried out ab initio molecular dynamics (MD) simulations of O_2 molecules co-adsorbed with a monolayer of water on Au(100), and discussed the promoting role of water in the ORR besides the solvation effects. The MD results show that the co-adsorption of oxygen species and H_2O molecules can promote the proton exchange between the O_2 molecule with a neighboring H_2O molecule, leading to the formation of hydroperoxyl (OOH) and hydroxyl (OH) on the Au surface, as shown in Figure 5.

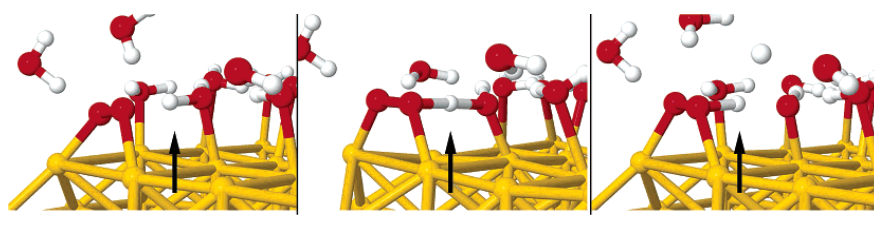


Figure 5. Snap shots from the molecular dynamics simulations depicting the process of proton exchange (left to right) between the oxygen molecule O_2 and a water molecule. The proton involved in the exchange is indicated with a black arrow. Reprinted with permission from reference (96). Copyright (2007) American Chemical Society.

The Role of Water in Other Au-Catalyzed Reactions

Water has a promoting effect on the catalytic activities of Au-catalyzed reactions, including carbon monoxide (CO) oxidation and alcohol oxidation reactions. Au nanoparticles supported on appropriate metal oxides have exhibited high catalytic activities toward the low-temperature CO oxidation reaction (5, 6, 100-111), at

temperatures as low as -70°C (101). By adding very little amount of water into the reactant feed stream, the catalytic activities of supported Au catalysts could be enhanced by at least two orders of magnitude (102). Different mechanistic understandings of the role of water in the CO oxidation reaction have been proposed (104), in which one theory is that water could help the activation of O_2 (102, 107-110) and hence enhance Au catalysts' activities. For the selective oxidation of alcohols in liquid water catalyzed by Au, water could help close the catalytic cycle by reducing O_2 and generate HO^- (112). Water could also promote Au catalysts' activities for aerobic oxidation of alcohols (113).

Perspective of Our Work

In this work, we explored the ORR activity of Au octahedral and cubic nanocrystals, which contain only one type of facet per particle, $\{111\}$ and $\{100\}$, respectively. Such surface tailoring of nanoscale objects permitted us probing the dependence of the ORR selectivity on Au surfaces with different facets. Combining with DFT calculations, we pose a new insight into the role of water in ORR selectivity on Au surfaces. O_2 and H_2O , as two essential and pervasive chemicals, are prominent in many areas of chemistry. However, the O_2 - H_2O interplay on metal surfaces, as well as its effect on electrochemical process, is not clear. Our computational studies elucidate that the unique facet-dependent and potential-dependent 4e-ORR activity on Au surfaces is likely to arise from surface proton transfers from co-adsorbed H_2O to dioxygen intermediates.

Experimental

Two monofacet Au nanocrystals, including octahedra and cubes, were synthesized using a solution-phase multi-step procedure (8, 9). First, the small-sized Au nano-octahedral seeds were prepared using a two-step procedure (114). They were condensed in 0.1 M cetylpyridinium chloride (CPC) solution and denoted as the CPC-capped seeds. Next, in the synthesis of Au octahedra, 200 μL of 10 mM HAuCl_4 , 26 μL of freshly prepared 100 mM L-ascorbic acid (AA), and 670 μL of the CPC-capped seed solution were added consecutively to 10 mL of 0.1 M CPC at 25°C and thoroughly mixed thereafter. The reaction continued for 3 h, and then the solution was centrifuged (10000 rpm, 10 min) and re-dispersed in 10 mL of 0.1 M CPC solution, denoted as small Au octahedra. 333 μL of 10 mM HAuCl_4 , 43 μL of freshly prepared 100 mM AA, and 5 mL of 0.1 M CPC solution with small Au octahedra was added to 12 mL of 0.1 M CPC at 28°C consecutively and thoroughly mixed after each adding. The reaction was left undisturbed for 6 h and stopped by centrifugation (8000 rpm, 10 min). The nanocrystal solution obtained was washed twice with Milli-Q water and concentrated, denoted as Au octahedra, and was used in this work. In the synthesis of Au cubes, 500 μL of 100 mM KBr, 100 μL of 10 mM HAuCl_4 , 150 μL of freshly prepared 100 mM AA, and 270 μL of the CPC-capped seed solution were added to 5 mL of 0.1 M CPC at 32°C consecutively and thoroughly mixed after each adding. The reaction was left undisturbed for 6 h and stopped by centrifugation (10000 rpm, 10 min). The nanocrystals solution obtained was washed twice with Milli-Q water and concentrated, denoted as Au cubes, for further characterizations and measurements. SEM characterization was conducted on a Hitachi S-4800 scanning electron microscope.

The thin-film electrode with Au nanocrystals was prepared by putting an aliquot of the aqueous nanocrystal suspension onto a polished electrode. A 5.0-mm diameter glassy carbon rotating disk electrode (RDE) (Pine Instrument) was used. After drying in vacuum,

the electrode was washed in ethanol and water prior to any electrochemical measurements. A platinum flag and a leak-free (Ag/AgCl, 3M NaCl) electrode were used as counter electrode and reference electrode, respectively. All the reported potentials were calibrated with respect to the RHE. ORR and TI UPD measurements were performed at room temperature with a Volta PGZ402 potentiostat and a BAS 100B electrochemical analyzer, respectively. The average number of electrons transferred per O₂ molecule (n) during the ORR was calculated from the slopes of the Koutecky-Levich plots at different potentials. The Koutecky-Levich equation (115, 116) is expressed as

$$j^{-1} = j_k^{-1} + j_L^{-1} = j_k^{-1} + B^{-1}\omega^{-1/2} \quad [1]$$

and

$$B = 0.62nFAD_{O_2}^{2/3}\nu^{-1/6}C_{O_2} \quad [2]$$

where j is the current density, j_k is the kinetic current density, j_L is the diffusion-limiting current density, n is the electron exchange number, F is the Faraday constant (96485 C mol⁻¹), A is the geometric area of the working electrode, and ω is the electrode rotation rate. In 0.1 M NaOH, the published values of the diffusion coefficient of O₂ ($D_{O_2} = 1.90 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) (25, 117), the kinetic viscosity of the solution $\nu = 1.02 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ using (118)

$$\nu = \frac{\eta}{\rho} \quad [3]$$

and $\eta = 1.027 \text{ mPa s}$, $\rho = 1.0039 \text{ g cm}^{-3}$ from reference (119), and the concentration of dissolved O₂ ($C_{O_2} = 1.21 \times 10^{-3} \text{ mol L}^{-1}$) (120) were used in the calculation.

The DFT calculation was done using Vienna Ab-initio Simulation Package (VASP) (121-125) with projector augmented wave method (126), and the Perdew–Wang functional (GGA-PW91) (127) within the generalized gradient approximation was used to describe exchange-correlation effects. Spin-polarized calculations were carried out for bare surface and non-spin-polarized calculations were considered for water-covered surface. According to our calculations, the presence of water on the surface can lead to spin quenching down. The cut-off energy was 400 eV and convergence of energy and forces were set to $1 \times 10^{-5} \text{ eV}$ and $0.01 \text{ eV}^{-1} \text{ \AA}$. All the slab models included a vacuum of 14 Å. Monkhorst-Pack (128) k-point sampling was used: $4 \times 4 \times 1$ for a 4-layer Au{100} in a (2×2) unit cell, $4 \times 3 \times 1$ for a 4-layer Au{100} in a (2×3) unit cell, and $3 \times 3 \times 1$ for a 4-layer Au{111} in a (3×3) unit cell. The bottom 2 layers of Au slabs were fixed at the bulk position, while the top 2 layers were allowed to relax with the adsorbates. 2/3 monolayer of water were included to model the effect of water on Au surfaces. The free energy of intermediates was calculated by the following steps: 1). RHE was chosen as reference electrode, and therefore G(OH⁻) was calculated according to reaction $\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$, where G(H⁺) was determined using G(H₂) following reference (129); 2). pH = 13 was considered. Accordingly G(H⁺) and G(OH⁻) were corrected with the following equation according to reference (129).

$$G(\text{pH}) = -kT \ln[\text{H}^+] = kT \ln[10 \times \text{pH}] \quad [4]$$

3). The solvation effect for OH^- and O_2H^- in solution was considered, achieved by adding the difference between gas phase energy and solution phase energy according to the standard value from the handbook (130); 4). The effect of water on the surface was described by one layer of H_2O molecules adsorbed on the Au surfaces, so that the reacting sites were surrounded by water on the surface.

Results and Discussion

Synthesis and Characterization

Our solution-phase synthetic methods permitted creating monofacet Au nanocrystals, including octahedra and cubes, with both narrow size distribution and well-defined single-crystalline surface. The scanning electron microscopy (SEM) images demonstrate that the Au octahedra with eight $\{111\}$ faces (Figure 6a) assemble via face-to-face contact with neighbor particles forming a Minkowski-like structure (131), and Au cubes with six $\{100\}$ faces (Figure 6b) pack closely with the four-fold square symmetry. The prepared Au octahedra have a yield of 95%, and an average edge length of 62 nm with the standard deviation of 3.3%; the synthesized Au cubes have a yield of 96%, and an average edge length of 48 nm with the standard deviation of 2.6%.

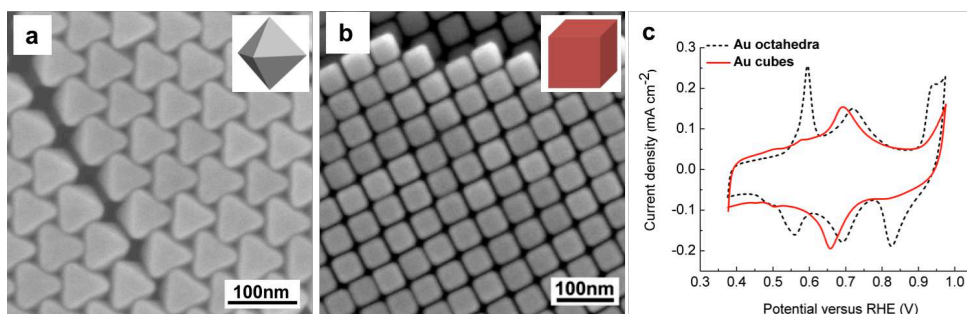


Figure 6. (a-b) Typical large-area SEM images of (a) Au octahedral nanocrystals and (b) Au cubic nanocrystals, the insets show the schematic demonstration of polyhedral shapes for the corresponding nanocrystals. (c) Thallium (Tl) UPD curve in Ar-saturated 5 mM $\text{TiNO}_3 + 0.1 \text{ M NaOH}$, sweep rate 50 mV s^{-1} .

Electrochemical characterization was carried out using thallium underpotential deposition (Tl UPD), as shown in Figure 6c, to check the surface cleanness and crystallinity of these shaped Au nanocrystals. The Tl monolayer phase and the co-adsorbed Ti^+-OH^- adlayer phases are very sensitive to the structure and quality of Au single-crystal surfaces, and the phase transition between these two phases generates sharp voltammetry peaks (132). The Tl UPD curves (Figure 6c) obtained for Au octahedra and cubes resemble those on the corresponding well-oriented clean Au(111) (132) and Au(100) (133) single-crystal surfaces, albeit with broadened peaks resulted from influences from the edges and corners of nanoparticle facets. The observed characteristic phase-transition features of the Tl UPD curves verify the high crystallinity and cleanness of the Au nanocrystals.

ORR on Au Nanocrystals

The ORR performances of Au nanocrystals were measured using the RDE technique in O_2 -saturated 0.1 M NaOH. The ORR curves (Figure 7a) for the octahedra and cubes, imitate those on the Au(111) and Au(100) single-crystal surfaces (25), respectively, and also are in good agreement with other groups' results for Au shaped nanocrystals (42, 43). The Au octahedra show a low onset potential (0.88 V), and a mass-transport limiting current of -3 mA cm^{-2} at $0.2 \sim 0.6 \text{ V}$. In contrast, Au cubes exhibit a high onset potential (0.98 V) with its ORR current exceeding that on octahedra.

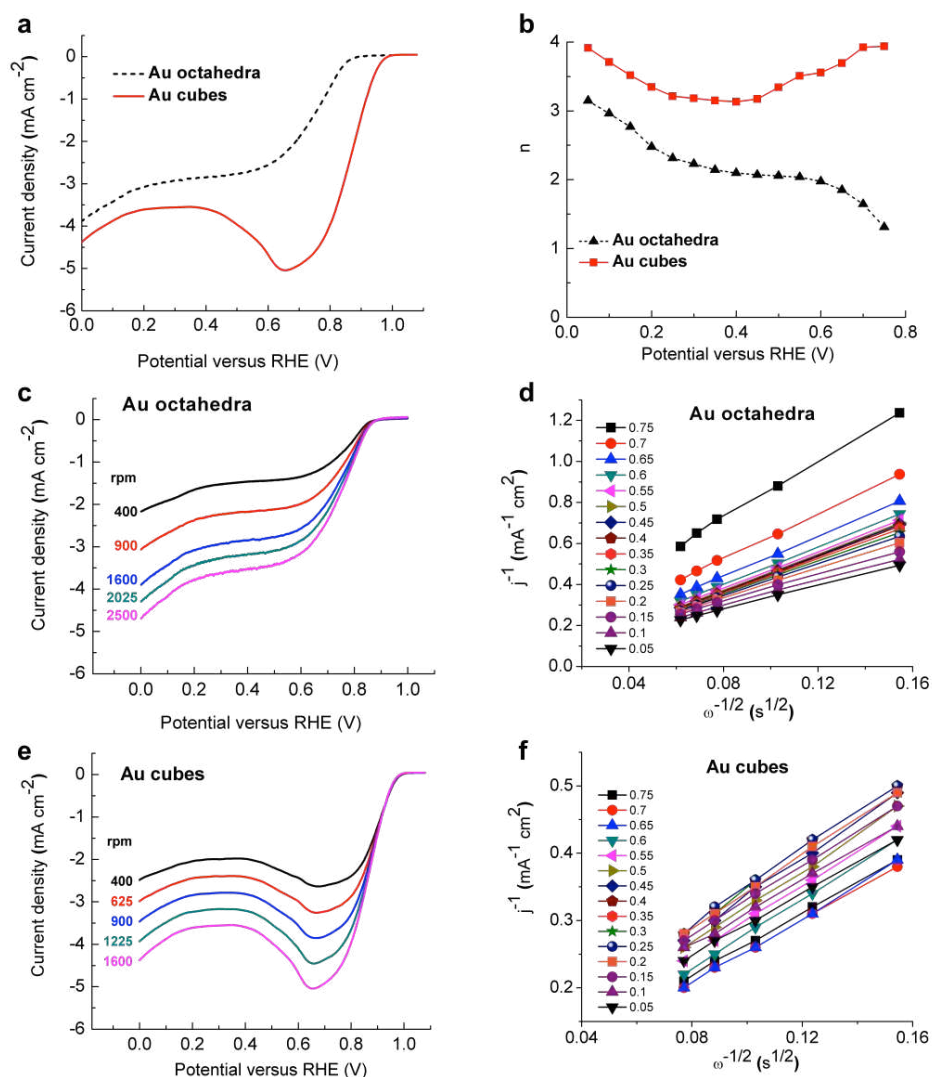


Figure 7. (a) ORR polarization curves measured on Au octahedra and Au cubes in O_2 -saturated 0.1 M NaOH at 50 mV s^{-1} and 1600 rpm. (b) Electron transfer number during the ORR as a function of potential calculated from data in (c, e) using the Koutecky-Levich equation. (c, e) ORR curves of the (c) Au octahedra and (e) Au cubes in O_2 -saturated 0.1 M NaOH at 50 mV s^{-1} and at different rotation rates. (d, f) Koutecky-Levich plot at different potentials (V versus RHE) obtained from (c, e), respectively. Loading: $100 \mu\text{g cm}^{-2}$ for octahedra, $130 \mu\text{g cm}^{-2}$ for cubes.

The average number of electrons transferred per O_2 molecule, shown as a function of potential (Figure 7b), was determined via the Koutecky-Levich plot (Figures 7d, 7f) using the polarization curves measured at different rotation rates (Figures 7c, 7e). The electrochemical results (Figures 7a, 7b) demonstrate that only a 2e ORR occurs on Au octahedra, while a 4e-to-2e pathway switch takes place on Au cubes. With decreasing potentials (i.e. increasing overpotentials) on Au cubes, the current (Figure 7a) continuously increases and reaches the maximum around 0.6 V, and then decreases to the plateau below 0.4 V, and at the potential close to 0 V it rises again due to the increased electron energy in the metal. Correspondingly, the electron number of Au cubes (Figure 7b) is initially close to 4, but drops to ~ 3 around 0.6 V, and then rises again at the potential close to 0 V.

Surface Proton Transfer from Co-adsorbed Water

The recent studies on water-metal interaction inspire us to re-examine the reaction mechanism for the ORR in base on Au surfaces, taking in account that water is the source of proton for the ORR in alkaline media. DFT calculations were carried out to gain insights for the ORR mechanisms, considering the Au surfaces without and with co-adsorbed water. The DFT-calculated free energy diagram for Au{111} with adsorbed water (Figure 8a) shows that O_2 adsorption is still endothermic and the 2e pathway remains energetically favorable, consistent with the electrochemical results (Figures 7a-b).

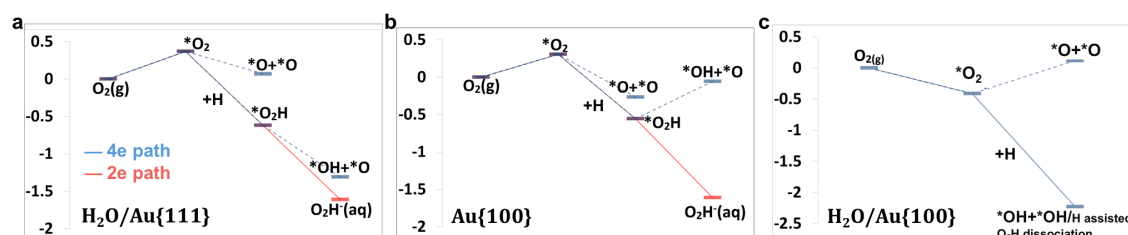


Figure 8. (a) DFT-calculated reaction free energy diagrams on (a) Au{111} and (b-c) Au{100} surfaces with (a, c) and without (b) adsorbed water. The reaction pathways with the lower energy are depicted by solid lines. “+H” denotes the protonation from solution, and “*” denotes the adsorbed species.

Under electrochemical conditions, water molecules are likely to adsorb on Au surfaces at high potentials, and desorb from Au surfaces at low potentials. Figure 8b shows that on bare Au{100} without the presence of co-adsorbed H_2O , the 2e-ORR pathway without the O-O bond breaking is the preferred pathway. O_2 prefers to get protonated from solution to become adsorbed O_2H^- , and later to dissolve in the phase of O_2H^- . However, when H_2O is co-adsorbed on Au{100} (Figure 8c), the 4e-ORR pathway becomes the preferred pathway. Upon the protonation from solution, the adsorbed O_2 is further activated with the assistance of a surface proton transfer from a nearby co-adsorbed H_2O , leading to the spontaneous O-O bond cleavage. Given that, with the potential increasing, the presence of co-adsorbed H_2O allows the transition from the 2e pathway to the 4e pathway for the ORR on Au{100}. Such mechanistic transition is also observed in our experiments (Figures 7a-b). The 4e-to-2e pathway switch around 0.6 V is attributed to the weakened water adsorption at low potentials. As reviewed in previous paragraph, the voltammetry peak in deaerated electrolyte (25) and the SERS peak at 820

cm^{-1} (32) in the 4e-ORR potential range were associated with hydroxyl (OH) chemisorption at the Au(100) surface site. However, a recent study (86) of water adsorption on Au using vibration spectroscopy reports a hydrogen bending mode at 730 cm^{-1} for the H_2O adsorbed from gas phase on Au surfaces, which decreases in the order of $\text{Au}(100) > \text{Au}(11,1,1) > \text{Au}(511)$ with a narrower {100} terrace width. These results reveal that instead of adsorbed OH, the SERS peak at 820 cm^{-1} (32) in the 4e-ORR region is more likely to be associated with the adsorbed H_2O .

Conclusions

In conclusion, monofacet Au nanocrystals with different shapes, including octahedra and cubes, which are enclosed by atomically well-defined nanocrystal surfaces, {111} and {100}, respectively, have been synthesized by a developed seed-mediated method. The comparability of the ORR and TI UPD behaviors in alkaline media between Au octahedra and Au cubes with their counterparts, Au(111) and Au(100) single-crystal surfaces, has bridged the gap for both catalytic activities and electrochemical characterizations between confined nanocrystal surfaces and extended single-crystal surfaces, indicating that these high-quality single-crystalline Au nanocrystals with different surface atomic structures can be employed as model systems to understand the ORR mechanisms in alkaline electrolyte. Together with DFT calculations, we propose that the surface proton transfer from co-adsorbed H_2O plays a critical role for the facet- and potential-dependent 4e-ORR on Au in alkaline electrolyte. When the geometric lattice structure of Au surface favors the co-adsorption of O_2 and H_2O , the surface proton transfer promotes the O-O bond break and therefore lead to the 4e-ORR on Au. The new insight can help in the understanding of mechanisms for other structure-sensitive catalytic reactions and assist the rational design of nanocatalysts. The monofacet nanocrystals used in this work could also serve as a powerful platform to substitute polycrystalline metal thin films currently used in studies on interfacial water and water-reactant interactions (63, 134), providing new opportunities for gaining in-depth understanding of the structures and behaviors of interfacial water on various solid substrates.

Acknowledgments

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Climbing Over the Activity Volcano Correlation By Biomimicking Vitamin B12: A Co Phthalocyanine Pyridine Axial Ligand Coordinated Catalyst for the Reduction of Molecular Oxygen

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CoN4 macrocyclic complexes like Co phthalocyanines (CoPc) have been extensively studied as electrocatalysts for the ORR but they preferentially promote the 2-e reduction of O₂ to give peroxide. In contrast, vitamin B₁₂, a naturally occurring CoN4 macrocyclic molecule alkaline media promotes the 4-electron reduction of O₂ to H₂O. Vitamin B12 possesses an imidazole axial back ligand and this seems to be the reason for its higher activity and selectivity for the 4-e reduction of O₂. To test this hypothesis, we synthesized a CoPc axially coordinated to pyridine anchored to carbon nanotubes (Co-Py-CNT). The Co center is therefore coordinated to 5 nitrogens as in vitamin B₁₂. The modified CoPcPy containing catalytic material was characterized by EPR and XPS spectroscopy. DFT calculations. According to our results the pyridine back ligand increases the Co-O₂ binding energy, making it more similar to VitB12, favoring the splitting of the O-O bond. The back ligand then plays a crucial role in modifying Co-O₂ binding energy which is a well know reactivity descriptor. A further evidence of this dramatic change in reactivity of CoPc by the presence of the "Py" back ligand is that it moves from the weak binding leg of a volcano correlation to the strong leg of the volcano. This might explain why nature uses a back ligand in cytochrome c to catalyze the ORR.

Introduction

This paper is dedicated to R.R.Adzic, who has made substantial contributions the understanding the electrocatalytic reduction of molecular oxygen (1,2). “Oxygen reduction is considered to be one of the most important electrocatalytic reactions because of its role in electrochemical energy conversion, several industrial processes, and corrosion” Adzic (2). In aqueous media alkaline media O₂ can be reduced via an outer-sphere one-electron process to give superoxide (only very high pH values) or via inner-sphere 2-electrons or 4-electrons to give peroxide (as HO₂⁻) or OH⁻ respectively, with analog process in acid media (2). The 4-e reduction process involves the splitting of the O-O and, importantly, delivers more energy. It involves then the formation of more than one intermediate (3-6). The complexity of the reaction determines the difficulties in

finding an adequate catalyst that will facilitate the rapid desorption of the different intermediates from the electrode surface without energy losses (6,8). A whole series of catalytic materials have been developed over the years (9-11) but to date the most stable and active catalysts are still based on Pt and Pt-containing alloys (12, 13). In order to avoid the use of Pt in fuel cells, non-precious metal catalysts (NPMC) have been developed by various groups (7, 9, 12-16). An important class of NPMC catalysts are MN₄ macrocyclics which are molecules inspired by nature like cytochrome *c* for Fe macrocyclics or vitamin B₁₂ (Vit. B12) for Co macrocyclics (17-24). The activity of these catalysts was discovered in 1964 when Jasinski (20) reported that Co phthalocyanine was active for O₂ reduction. MN₄ macrocyclics are versatile catalysts that have been investigated for a great variety of electrochemical reactions. Just to mention a few: CO₂ reduction (25, 26), oxidation of L-cysteine (27), cysteamine (28) hydrazine (26,27,29-33), thiocyanate (34), nitric oxide (35) several thiols (36-38). Vit. B12 was discovered as an electrocatalyst for the ORR in 1987 (39). Vitamin B12 is also a versatile catalyst that promotes the cysteine/cysteine redox process (40,41), the oxidation of glutathione (42) of 2-aminoethanethiol (43) and of hydrazine (44) so essentially parallels the behaviour of Co phthalocyanine. Concerning the ORR process, in general CoN₄ macrocyclics promote the reduction of O₂ via 2-electrons only and Vit. B12 is one of the few exceptions of Co containing catalysts (45,46) that also promotes the 4-e reduction of O₂. An important structural difference between vit.B12 and Co phthalocyanine (CoPc) for example is that vit.B12 possesses an imidazole axial ligand whereas Co does not. These axial ligands are not innocent and play an important role by modulating the metal active site, as it occurs in cytochrome *c* (19). Zagal and Koper, have recently published a review (46) where the activity of a great variety of MN₄ macrocyclics is compared versus two reactivity parameters: the M(III)/M(II) redox potential of the complexes and the M-O₂ binding energy. Both comparisons give a volcano correlation compared. The binding energy volcano correlation involves two regions: the ascending region corresponding to weak binding energies and the falling region involves the strong binding catalysts. The catalysts on the weak binding region are 2-electron catalysts and the strong binding region catalysts promote the 4-e reduction of O₂. As expected, CoPc appears in the weak binding region and vit.B12 in the strong binding region (41). It is interesting to point out that for example, when comparing the activity of pure metals for ORR Pt appears on the strong binding region of the volcano correlations and promotes the 4-e reduction whereas Au, a weak binding catalyst only promotes the reduction of O₂ via 2-e. It seems that strong binding of ORR intermediates requires splitting the O-O bond. In this manuscript we review recent data on the influence of the axial ligand on the catalytic activity of CoPc. When anchored on gold, CoPc, the presence of an axial ligand increases its activity and the magnitude of this effect depends on the nature of the axial ligand. While the synthesis and characterization of CoPc with various axial ligands has been reported before (47-57), to the best of our knowledge, the electrochemical properties of this complex (i.e. CoPc-Py) have only been compared with those of vit.B12 (58) only recently (59). With the CoPc-Py-CNT it is observed that it somehow mimics the activity of vit.B12 (58,59).

Experimental

Preparation of electrodes

We used double walled carbon nanotubes (CNTs) as substrates for immobilizing the Co

complexes, instead of single or multi-walled CNT as they exhibit its higher purity (>90%) (53, 54). They were obtained from Nanocyl, Belgium and used as received. High purity vitamin B12 was obtained as cyanocobalamine from Merck (Kenilworth, NJ, USA). Cobalt phthalocyanine (CoPc) and 4-aminopyridine (Py), 2,2-diphenyl-1-picrylhydrazyl (DPPH), N,N-dimethylformamide (DMF), isopropyl alcohol, H₂SO₄, NaOH, K₂HPO₄ were obtained from Sigma (St. Louis, USA). Similar to a procedure reported before (48-50), the functionalization of the CNT with Py was achieved using diazonium reaction. 5 g of NaNO₂ was dissolved in 10 ml of water; 7 g of pyridine and 1 g of DPPH were dissolved in 5 ml 4 M HCl; DPPH was used as radical scavenger to avoid the polymerization of pyridine (Py) which can lead to the formation of multilayers (54). A dispersion of 0.1 g of CNT were dispersed in 200 ml DMF. This dispersion of CNTs was added to a solution containing NaNO₂ and Py. Vitamin B12 of high purity was obtained as cyanocobalamine from Merck (Kenilworth, NJ, USA). The modified carbon nanotubes (Py-CNTs) were separated by filtration and washed with water and isopropanol, and finally at 80° C. The Py-CNT were then suspended in DMF and chemically modified with CoPc by refluxing the mixture in N₂ at 150° C. 0.1 M K₂HPO₄ aqueous solution of vitamin B12 (10⁻³ M), were sonicated with CNT (1 mg ml⁻¹) with the purpose of preparing vitamin B12-CNT dispersions (31, 55, 56). Modification of the electrodes was conducted using an ink of CoPc-Py-CNT prepared by dispersing 1 mg of CoPc-Py-CNT in 1 ml of a solution of 25% volume isopropyl alcohol and 75% H₂O. A loading of 0.1 mg cm⁻² of the catalyst was achieved by placing a drop of ca.10 µl of the ink on the surface of the working electrode and let to dry. The working electrode was a highly oriented pyrolytic graphite disk of 5 mm diameter (edge orientation) surrounded by a Pt ring, mounted in a Teflon rotating Pt ring disk electrode and a MSR rotator all from Pine Instruments USA.. The graphite disk surface was roughly polished prior to modification with 800 grit emery paper. The surface of the electrode was modified with the two Co complexes: with the ink containing CoPc-Py-CNT or with 10 µl of aqueous solution of Vit.B12-CNT (1 mg ml⁻¹). A KCl saturated Ag|AgCl was used as reference and all potentials are reported vs. this electrode.

Au electrodes modified with SAMs of aromatic thiols and further modified with CoPc were prepared according to procedures previously reported for FePc and CuPc (63-66). These materials were characterized using e.p.r. and XPS as reported before (59)

Electrochemical measurements

Electrochemical experiments were performed on an Autolab PGSTAT 302N with a bipotentiostat module (Utrecht, The Netherlands). RRDE experiments were conducted polarizing the ring 0.65 V vs Ag|AgCl (saturated KCl).

Theoretical calculations

Theoretical calculations were conducted using a spin-polarized density functional theory (DFT) employing the Quantum-ESPRESSO *ab initio* package (55,56). The generalized gradient approximation (GGA), with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange-correlation potential for systems with covalent functionalization (56). For systems with non-covalent functionalization the van der Waals functional (vdW-DF2) (57) was employed. Kohn-Sham eigen-functions were expanded on a plane- waves basis set where the interaction between valence electrons and ion cores are depicted by ultrasoft pseudo-potentials (60). Converged results have been achieved by

using cut-off energies of 35 Ry on plane waves and of 280 Ry on electronic density. Calculations were conducted in large unit cells, involving up to 359 atoms, with periodic boundary conditions. The sampling in the irreducible part of the Brillouin zone was restricted to the Γ point.

Discussion

Oxygen reduction promoted by CoPc directly adsorbed on gold or anchored via axial ligands

Fig. 1 shows an artistic view of the different configurations of a metal phthalocyanine, directly adsorbed on gold (111) or linked to gold via two different axial ligands (63-66). The catalytic activity of complexes in configurations like in Fig.1 have only been reported for FePc and CuPc but not for CoPc (63-66)

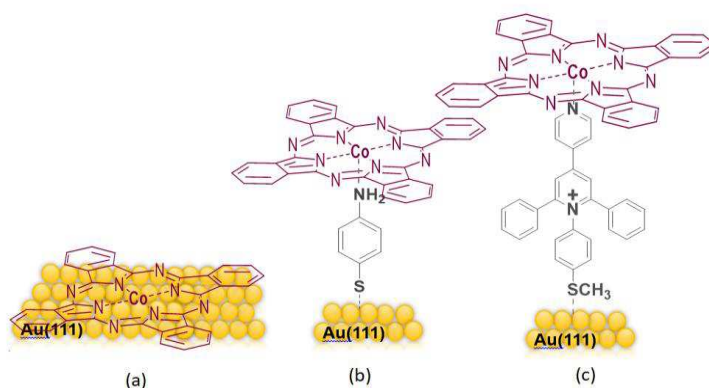


Figure 1. Different configurations of a metalphthalocyanine anchored via SAMs on Au (111) for O₂ reduction.

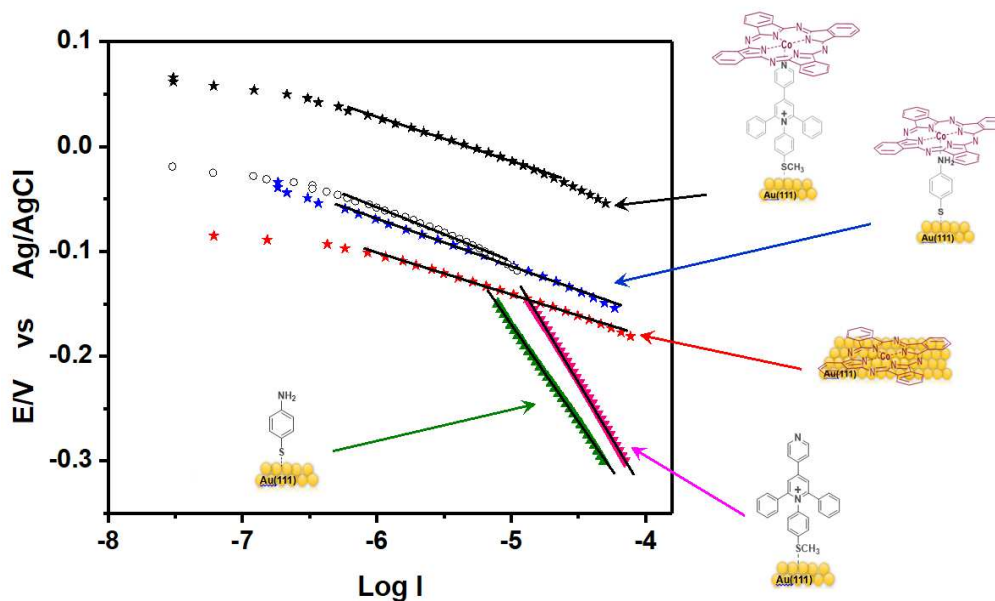


Figure 2. Tafel plots for O₂ reduction in 0.1 M NaOH on clean Au(111) surface, CoPc adsorbed directly on Au(111), CoPc-linked-SAMs of 4-ATP on Au(111) and CoPc-linked-SAMs of MDDP on Au(111).

Fig. 2 illustrates Tafel plots for ORR obtained in alkaline media for the three different configurations of CoPc on Au(111). It is clear in the Figure that the highest activity is observed when CoPc is linked to the Au surface using 1-(4-Mercaptophenyl)2,6-diphenyl-4-(4-pyridyl)pyridinium tetrafluoroborate (MDDP) as an axial ligand, which is much bulkier than 4-aminothiophenol (4-ATP). CoPc directly adsorbed on Au shows the lowest activity of the three CoPc configuration indicating the beneficial effects of the axial ligands. The Tafel slope is ca. -0.060V for the three cases indicating that the electron transfer mechanism is not altered by the special configuration of CoPc. The very inclined Tafel lines observed for Au only covered with a monolayer of the aromatic thiols shows that the exhibit poor performance for ORR and the slopes ca. 0.5 V/decade indicate the presence of an electrical resistivity, so Au is passivated. The high activities observed in the presence of CoPc can only be attributed to its presence in the outermost portion of the SAMs. Similar results have been reported for FePc (63-66) even though FePc is a 4-e reduction catalyst for ORR. CuPc is a poor ORR catalyst and its activity practically does not change in the presence of axial ligands as illustrated in Fig.1 (65). No rotating ring experiments could be conducted with the gold sheets employed (63,64,66) in order to quantify the amount of peroxide produced.

Oxygen reduction of CoPc in the presence of axial ligand anchored to CNTs and comparing with the performance of vit.B12

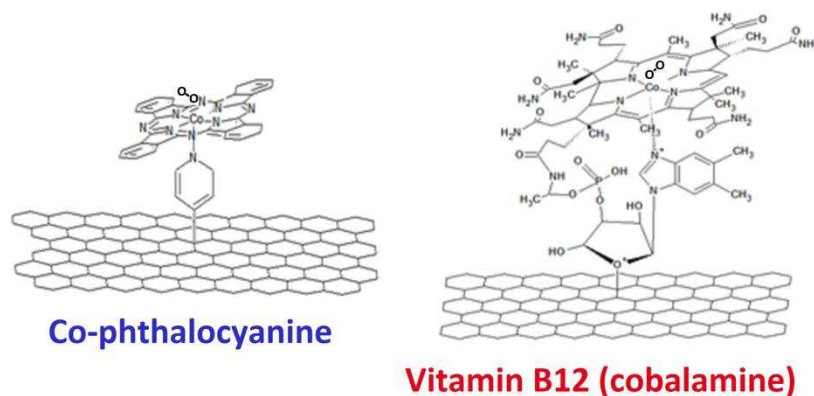


Figure 3. Artist's view of Co phthalocyanine and Cobalamine anchored on a carbon nanotube via an axial ligand. O_2 is shown interacting with the Co center (Reproduced by permission from Elsevier (59)).

CNTs covalently modified with pyridine moieties has been well documented in previous work (65,66). Coordination of CoPc to pyridine has been reported before (50). CoPc shows a similar behavior to FePc and both complexes undergo-facile coordination in the presence of strong bases (48). In previous work we have shown Epr data that indicates that CoPc does coordinate to pyridine not only in solution but also when pyridine is linked to CNTs (Py-CNT) (59). CoPc has been extensively characterized electrochemically both in the presence and in the absence of CNT (74-76). For both cases, only one completely reversible redox peak at -0.580 vs. Ag|AgCl (KCl, saturated), is reported, corresponding to the Co(II)/(I) transition (73-75). The Co(II)/(I) and the Co(III)/(II) redox couples in the CoPc-Py-CNT complex appears at higher potentials than in the Vit.B12 (≈ 0.250 V higher potentials), probably because the ligands in the macrocyclic of CoPc-

Py have a higher electron withdrawing character (59). The polarization curves for electrodes modified with Vit.B12-CNT and CoPc-Py-CNT in a 0.1 M NaOH solution saturated with O_2 at various rotation speeds (from 200 to 1600 rpm) are reported in Fig 4 a) and b) respectively. The polarization curves of the CoPc-Py-CNT and VB12-CNT electrode in 0.1 M NaOH solution (see, Fig. 2) display current plateaus in the high-polarization range. The onset for the ORR starts at -0.05 for both complexes but while the mass transport limiting catalytic current is reached already at -0.550 V for the CoPc-Py-CNT complex this happens only below -0.8 V for the Vit B12-CNT catalyst.

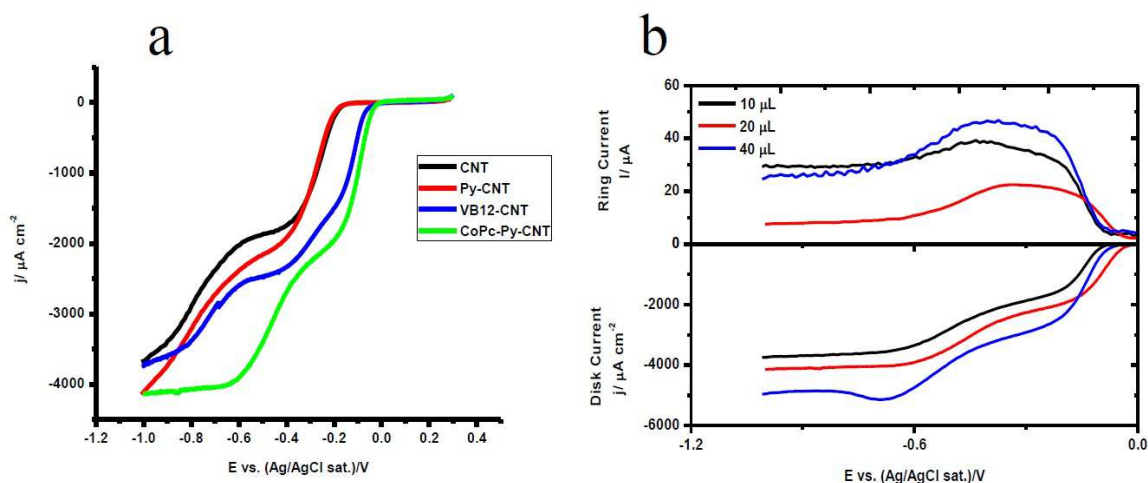


Figure 4. (a) Comparative polarization curves for the ORR of electrodes modified with CNT, Py-CNT, VB12-CNT, CoPc-Py-CNT with rotation speed of the electrode of 1200 rpm. b) ORR current on the disk and H_2O_2 oxidation current at the Pt ring electrode for electrodes modified with different amounts of CoPc-Py-CNT ink. Reproduced by permission of Elsevier (59)

Apparently the difference in potential for the Co(II)/(I) redox couples in the 2 catalysts is reflected in the catalytic activity and in fact the mass transport limiting current is reached at 0.250 V which is close the potential of the Co(II)/Co(I) redox couple (59). The peroxide yield can be monitored at the ring disk electrode where the amount of H_2O_2 produced during the ORR is measured. At low overpotential, in the mixed mass transport and kinetic controlled region, high amounts of H_2O_2 were produced with a maximum at -0.35 V with both catalysts. The production of H_2O_2 sharply decreases for the CoPc-Py-CNT catalyst while it takes an extra 0.250 V for decreasing with the Vit.B12-CNT molecule. In conclusion both catalysts present a bell shaped curve for H_2O_2 production, but for the Vit.B12-CNT catalyst it takes and extra 0.250 V to reach the steady mass transport limited current, probably because the Co(I) is formed only at lower potentials (starting from -0.65 V).

The total number of electrons determined by Koutecky-Levich extrapolation for the CoPc-Py-CNT and Vit.B12-CNT catalysts can be estimated. A maximum of 3.2 electrons for the ORR was obtained with the VB12 catalyst, indicating a mixed process of 4 and 2 electrons. A similar situation is observed with CoPc-Py-CNT with a total number of electrons of 3.0. Tafel plots in the low polarization linear region exhibit almost identical slopes for both catalysts with values that vary from -0.049 to -0.052 V decade⁻¹. These

values suggest a common ET mechanism that probably involves a fast one-electron transfer step followed by a chemical rate-determining step.

Fig. 5 illustrates the stable geometries of the O_2 molecule interacting with the Co center. The total energy and the structural properties of the molecule in the absence of O_2 and when O_2 is adsorbed onto the five coordinated Co atoms of Vit.B12 or CoPc-Py-CNT were investigated for the allowed spin configurations (results reported in (55) with the spin –polarized DFT calculation with the Quantum-ESPRESSO ab initio package (56). The calculations indicate that the minimum energy E_0 for Vit.B12 occurs when the molecule has a ground-state magnetic moment of $m = 1 \mu_B$. O_2 is adsorbed in the end-on configuration with bounding distances d that are in agreement with previously reported results for similar molecules (56, 77). The Co- O_2 binding energy in Vit.B12 is at the lowest for $m=2 \mu_B$ (0.66 eV), while it is 0.88 eV for $m=1 \mu_B$ and 0.66 for $m=0 \mu_B$. In a similar way, for the CoPc-Py-CNT system the $m = 3 \mu_B$ configuration exhibits the highest energy ($E_0 + 0.15$ eV), while the states $m = 0 \mu_B$ and $m = 2 \mu_B$ are only slightly less probable than the $m = 1 \mu_B$ with higher energies of 0.06 eV and 0.04 eV, respectively. The total energy for the molecule in the presence of O_2 is at the highest when $m=3 \mu_B$ ($E_0 + 0.15$ eV), while the situations with $m=0 \mu_B$ ($E_0 + 0.07$ eV) and $m=2 \mu_B$ ($E_0 + 0.04$ eV) showed very similar energy to the $m=1 \mu_B$ with the E_0 configuration. The binding energy of O_2 to the Co in CoPc-Py-CNT is at the lowest for $m=3 \mu_B$ (0.52 eV) while for $m=1 \mu_B$ it is 0.66 eV. The net effect of the axial ligand on CoPc is to increase the binding energy Co- O_2 compared to that in the absence of this back ligand. Hoptheticallylly this should increase its catalytic activity according to the volcano-correlation predictions reported recently (46). When comparing the activity of a series of MN4 macrocyclics for the reduction of O_2 , a plot of activity as $(\log i)_E$ versus the M- O_2 binding energy CoPc appears on the weak-binding leg of the volcano and vit.B12 appears on the strong binding leg of the correlation (46).

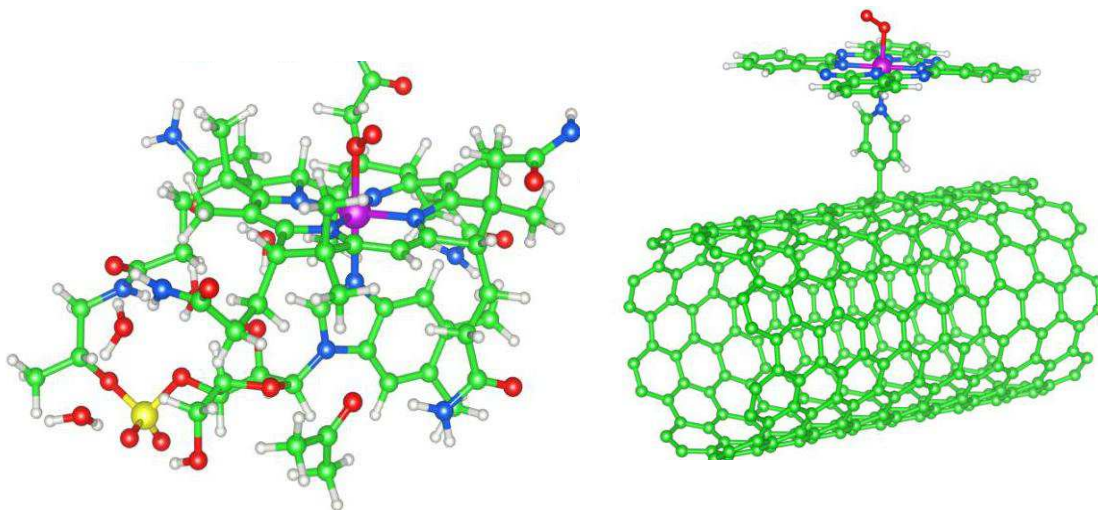


Figure 5. Stable geometries of the O_2 molecule adsorbed with side-on configuration on the Co metal center of Vit.B12 and of CoPc-Py-CNT. Calculated according to (59), reproduced by permission from Elsevier.

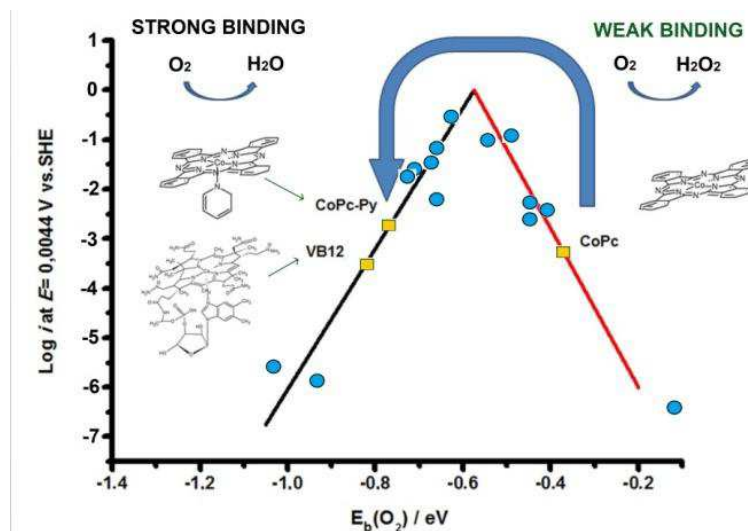


Figure 6. Qualitative volcano plot of activities versus theoretically calculated binding energies for Co-O₂ showing the change in position of CoPc by the presence of an axial ligand (reproduced by permission from Elsevier (59))

Fig. 6 shows a schematic volcano correlation adapted from (46) that essentially illustrates that the presence of the pyridine axial ligand dramatically modifies the Co-O₂ binding energy and seems to move CoPc from the weak binding leg of the volcano correlation to the strong binding leg. This seems to favor the splitting of the O-O bond as lower peroxide yields are observed for the CoPc with axially bound pyridine. This seems to mimic the action of vit.B12 which shows similar peroxide yields with a number of electrons greater for ORR greater than 3. It would be interesting to test a back ligand that does not change the Co-O₂ binding energy so dramatically so it pushes CoPc to the top of the volcano correlation on the weak binding side. Our results show once more that the activity of MN4 complexes is very sensitive to the coordination environment that affects essentially the electron density on the metal center and its energy levels. This will affect the coordination ability of the metal to bind extra planar ligands like O₂. We have shown in several papers that substituents on the ligand modulate these parameters (46) and now axial is also an important parameter, which has also been proposed by other authors as a way of improving the catalytic activity of MN4 macrocyclics (56,63-66).

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(Invited) Development of Highly Active and Durable Hybrid Compressive Platinum for Polymer Electrolyte Membrane (PEM) Fuel Cells at USC

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A highly active and stable catalyst/support system is developed by using a two-step process. In the first step, activated carbon composite support (ACCS) is synthesized that retains its activity after accelerated stress test (AST). A 30% Pt/ACCS catalyst shows no loss of mass activity and power density after 5000 cycles at 1.0-1.5 V while the commercial Pt/C and Pt/290G catalysts show drastic mass activity losses (57.5% and 66.2%, respectively) and power density losses (88.7% and 84.0%, respectively). In the second step, compressive Pt lattice (Pt^{*}) is synthesized through a USC-developed annealing procedure to diffuse Co atoms previously embedded in the support into Pt. The 30% Pt^{*}/ACCS shows high initial power density (rated) of 0.174 g_{Pt} kW⁻¹ and high stability of 24 mV loss at 0.8 A cm⁻² with an electrochemical surface (ECSA) loss of 42% after 30000 cycles (0.6-1.0 V). A carbon based support is synthesized which is stable under simulated start up/shut-down operating conditions.

Introduction

Polymer electrolyte membrane fuel cells (PMFC) are promising power generating devices for future vehicles. However, cathode durability, cost, and performance are some of the key issues preventing the commercialization of PEMFCs for automotive applications (1). The objective of this work was to develop unique hybrid cathode catalyst (HCC) through interaction of highly-active and stable compressive Pt lattice catalyst (Pt^{*}) with catalytically active carbon composite support (ACCS). The specific objectives were to increase the synergistic effect of the catalytic sites present in the support and those in suppressed lattice Pt^{*} catalyst. The following constraints were addressed when developing the hybrid catalyst: (i) chemical and electrochemical stability at high potentials, low pH and high temperature, (ii) the support should possess an onset potential and kinetic activity similar to that of platinum, (iii) development of highly active and stable Pt shell Co core catalyst.

Experimental

Synthesis of Activated Carbon Composite Support and Compressive Pt-lattice catalyst

The activated carbon support (ACCS) was prepared using the procedure developed in the Center for Electrochemical Engineering at University of South Carolina (2-14). The Pt/ACCS was synthesized using a modified polyol method (7, 9, 11).

Compressive lattice Pt*/ACCS catalyst was synthesized by annealing the Pt/ACCS sample with polyaniline as the protective coating. USC-developed process yields uniform particle size distribution with 3-4 nm Pt* catalyst particles. The polyaniline-coated Pt/ACCS was then subjected to heat-treatment from 300 to 900 °C under reducing atmosphere. During the controlled heating process, the Co which is incorporated into ACCS support diffuses to the surface and forms Pt*/ACCS catalyst. The electrochemical durability of the Pt/C, Pt/ACCS and Pt*/ACCS cathode catalysts were examined using AST protocols suggested by U.S. DRIVE Fuel Cell Tech Team.

Results and Discussion

Carbon Support Characterization and Support Stability Test

The crystallite thickness (L_c) calculated by Scherer's formula and the interlayer spacing (d_{002}) (nm) obtained from Bragg's law are used as the factors to determine the degree of graphitization of carbons. Higher L_c value of the (002) peak and lower d_{002} number imply a higher degree of graphitization (6, 8-9). The ACCS shows L_c value which is almost twice higher than that of Ketjenblack EC-300J and the lowest d_{002} of 0.349 (nm) when compared to Ketjenblack and Ensaco 290G. XRD indicated that the higher degree of graphitization observed for ACCS when compared with the Ketjenblack EC-300J can be attributed to the higher thermal stability of ACCS. The hydrophilic/hydrophobic properties of ACCS were tested by dispersing the carbon supports in water hexane mixture. The results indicated that ACCS support shows dispersion mainly in the hexane phase attributed to the higher degree of its hydrophobic character when compared with Ketjenblack EC-300J. The enhanced hydrophobic property of ACCS was also confirmed by the contact angle measurements. The contact angle of 132° estimated for ACCS was much greater than that for Ketjenblack EC-300J of 38°, indicating an enhanced hydrophobicity. The enhanced hydrophobic property of ACCS minimizes water adsorption resulting in less carbon corrosion and as it will be shown later increases H₂/air cell performance in the mass transport region. The functionalized ACCS support remains stable dispersion during Pt deposition in aqueous media. USC activation process uses organic molecules containing hydrocarbon and acid group. The stability was attributed to the grafting of functional groups with negative charges which provides electrostatic stability required for colloidal dispersion (6-9). After Pt deposition, the functional groups were removed from carbon surface. The support stability tests were carried out by subjecting the MEAs to a potential cycling test (1.0-1.5 V, 5000 cycles) to simulate the start-up/shut-down conditions of an automotive PEMFC. Oxidation of the carbon surface increases its hydrophilicity and affects water removal, resulting in an increased mass-transfer resistance. In addition, oxidation of carbon increases the electrical resistance of the catalysts, which leads to the detachment or aggregation of catalyst particles, and damages the cathode catalyst layer structure. Furthermore, platinum increases the corrosion rate by catalyzing the carbon oxidation.

Fig. 1 shows H₂-air fuel cell polarization curves for 30% Pt/ACCS and 30% commercial Pt/C (TKK) catalyst. After 5000 cycles, the Pt/ACCS shows no loss in H₂-air performance indicating excellent support stability with no potential loss after 5000 cycles (9). On the other hand, commercial 30 % Pt/C (TKK) catalyst shows

69.5% power density loss only after 1000 cycles and a further decrease to 88.7% after 5000 cycles, (Fig. 1.b). The 30% Pt/ACCS catalyst shows no loss of mass activity after the support stability test while commercial Pt/C (TKK) shows 90% loss (6, 9).

The support stability of ACCS was attributed to the higher degree of graphitization of ACCS than Ketjenblack EC-300J. The higher H₂-air fuel cell performance of Pt/ACCS is due to (i) optimized support properties such as BET surface area which resulted in thin catalyst layer thus favoring effective mass-transfer to the Pt catalytic sites and (ii) hydrophobicity of the ACCS support which results in better water removal during high current operation. Also, the results indicated that Pt/ACCS with the ultra-low Pt loading at operating conditions exhibits excellent support stability due to: (i) synergistic effect through combined activity of the catalytic sites present in the ACCS-support and in Pt, (ii) the well distributed catalyst nanoparticles and (iii) increased metallic Pt⁰ surface concentration due to the fact that the pyridinic-N present in the support played a role of oxide-cleanser confirmed by physico-chemical and electrochemical analysis.

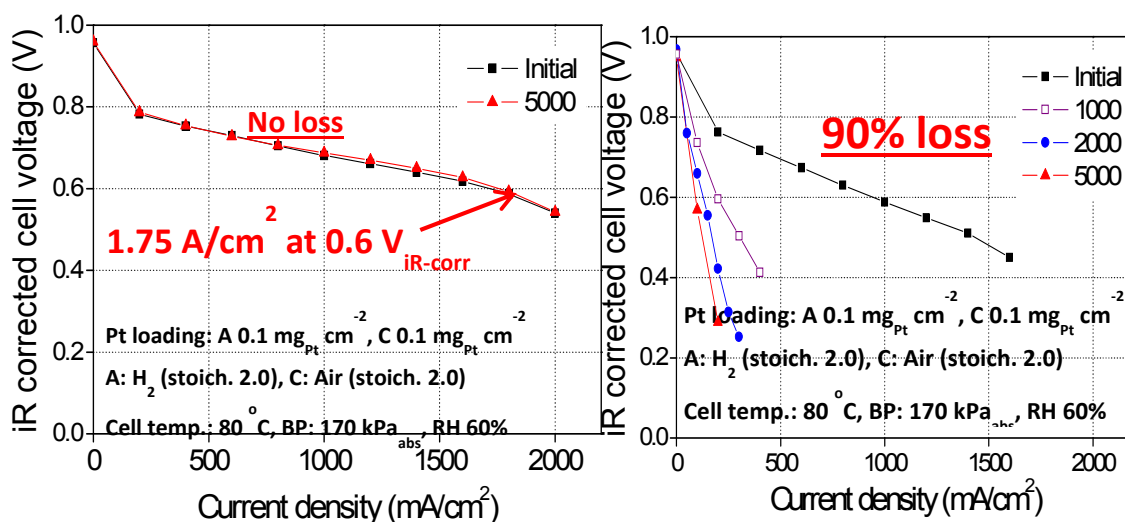


Fig. 1(a) Support stability of 30% Pt/ACCS under 1.0-1.5V potential cycling for 5000 cycles.

Fig. 1(b) H₂-air PEMFC polarization curves of commercial Pt/C.

Mass activities under H₂-O₂ operating conditions at 0.9 V_{iR-corr} were measured before and after support stability test to examine the kinetic performance changes of the catalysts (Figs. 2a and 2b). The 30% Pt/ACCS catalyst shows no loss of mass activity after the support stability test, while commercial Pt/C (TKK) shows 57.5% loss (6,8-9).

Development of Ultra-Low Highly Active and Durable Hybrid Compressive Platinum Lattice Catalysts for PEM Fuel Cell

Compressive platinum lattice catalyst (Pt*/ACCS) was prepared using a methodologies developed at USC (4-13). The amount of Co used as a doping material targeted different atomic ratio of PtCo in Pt*/ACCS catalyst. After annealing the sample of Co-doped Pt/ACCS catalyst at 800 °C for 4 h in absence of protective

coating, the peak positions 2θ of Pt increased from 39.81° to 40.92° indicating a formation of compressive Pt lattice. However, the particle size of annealed sample increased to 6.7 nm from initial diameter of 2.9 nm of Pt/ACCS catalyst estimated before the heat treatment. The large Pt particle size results in small ECSA and poor fuel cell performance. When the annealing was carried out in presence of protective coating, the estimated particle size was in the range of 3.2 nm, while the peak position shifted to 2θ of 40.92° . The pristine Pt/ACCS shows uniform Pt dispersion on the ACCS. Without the protective coating, large particles are seen in the range between 8 and 20 nm. In presence of protective coating on catalyst surface, a uniform particle distribution is observed, with a particle size in the range between 3 and 4 nm (9).

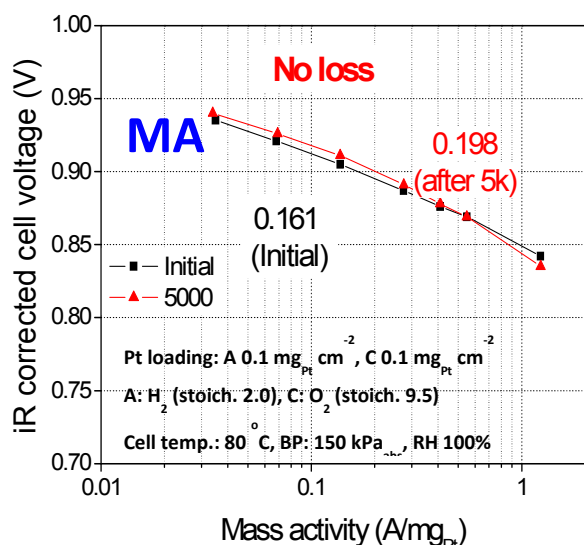


Fig. 2a No loss of mass activity for 30% Pt/ACCS under 1.0-1.5 cycling.

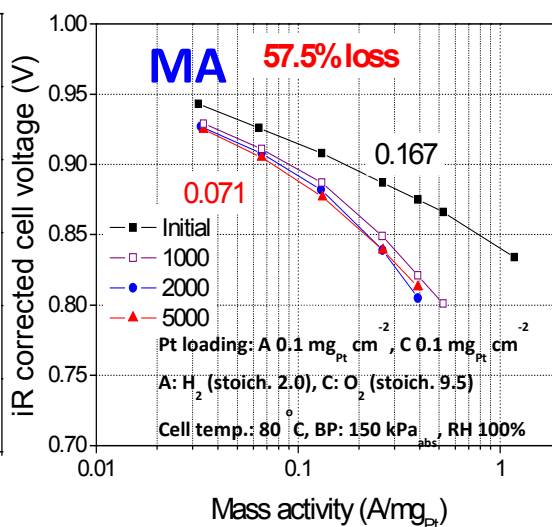


Fig. 2b Mass activity loss for 30 % TKK catalyst under 1.0 -1.5 cycling

The effect of annealing temperature on the particle sizes of Pt*/ACCS was studied in the temperature range between 300 and 900 °C. The corresponding XRD patterns are shown in Fig. 3. The Pt (111) peak is shifted to higher 2θ values as the annealing temperature is increased. Above annealing temperature of 800 °C, 2θ values of the Pt (111) peak are stabilized which indicates a completion of Pt compressive lattice formation. The peak shift is linearly increases up to approximately 700 °C and levels off above 800 °C. Co present within the ACCS diffuses to the catalyst surface forms Co doped Pt lattice which is confirmed by the Pt* peak shift. Our previous XRD study indicates the presence of Pt and PtCo phases after 0.5 h heat treatment at 800 °C (11). Single phase compressive lattice Pt catalyst is formed after 2 h. The shift in 2θ can be varied by adjusting the heat treatment time. The results indicated that compressive Pt lattice is formed by increasing temperature to and above 800 °C (6, 9).

The results clearly indicated that choosing the annealing temperature in the range between 700 and 800 °C to synthesize Pt*/ACCS catalyst will maximize the Pt* formation while maintaining good particle size of Pt.

Formation of Pt-shell Co-core structure on Pt* catalyst is shown in Fig. 4. As shown in Fig. 4, Co which is present within the ACCS diffuses during controlled annealing in the presence of a protective coating to form Co-doped catalyst.

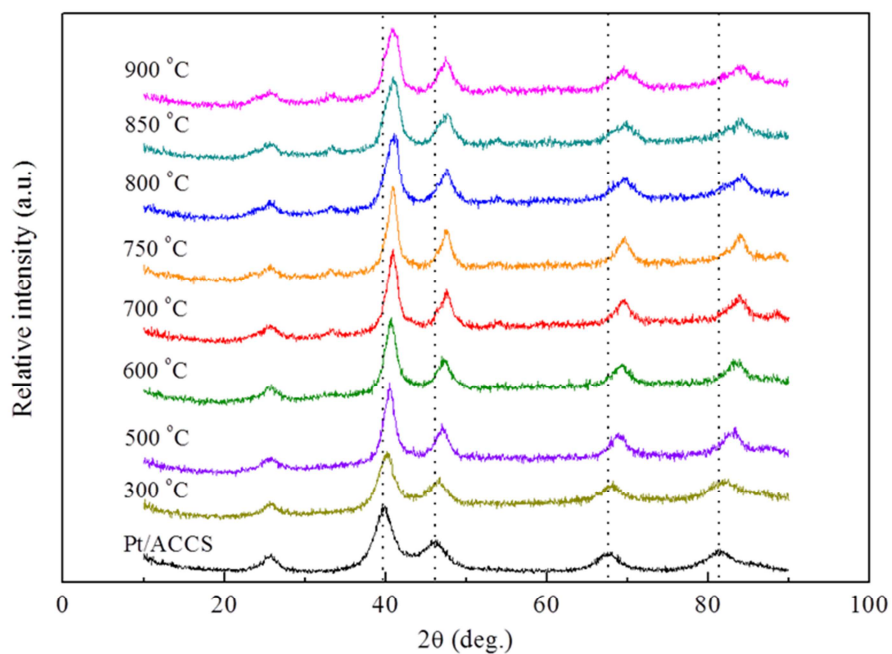


Figure 3. XRD patterns for Pt/ACCS and Pt*/ACCS catalysts.

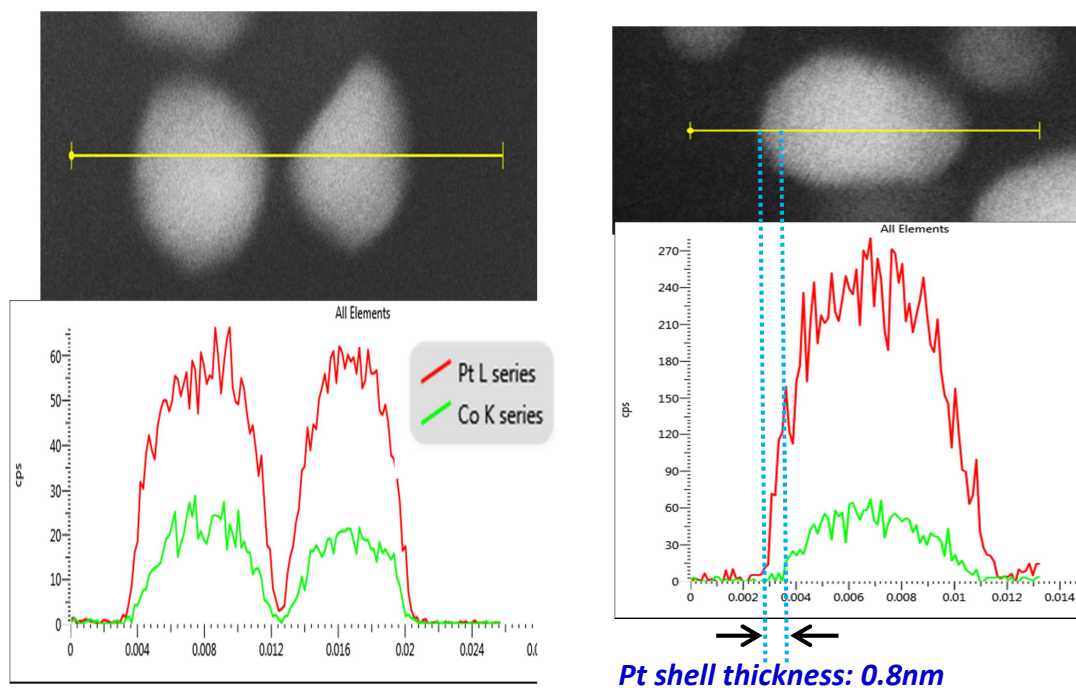


Fig 4. Line scan confirms the existence of Co within the core of the catalyst particle and a Pt shell thickness of 0.5-0.8 nm (Core-shell structure).

Effect of Annealing Temperature on Catalyst Mass Activity

The mass activities of Pt/ACCS and Pt*/ACCS catalysts at $0.9 V_{iR-corr}$, annealed at different temperatures under H_2/O_2 condition are shown in Figs. 5 (a). The mass activities of Pt*/ACCS catalysts showed more than two times higher values ($> 0.40 A mg_{Pt}^{-1}$) than that of Pt/ACCS catalyst ($0.193 A mg_{Pt}^{-1}$). The mass activity gradually increased to $0.492 A mg_{Pt}^{-1}$ at $700 ^\circ C$. The observed increase in mass activity can be attributed to an increase of Pt* lattice formation as a function of annealing temperature due to formation of Pt shell-Co core catalyst as described in conclusion. At $900 ^\circ C$, a decrease of mass activity was observed because of the agglomeration of Pt particles and large particle size of Pt. ECSA decreases as heat treatment temperature increases due to particle size increase. The H_2 /air fuel cell performance was investigated in order to evaluate the performance of Pt/ACCS and Pt*/ACCS under automotive operating condition (Fig. 5b). Initially when the measurements were performed at $0.7 V_{iR-corr}$ (mixed ohmic and mass transfer region), the results indicated that Pt*/ACCS catalysts showed $100 mA cm^{-2}$ higher current densities than Pt/ACCS catalyst under H_2 /air polarization. The current densities of $1186 mA cm^{-2}$ and $1143 mA cm^{-2}$ were observed at $0.7 V_{iR-corr}$ for $700 ^\circ C$ and $800 ^\circ C$ annealed Pt*/ACCS catalyst respectively compared with $1011 mA cm^{-2}$ estimated for Pt/ACCS catalyst.

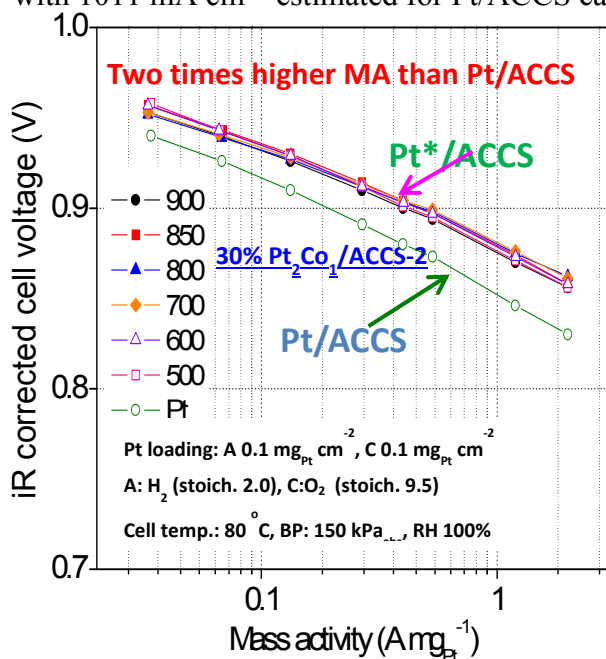


Fig. 5(a) Effect of annealing temperature on mass activity.

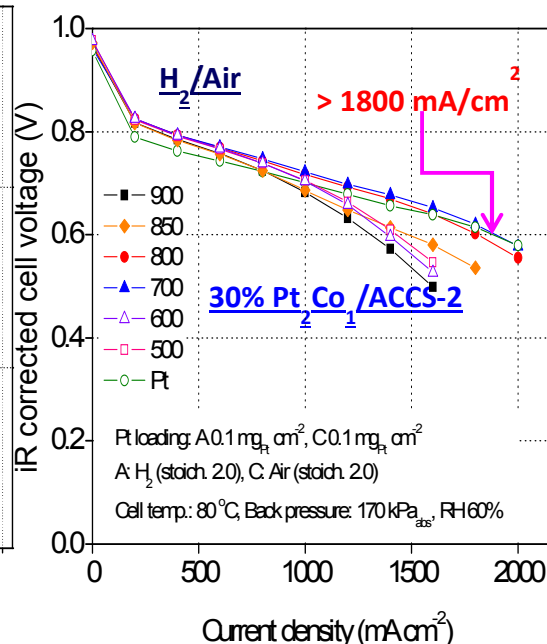


Fig. 5b. Effect of annealing temperature on H_2 -air performance.

The H_2 /air performance of Pt*/ACCS catalyst at mass transfer limitation region at $0.6 V_{iR-corr}$ shows similar performance when compared to Pt/ACCS catalyst. The current densities of $1889 mA cm^{-2}$ and $1800 mA cm^{-2}$ were observed at $0.6 V_{iR-corr}$ for $700 ^\circ C$ and $800 ^\circ C$ for annealed Pt*/ACCS catalysts, respectively. These performances are similar to those of the pristine Pt/ACCS catalyst of $1884 mA cm^{-2}$ at $0.6 V_{iR-corr}$. Lower performances than Pt/ACCS catalyst were observed in the case of catalysts

synthesized below 600 °C and over 850 °C. For the catalysts annealed below 600 °C, the low H₂/air performances are due to the residual coating materials on Pt particles which cover the active site of Pt. The performance of the catalysts annealed over 850 °C is attributed to the large Pt particle size and agglomerations. The reason for observed phenomenon is the fact that the H₂/air performance is mainly controlled by the kinetic performance of the catalyst at the low current density region but is mostly controlled by the mass transfer limitation including O₂ concentration and water removal at the high current density region. Furthermore, for both Pt/ACCS and Pt*/ACCS, only pure Pt will be present on the catalyst surface at applied potentials of 0.6-0.7 V due to the electrochemical reduction of Pt oxides at that potential. Various Pt/Co ratio in the range of Pt₄Co₁/ACCS to Pt₁Co₁/ACCS were synthesized using the same Co doping process and annealing conditions of 800 °C for 4 h. The effect of the Pt/Co ratio on the particle size and Pt structure is shown in Fig. 6. All Pt*/ACCS catalysts with various Pt/Co ratios showed peak shifts in XRD. The Pt*/ACCS catalyst synthesized with a higher amount of Co exhibited a higher shift in the 2θ angle indicating more active sites of compressive Pt* lattice have been formed during annealing process. Furthermore, Pt particle sizes of the Pt*/ACCS catalysts measured by XRD patterns showed the values in the range of 3-4 nm which were well maintained after annealing due to the controlled annealing with protective coating procedure

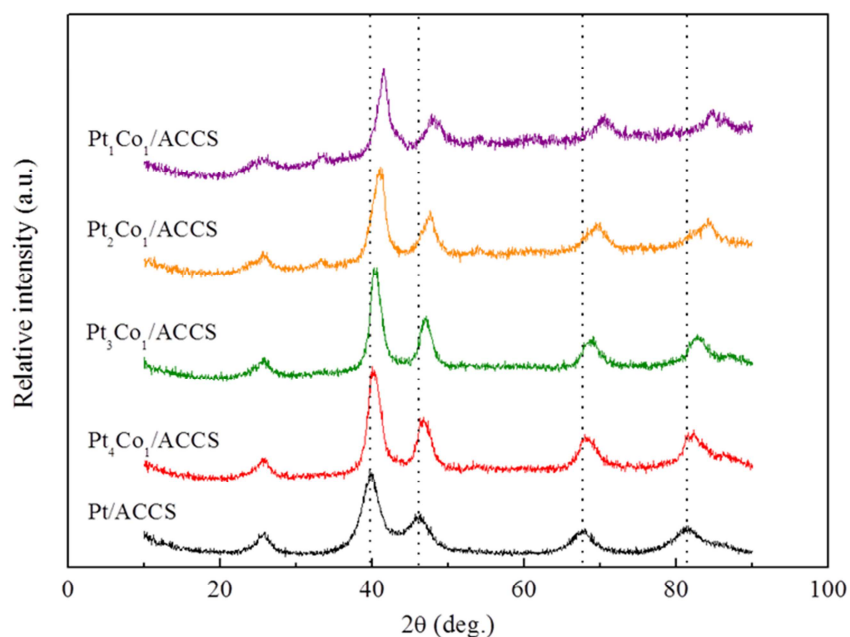


Fig. 6 XRD patterns for Pt/ACCS synthesized with various Pt/Co ratios.

As shown in Fig. 7(a), as the Co amount increases in the Pt*/ACCS catalyst, mass activity also increases due to the formation of a more compressive Pt lattice active sites. Most of Pt*/ACCS catalysts annealed at various temperatures showed Pt (111) 2θ values higher than 40.50° and mass activities above 0.40 A mg_{Pt}⁻¹. The H₂/air fuel cell

performance for Pt/ACCS and Pt*/ACCS synthesized with various Pt/Co ratios are shown in Fig. 7(b). The H₂/air fuel cell performance of Pt₂Co₁/ACCS and Pt₃Co₁/ACCS catalysts showed similar performance (1847 mA/cm²) with that of the Pt/ACCS catalyst.

The Pt₁Co₁/ACCS catalyst showed lower H₂/air fuel cell performance (1230 mA cm⁻²) when compared to that of the pristine Pt/ACCS catalyst (1884 mA cm⁻²) due to excess Co amount in the Pt₁Co₁/ACCS catalyst. Based on the physical and electrochemical properties of various Pt*/ACCS catalysts with different Pt/Co ratios, a catalyst with a composition of Pt₃Co₁/ACCS catalyst annealed at 800 °C for 4 h was selected and subjected to support stability and catalyst stability studies under 1.0-1.5 V and 0.6-1.0 V potential cycling conditions, respectively.

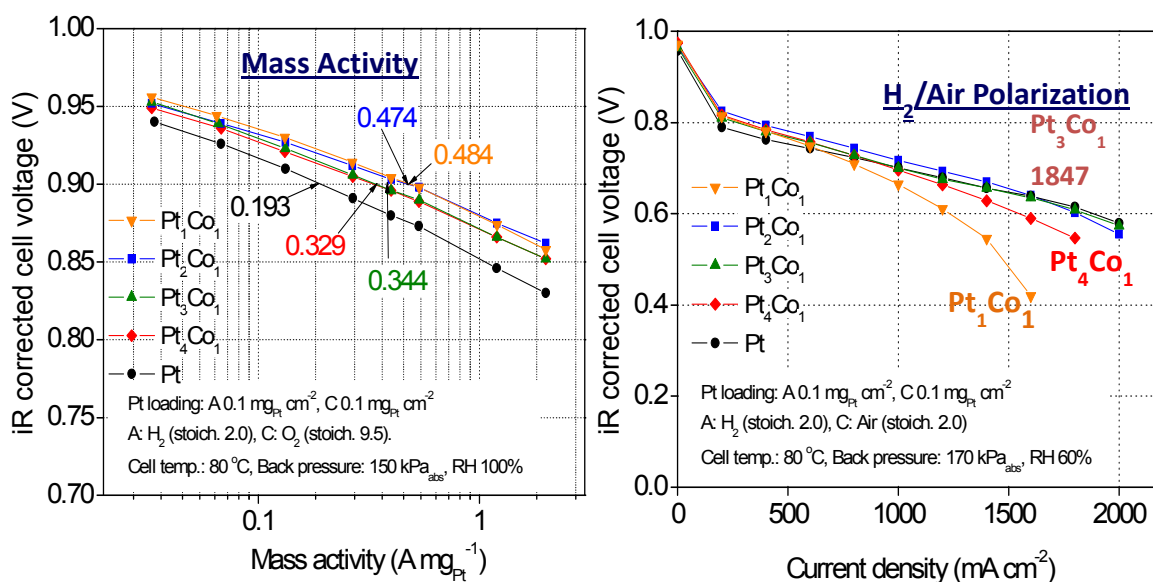


Fig. 7(a) Comparison of mass activities Fig. 7 (b) H₂/air polarization results for Pt/ACCS and Pt*/ACCS with various Pt/Co ratios.

The H₂/air fuel cell performance and mass activity of 30% Pt₃Co₁/ACCS subjected to 1.0-1.5 V potential cycling test is shown in Fig. 8(a) and 8(b). The Pt*/ACCS (30% Pt₃Co₁/ACCS) catalyst showed an initial potential of 633 mV_{iR-corr} at 1.5 A cm⁻² and a potential loss of 8 mV at 1.5 A cm⁻² after 5000 potential cycles between 1.0 and 1.5 V, Fig. 8 (a). Fig. 8(b) shows reproducibility of initial performance of mass activity for five MEAS. The commercial Pt/C catalyst showed 481 mV_{iR-corr} at 1.5 A cm⁻² for initial performance and no activity after only 1000 cycles between 1.0-1.5 V. The initial mass activity of the 30% Pt*/ACCS catalyst is in the range of 0.331-0.349 A mg_{Pt}⁻¹.

After 5000 cycles at 1.0-1.5 V the catalyst showed 0.171 A mg_{Pt}⁻¹ a value in the range of the initial performance of the commercial catalyst. The good support stability of Pt*/ACCS is attributed to the stable AC support.

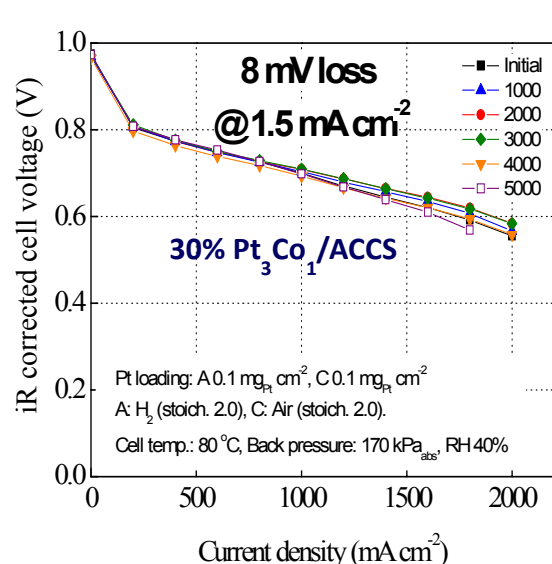


Fig. 8 (a) Support stability of 30 % $\text{Pt}_3\text{Co}_1/\text{ACCS}$ (1-1.5 V cycles)

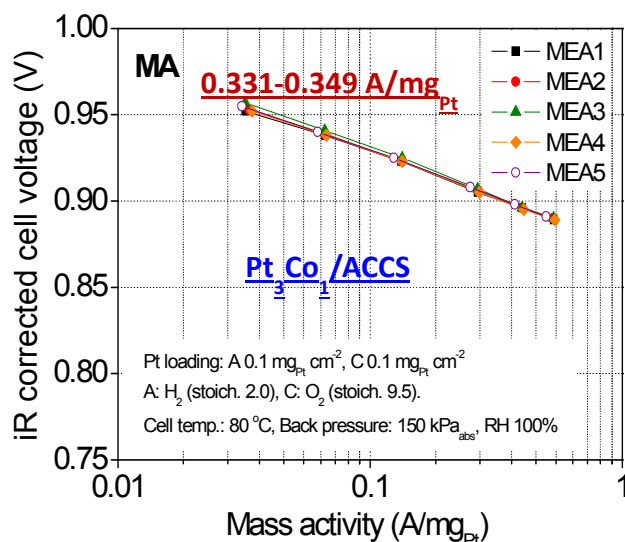


Fig. 8(b). Initial performance of mass activity of 30% $\text{Pt}_3\text{Co}_1/\text{ACCS}$

Fig. 9 (a) shows the H_2/air fuel cell performance of Pt^*/ACCS ($\text{Pt}_3\text{Co}_1/\text{ACCS}$) catalyst tested in 25 cm^2 MEA subjected to 0.6-1.0 V potential cycling test (30,000 cycles).

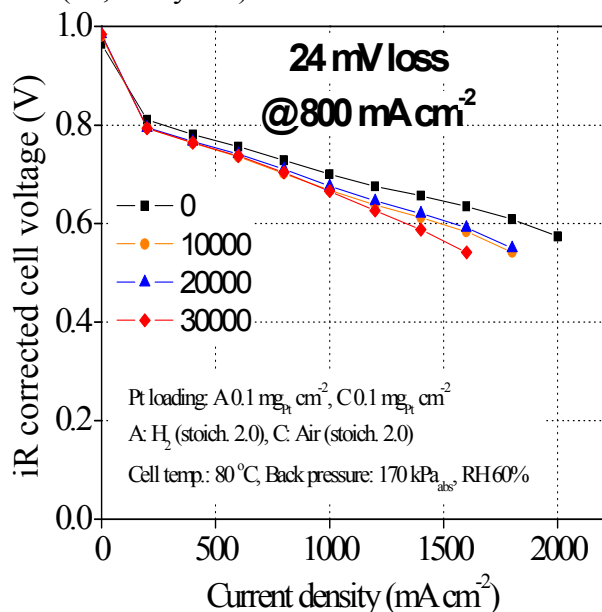


Fig. 9 (a) The catalyst stability test (0.6-1.0V) potential cycling for 30000 cycles) of 30%

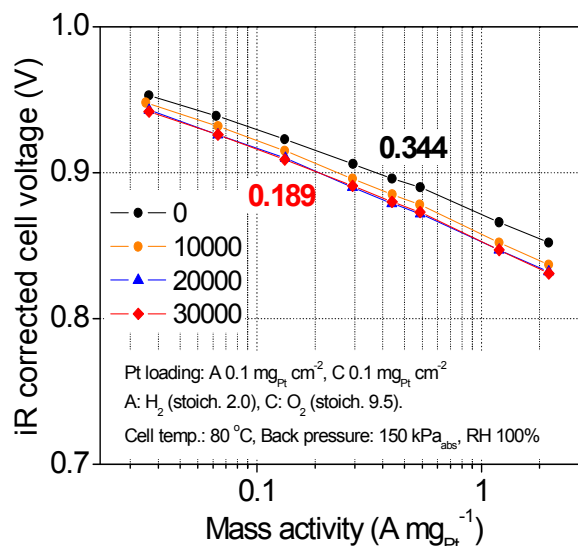


Fig. 9. (b) Mass activity loss after 30000 cycles (0.6-1.0V).

Pt^*/ACCS ($\text{Pt}_3\text{Co}_1/\text{ACCS}$) catalyst showed an initial potential of $729 \text{ mV}_{\text{iR-corr}}$ at 0.8 A cm^{-2} with a potential loss of $24 \text{ mV}_{\text{iR-free}}$ at 0.8 A cm^{-2} after 30000 potential cycles between 0.6 and 1.0 V. The 30% $\text{Pt}_3\text{Co}_1/\text{ACCS}$ catalyst showed high initial current due to

optimized catalyst layer thickness. The commercial Pt/C showed an initial potential of 696 mV_{iR-free} at 0.8 A cm⁻² and no activity at 0.8 A cm⁻² after 30000 cycles. Mass activity in Fig. 9 (b) from 0.344 A/mg_{Pt} decreases to the initial performance of Pt/C catalyst of 0.189 A/mg_{Pt}.

Mitigation of Pt dissolution in Pt*/ACCS

Line scanning analysis before and after the cycling test of 30000 cycles (0.6-1.0 V) is shown in Fig. 10.a

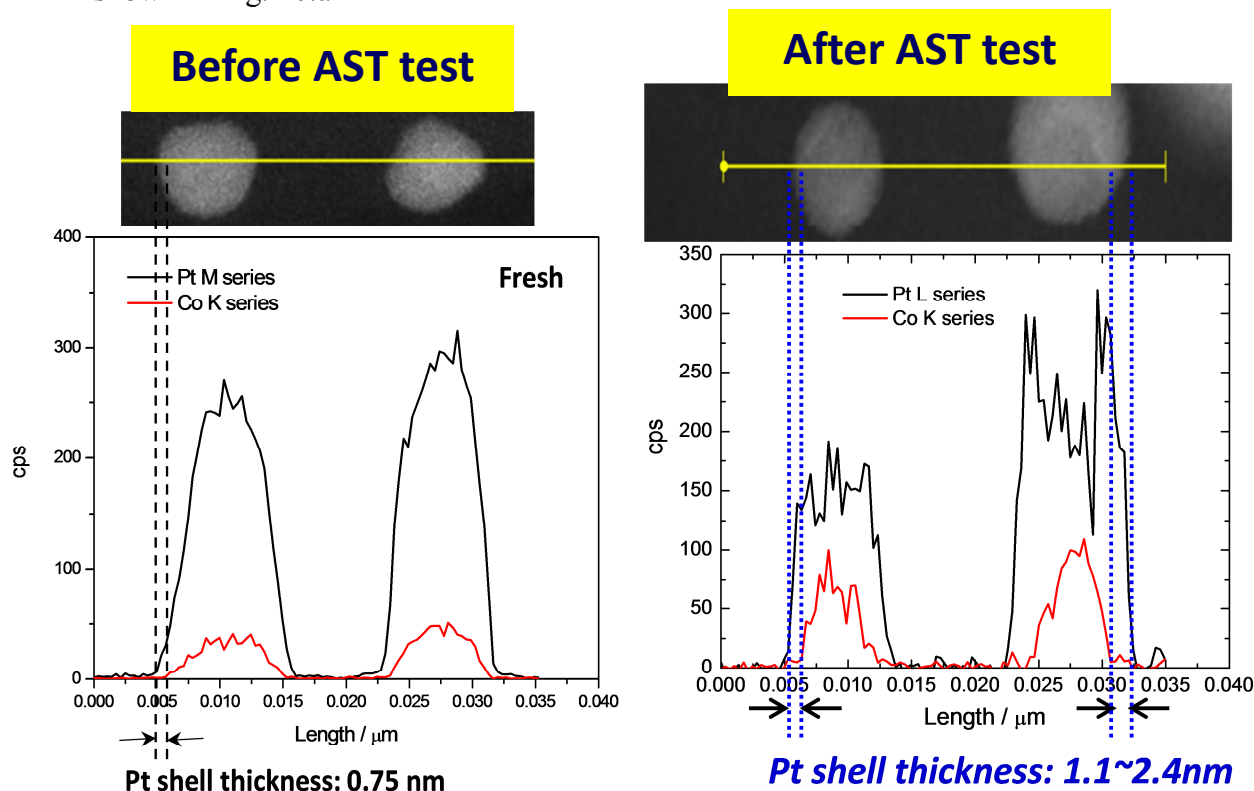
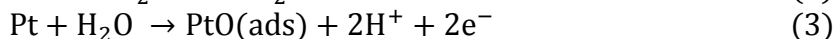
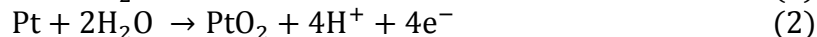
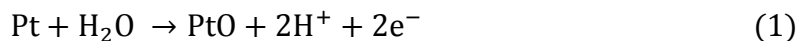


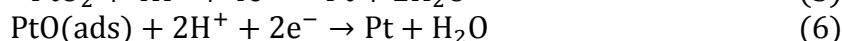
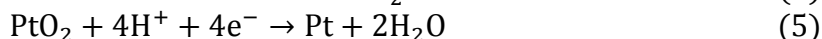
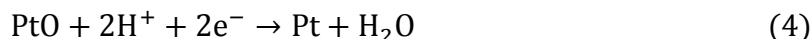
Fig. 10(a) Line scan analysis before stability test.

Fig. 10(b) Line scan analysis after catalyst stability test.

The results indicated that the Pt shell thickness increases from 0.7-0.8 nm (2-3 monolayers) to as high as 2.4 nm (8-10 monolayers). In core shell catalyst, Pt shell with 2-3 monolayers show highest activity for ORR. After cycling of 30000 cycles (0.6- 1.0 V), Pt shell thickness increases to 8-10 monolayers which decreases the ORR activity due to Pt redistribution. Our rotating ring disk electrode studies (RRDE) on 30% Pt*/ACCS catalyst indicated a shift in Pt-OH formation of 40 mV when compared with Pt/C or P/ACCS. The potential shift for Pt oxidation to higher values as indicated by the higher open circuit voltage (OCV) increases the mass activity in average from 0.15 to 0.4 A/mg_{Pt}, due to the suppression of Pt oxide formation which has much lower exchange current density for ORR ($i^0=1.7 \times 10^{-10}$ A/cm²) when compared to pure Pt ($i^0=2.8 \times 10^{-7}$ A/cm²). During potential cycling from 0.6-1.0 V, Pt oxides are formed according to the following reactions:

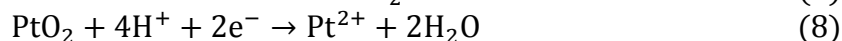


In the reverse scan from 1.0 to 0.6 V, Pt oxides are reduced to Pt according to the following reactions:



The potential shift for Pt oxidation to higher values increases the mass activity (from 0.15 to 0.4 A mg_{Pt}⁻¹) as discussed above due to the suppression of Pt oxide formation. Besides the effect of higher mass activity, the Pt* catalyst also illustrates much higher support and catalyst stability when compared to the pure Pt catalyst.

Pt dissolves during potential cycling conditions according to Eq. (7) and Eq. (8). Thus, less Pt oxide formation in the forward scan due to higher Pt oxidation potential in the case of the Pt*/ACCS catalyst alleviates Pt dissolution in the reverse scan and enhances the catalyst stability.



Conclusion

The ultra-low Pt cathode catalyst development project at the University of South Carolina (USC) has developed highly-stable activated carbon composite supports (ACCS) as well as highly-active and stable compressive Pt lattice cathode catalysts, Pt*/ACCS that retains their activity after accelerated stress tests to simulate start-up/shut-down and driving potential cycling. ACCS was synthesized with optimization of: (i) BET surface area, porosity, pore-size and distribution, (ii) hydrophilic/hydrophobic ratio, (iii) structural properties (amorphous/crystalline ratio), and (iv) Pt-support interaction through inclusion of active surface functional groups. For the first time we report a carbon based support which is stable under simulated start-up/shut-down operation conditions. The compressive Pt lattice catalyst (Pt*) was synthesized through a USC-developed annealing procedure that controls the particle size during annealing and forms several monolayers of Pt* by diffusing Co atoms into Pt which is deposited on ACCS support. The Pt*/ACCS shows high rated power density (0.174 g_{Pt} kW⁻¹), excellent support stability (8 mV loss at 1.5 A cm⁻²), and enhanced catalyst durability (24 mV loss at 0.8 A cm⁻²) under AST conditions. The fuel cell performance of the Pt*/ACCS catalyst, support stability under 1.0-1.5 V potential cycling and catalyst stability under 0.6-1.0 V potential cycling were evaluated using a 25 cm² MEA. The Pt*/ACCS catalyst showed an initial mass activity of 0.344 A mg_{Pt}⁻¹ at 0.9 V_{iR-corr} and an initial power density (rated) of 0.174 g_{Pt} kW⁻¹. The support stability under 1.0-1.5 V potential cycling showed a mass activity loss of 50%, a potential loss of 8 mV at 1.5 A cm⁻², and an ECSA loss of 22% after 5000 cycles. The catalyst stability under 0.6-1.0 V potential cycling showed a loss of mass activity

of 45%, a potential loss of 24 mV at 0.8 A cm^{-2} , and an ECSA loss of 42% after 30000 cycles which were improved over those of the Pt/ACCS catalyst. The improved catalyst stability of Pt*/ACCS is attributed to a lower formation of Pt oxide in the forward scan of 0.6-1.0 V due to a higher Pt oxide formation potential than Pt/ACCS which leads to less dissolution of Pt in the backward scan of 1.0-0.6 V. The Pt*/ACCS catalyst which showed high initial fuel cell performance, good support stability, and good catalyst stability would be an ideal cathode catalyst candidate for automotive application PEMFC.

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Abbervations Used in the paper

USC – University of South Carolina
 MES-Membrane Electrode Assembly
 PEMFC- Polymer Electrolyte Membrane Fuel Cell
 BET-Surface Area - Brunauer-Emmett-Teller Surface Area

Pt^{*}/ACCS – Compressive platinum lattice catalyst deposited on activated carbon support

Fabrication and operation under the same conditions: oxygen reduction on electrodeposited manganese oxide

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The recharging behavior and oxygen reduction electrocatalysis in alkaline solutions are compared for two types of birnessite materials potentiostatically electrodeposited by means of either anodic oxidation of Mn(II) in a neutral solution, or cathodic reduction of permanganate in alkaline medium. Fabrication and operation conditions are very close for the latter material, which demonstrates higher stability and activity. The reversible capacities of both materials exceed 500 F/g.

Introduction

We dedicate this work to Professor Radoslav Adzic. His works are inspirational for two topics combined below, oxides deposition and oxygen reduction reaction (ORR). For the former topic, Markovic and Adzic's observation of 2D oxides formation (1) is of crucial importance. As for ORR, this Adzic's favorite research area is widely known and does not require special comments, being a matter of classics.

We take a risk to present a study of electrodeposited manganese oxides. In spite of the very long scientific and technological history of these materials, there are still some missing aspects. Actually, to develop the oxide electrocatalysis for alkaline media we need to deposit the oxide at as high pH as possible, to make fabrication and operational conditions closer. The traditional anodic deposition from Mn(II) precursors excludes alkaline medium. As for deposition from neutral solutions, it can be arranged only in the presence of some complexing agents. The alternative cathodic deposition from permanganate solutions allows for neutral and alkaline conditions. This less known process recently attracted attention as a tool to fabricate the materials for supercapacitors (2-13). The cathodic deposition from neutral permanganate solutions under potentiostatic (2, 4, 6), galvanostatic (3, 5), pulse (9) and voltammetric (10) modes was reported. Typically, this process results in the formation of either X-ray amorphous oxides (5, 7), or of birnessite, the cation-doped MnO₂ phase stable in neutral and alkaline media. Publications on the deposition from alkaline solutions are more rare (7, 13), and no systematic optimization of deposition modes was reported for this process. ORR on cathodically deposited manganese oxide was tested only for neutral medium (12), and the observed activity was less impressive than for chemically synthesized manganese oxides (14).

Rather important advantage of electrodeposited oxides for electrocatalysis is the possibility to avoid carbon binder, but this goal can be achieved only if the deposits are

conductive enough and mechanically stable. Typically, deposition potential/current can strongly affect these properties of the resulting oxides, as well as their crystal structure and microstructure. In what follows we report the data for the optimized electrodeposition procedure, which allows for formation of oxides with a reasonable conductivity, high capacity, and high enough ORR activity at low overvoltages. We also present the data for more traditional anodic deposition from neutral medium for deposition potential optimized in a similar manner. To avoid the effects of the complexing agents, we limit ourselves to pH 6 (acetic buffer). Solutions with additives allow to reach pH 8 at most (15, 16), which is still very far from pH of alkaline solutions employed in electrocatalysis.

The data for electrodeposited oxides prepared from the alternative precursors are compared below with the data for a more conventional chemically prepared MnO_2 .

Experimental

Cathodic deposition of the manganese oxide at potential $E = 0.88 \text{ V}$ vs. reversible hydrogen electrode (RHE) was carried out from the $0.02 \text{ M KMnO}_4 + 1 \text{ M NaOH}$ bath prepared immediately before the experiment. KMnO_4 (Reachim) was recrystallized from Milli-Q deionized water. NaOH (50 %, extra pure, Acros Organics) was used without further purification. Module EM-04 (Volta) with a rotating disc electrode (glassy carbon, 2 mm diameter) was applied in combination with platinum foil as a counter electrode and Hg/HgO (1 M NaOH) as a reference electrode. Hg/HgO potential was 0.93 V (RHE). The electrode covered with oxide was washed twice in 6 ml of 1 M NaOH .

The bath for anodic deposition of the manganese oxide at $E = 1.04 \text{ V}$ (RHE) was $0.1 \text{ M Mn}(\text{CH}_3\text{COO})_2$ in 0.5 M acetic buffer, pH 6. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (99.99 %, Aldrich), glacial acetic acid (99.8 %, Panreac) and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (puriss. p.a., Sigma-Aldrich) were used without additional purification. The value of pH was controlled with “Anion 4100” pH-meter (Russia). The electrochemical cell with a glassy carbon rotating disc electrode (Sigradur, 5 mm diameter) was combined with Ag/AgCl (KCl sat.) and platinum foil used as reference and counter electrodes, respectively. The electrode covered with oxide was washed in 5-7 ml of pure H_2O and transferred to 1 M NaOH for subsequent measurements. Potential of Ag/AgCl electrode in 1 M NaOH was 1.014 V (RHE).

Autolab PGSTAT100 (EcoChemie, Netherlands) was used in all electrochemical experiments. All voltammetric tests were arranged in 1 M NaOH as the background solution. Both deposition and voltammetric experiments in the absence of O_2 were performed at the stationary electrode. All potentials in the text below are given in the RHE scale. All current densities (i) are reported per geometric surface area.

High purity Ar (99.998 %) was bubbled for at least 20 min before measurements for deairation of all solutions. To study the ORR activity, 1 M NaOH was saturated with pure O_2 (99.5 %). After 20 min of O_2 bubbling, the voltammogram was measured on the rotating working electrode (900, 1600, and 2500 rpm) starting from 1.2 V (RHE) at 2 mV/s scan rate.

To determine the coulometric thicknesses and current yields of the cathodically deposited oxide, additional experiments were performed using a large glassy carbon support (geometric area 21 cm^2), which was subsequently transferred to pure water and washed 4-5 times in new portions of pure water. At lower deposition charges Q_d the films appeared to be mechanically stable, and the current yield could be determined by weighting the dry electrode before and after the deposition. For thicker films, the

spontaneous deposit peeling from the support took place in water, so the solid fragments were collected from the bottom of the flask, dried and weighted. In this case the loadings can be slightly underestimated because of the loss of the minor portion of the oxide. For anodic deposition, the oxide quantity was estimated directly from Q_d . In both cases MnO_2 stoichiometry was assumed.

X-Ray diffraction patterns were collected on Rigaku D/Max RC diffractometer (Bragg-Brentano geometry, $\text{CuK}\alpha$ radiation) in the range $2\theta=5-75^\circ$. Phase identification was performed using ICDD PDF2 database (17). Samples for the analysis were obtained in a manner similar to the preparative cathodic electrodeposition, in order to collect 5-10 mg of a specimen.

Scanning electron microscopy (SEM) images of cathodically and anodically deposited films were registered using JEOL JSM 6490 LV and JSM 6460 LV microscopes, respectively, both with tungsten cathodes operated at 30 kV. Images were collected in a secondary electrons signal. Energy-dispersive spectra (EDS) were measured with INCA X-sight (Oxford Instruments). For qualitative treatment of EDS data, Microanalysis suite software (Oxford Instruments) was used. Imaging of cathodically formed film was performed for the fragments peeled from the support during washing. These fragments were placed on a carbon duct tape before measurement. Anodically deposited films were imaged directly on the glassy carbon support, which was washed carefully by pure water, dried and placed into the microscope chamber.

Results and discussion

Current transients (Fig. 1) were practically featureless, with a slight manifestation of current maxima in the case of anodic deposition (dashed curve 2 in Fig. 1).

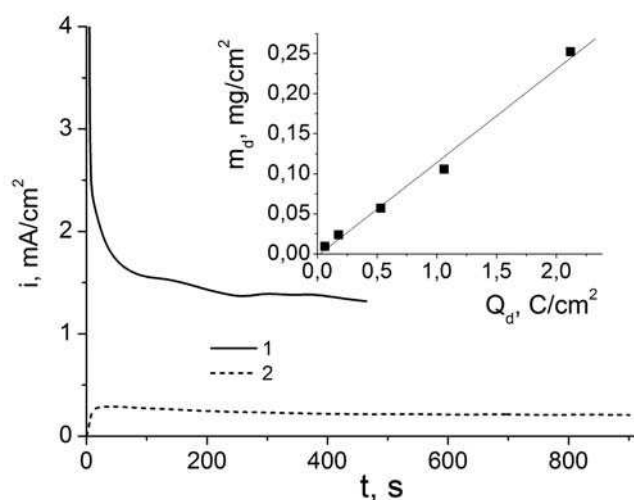


Figure 1. Current transients for the manganese oxide deposition at optimized potentials: cathodic deposition from 0.02 M KMnO_4 in 1 M NaOH at 0.88 V (RHE) (1) and anodic deposition from $\text{Mn}(\text{CH}_3\text{COO})_2$ in 0.5 M acetate buffer, pH 6, at 1.04 V (RHE) (2). The inset shows the dependence of the oxide loading on the deposition charge for the cathodically deposited film.

No parallel processes are thermodynamically possible at the potential used for anodic deposition, and all the charge is spent for oxide formation exclusively. Contrary, in the course of cathodic process, permanganate undergoes various parallel and subsequent transformations, and the oxide yield appears to be $(40 \pm 6) \%$. The transients in Fig. 1 correspond to very similar oxide loadings (85 and $91 \mu\text{g}/\text{cm}^2$ for cathodic and anodic deposition, respectively), despite the currents are much higher in the former case, and the deposition time is comparable. No effect of the pre-deposited oxide on the current yield was observed: in a wide interval of oxide thicknesses the loading was proportional to Q_d (see Fig. 1 inset). This means that controllable fabrication of the catalysts with desired loadings by means of cathodic deposition is possible, despite of complex electrochemistry of the permanganate precursor.

To test the rechargeable behavior of the deposits in alkaline solution, we started with slow scan rates and the cathodic potential limit of 0.7 V (RHE) (Fig. 2). We observed the decrease of the total charge in initial cycles, with subsequent stabilization (when further decrease of capacity is below 1-2%). According to Ref. (14), the irreversible reduction of various chemically synthesized manganese oxides (reductive degradation) can be excluded above this limit. Actually, the charge values at the anodic and cathodic scans are equal. However, the electrochemical response looks reversible only when we increase the cathodic limit up to 0.8 V (RHE) (curve 3 in Fig. 2). The capacities (Fig. 2, inset) calculated for 0.7 – 1.2 V (RHE) interval are proportional to the loading, and the values for both types of deposits are very similar.

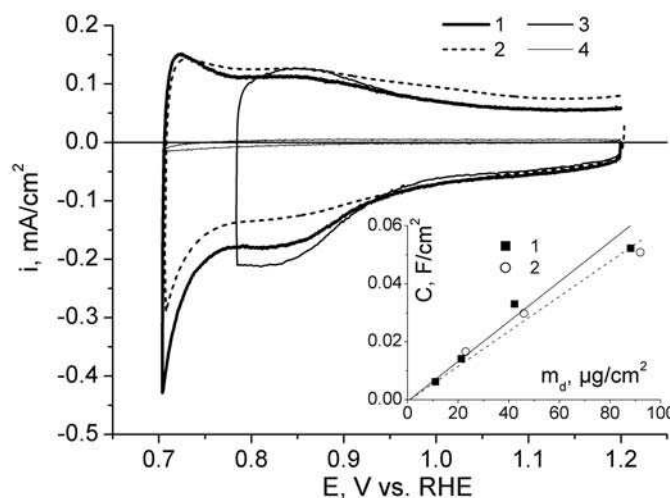


Figure 2. Voltammograms of cathodically (1, 3) and anodically (2) deposited manganese oxides in 1 M NaOH, (4) is the background curve for glassy carbon. Loadings are 85 and $91 \mu\text{g}/\text{cm}^2$, respectively. Seventh cycles are shown, scan rate is $2 \text{ mV}/\text{s}$. The inset presents the dependence of films capacity on the loading.

The difference in recharging behavior of cathodically and anodically deposited films becomes evident in our experiments with various scan rates (Fig. 3A). Manifestations of Ohmic drop are very pronounced for anodically deposited films (the capacity decrease starts already at 10 – $20 \text{ mV}/\text{s}$). In addition, the anodically deposited films tend to partial peeling in the course of recharging. Thin cathodically deposited films are less resistive,

more stable and demonstrate faster recharging. Their specific capacity remains above 500 F/g up to 100 mV/s scan rate, and approaches 300 F/g at 1 V/s. The observed capacity values are 2-3 times higher as compared to manganese oxides cathodically deposited from neutral solutions and tested in neutral solutions as well (2-6, 8, 9, 11).

Surely if one would like to consider supercapacitor applications in alkaline medium, this difference provides no serious advantage, because the potential window available in neutral solutions is wider. However, we consider the capacity data as a necessary part of material characterization protocol before going to electrocatalysis. In respect to this aspect, the data in Figs. 2 and 3A allow to conclude that both electrodeposited materials are homogeneously rechargeable, at least in the loading interval reported above. This means that if the deposits are porous, the pores are permeable for solution and do not induce the pronounced limitations for electrochemical reactions.

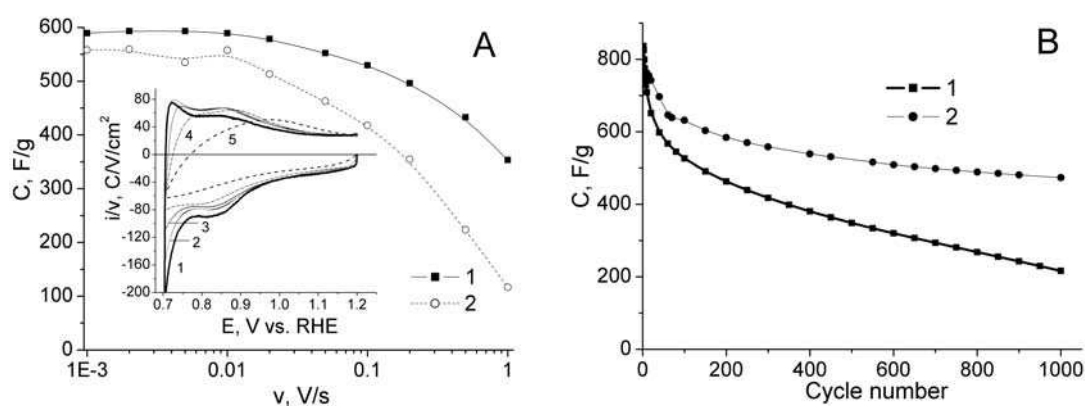


Figure 3. Specific capacities of cathodically (1) and anodically (2) deposited manganese oxides at various scan rates (A). Loadings are 85 and 91 $\mu\text{g}/\text{cm}^2$, respectively. The inset shows the voltammograms of the cathodically deposited oxide at 2 (1), 10 (2), 50 (3), 200 (4), and 1000 (5) mV/s measured in 1 M NaOH. The capacity evolution (B) for the cathodically deposited manganese oxide during the potential cycling at 100 mV/s in the intervals (0.7-1.2) (1) and (0.8-1.2) (2) V (RHE). This stability test was started for as deposited films without preliminary slow cycling, this is the reason of lower capacity in Fig. 3A (7th cycle at 2 mV/s).

To estimate degradation stability, we performed the accelerated test by means of cycling at 100 mV/s scan rate with various cathodic limits (Fig. 3B). The pronounced decrease of the specific capacity (200 F/g after 1000 cycles) was observed for wider potential window (0.7-1.2) V (RHE). Degradation is less pronounced when the cathodic limit is 0.8 V (500-550 F/g, Fig. 3B, curve 2). The behavior of the anodically deposited oxide is similar. The limited stability at 0.7 V (RHE) should not be considered as disadvantage for ORR applications, because operation of the ORR cathode at potentials above 0.8 V RHE is even preferable.

From the first glance, it is difficult to correlate the results on oxides recharging with the electron microscopy morphological data (Fig. 4). The cathodically deposited oxide looks like the compact solid, at least on the sub-micrometer scale (Fig. 4, A), when the anodically deposited film demonstrates the pronounced dispersion (Fig. 4, B). The same type of flakes is well known for microstructures of the anodically deposited manganese

oxides. The flake-like morphology is well-known also for the oxide cathodically deposited at higher overvoltages (3, 4, 6, 8, 9, 11, 12). XRD data (Fig. 5) confirm that both deposits consist of strongly disordered birnessite, and no other crystalline phases can be detected. The almost complete absence of basal reflections ((001) at $2\theta \approx 12.4^\circ$, (002) at $2\theta \approx 24.9^\circ$) indicates the loss of the stacking order in the direction perpendicular to the Mn-O layers. Such a case, complicated with the layers bending, was analyzed in (18). Large asymmetry of in-plane reflections, in addition to the absence of basal reflections, indicate the turbostratic disorder, observed for synthetic K-birnessite (19). The data on oxygen stoichiometry and cation content in our birnessite samples will be discussed in a separate communication.

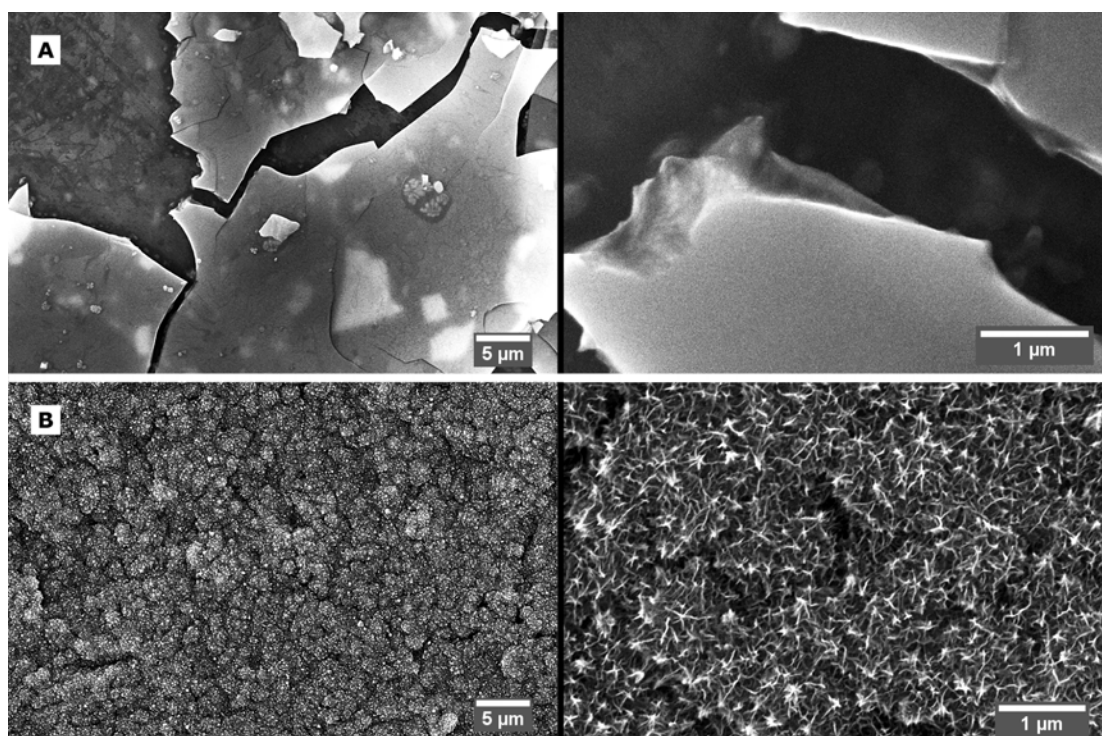


Figure 4. SEM images of cathodically (A) and anodically (B) deposited manganese oxides at two magnifications. Loadings are 85 and 91 $\mu\text{g}/\text{cm}^2$, respectively. Images A correspond to oxide peeled from the support, to show the absence of flakes at the cross-section (visible at the right image).

The electrocatalytic test (Fig. 6) demonstrates much higher activity of the cathodically deposited sample, for which the current is approaching the theoretical value for the 4-electron limiting diffusion current. The ORR onset potential for this material exceeds 0.9 V (RHE), being comparable with onset potentials of the most active chemically synthesized oxides operating with carbon binders at similar loadings (14). For the anodically deposited oxide with the very close loading, the onset potential is shifted to lower potentials (dashed curve 2 in Fig. 6). ORR currents remain practically unchanged after the preliminary film cycling during 1000 cycles in the background solution if the cathodic limit does not exceed 0.8 V (RHE) (curve 3).

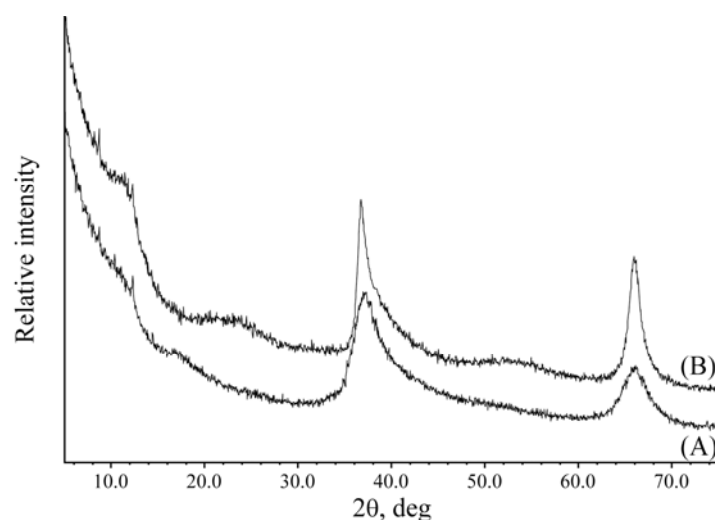


Figure 5. X-ray diffraction patterns of the cathodically (A) and anodically (B) deposited manganese oxides.

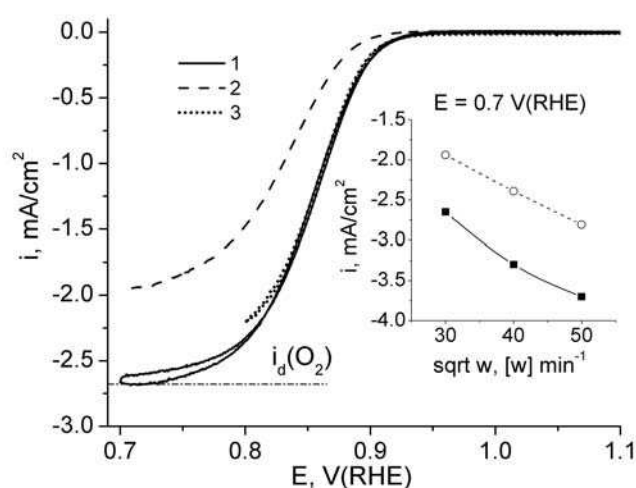


Figure 6. Oxygen reduction currents measured at RDE (900 rpm) for cathodically (1, 3) and anodically (2) deposited manganese oxides. Capacitive contribution is subtracted. Loadings are 85 and 91 $\mu\text{g}/\text{cm}^2$, respectively. Curve 3 corresponds to the electrode after degradation test (1000 cycles, (0.8-1.2) V (RHE), 100 mV/s, see Fig. 3B). The inset shows the limiting currents dependence on rotation rate.

To compare the specific activities of materials under discussion, we treated ORR data in frames of Koutecky-Levich equation. The limiting diffusion current i_d (A/cm^2) was calculated as follows:

$$|i_d| = 0.62nFD^{2/3}v^{-1/6}\omega^{1/2}C \quad , \quad [1]$$

the parameters for 1 M NaOH at 25°C were: O_2 concentration under saturation $C=8.4 \cdot 10^{-7} \text{ mol}/\text{cm}^3$, the O_2 diffusion coefficient $D=1.65 \cdot 10^{-5} \text{ cm}^2/\text{s}$ (20), the kinematic

viscosity of the electrolyte $\nu=0.011 \text{ cm}^2/\text{s}$, $n=4$, Faraday constant $F=96500 \text{ C/mol}$. The kinetic current i_k (electrocatalytic activity) was calculated from

$$1/|i_f| = 1/|i_k| + 1/|i_d| \quad . \quad [2]$$

The kinetic currents were normalized to oxide loadings to obtain the specific catalytic activity.

Table 1 presents the comparison of specific activities for electrodeposited materials under study and chemically synthesized $\beta\text{-MnO}_2$ (pyrolusite) studied earlier with a carbon binder (14). One can see that cathodically deposited carbon-free sample demonstrates the same activity as $\beta\text{-MnO}_2$. Its expected additional advantage is higher stability in alkaline medium, in which birnessite is more stable than pyrolusite. The most possible reason of the lower activity demonstrated by our anodically deposited oxide is its higher resistance, which presents the same problems as we always meet for less conductive chemically synthesized oxides.

TABLE I. Specific activity of manganese oxides in ORR reaction currents at 0.85 V (RHE)

Sample	Loading, $\mu\text{g/cm}$	Currents value, A/g
Anodically deposited at 1.08 V (RHE)	91	10.5
Cathodically deposited at 0.88 V (RHE)	85	28
Chemically synthesized $\beta\text{-MnO}_2$ with C-binder (14)	91	24

Conclusions

As the real surface area of electrodeposited oxides remains unknown at this stage, we cannot compare the specific activities per real surface area, quantitatively. However, a rough estimate of the surface areas from the capacity is possible. This estimate demonstrates that the surface areas of both electrodeposited samples are close and exceed the surface area of the chemically synthesized $\beta\text{-MnO}_2$. As both anodically and cathodically deposited samples consist of one and the same disordered crystalline phase and have similar dispersion, we can assign the difference in their ORR electrocatalytic behavior either to morphological difference, or to some tiny difference in stoichiometry.

The morphological difference is of interest on its own: what factors can force the material tending to flake-like ‘shaggy’ morphology to form very dense porous layers? One cannot exclude some difference in the density of nucleation centers at the surface of glassy carbon in neutral and alkaline solutions, but it is difficult to imagine that this difference is significant. We can assume that the most important difference can go from precursors chemistry: for cathodic deposition, it is highly probable that the solid oxide is formed in certain chemical step, by analogy with the chemical deposition of birnessite. Possibility to fabricate birnessite samples with either flake-type or dense morphology controlled by solution pH and the permanganate concentration was observed, e.g., in Ref. (21). More precise structural and compositional study of cathodically deposited samples is in progress.

Acknowledgments

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Chapter 4

Poster Session

The effect of synthesis temperature on Pd-H catalyst structure for alkaline direct formate fuel cells

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Keywords: Pd catalyst, Formate oxidation, Alkaline medium

Abstract

Palladium on a carbon support, electron-enriched by hydrogen incorporation to form Pd (Pd-H/C), was synthesized *via* dimethylamine borane complex at multiple temperatures and used for the oxidation of formate (HCOO^-). Physicochemical analysis revealed no significant changes in the Pd-H/C structures, with changes in only the particle size and dispersibility. The electronic effect of H was confirmed by physicochemical and electrochemical analysis and by the comparison of synthesized Pd-H/C with commercial Pd/C. The catalyst synthesized at 0 °C showed best catalytic activity for the oxidation of HCOO^- because it possessed the largest electrochemical surface area due to its smallest particle size and best dispersibility.

Introduction

Direct liquid fuel cells (DLFCs) have received much attention due to their safety, transportation, storage, and utility. Among them, fuel cells using formate (HCOO^-) as a fuel in alkaline media have attracted the greatest focus due to their faster oxidation kinetics than those of formic acid (HCOOH) in acidic media and higher theoretical voltage than that of methanol and ethanol.¹⁻⁵ Carbon monoxide is an inevitable product from the oxidation of formic acid and HCOO^- on platinum (Pt) surface and can poison the catalyst, but HCOO^- is the predominant form in alkaline media, and there is no poisoning effect on palladium (Pd) surface.⁶⁻⁹ The oxidation of HCOO^- in alkaline media with Pd catalysts has been investigated since 1969, and many researchers have reported studies of direct HCOO^- fuel cells (DFFCs) that showed remarkable power performance.^{6,10,11} Nevertheless, the catalytic activity of Pd for HCOO^- oxidation can still be improved. From a mechanistic study perspective, decreasing the chemisorption strength of the adsorbed hydrogen (H_{ads}) plays a key role in enhancing the catalytic activity of the oxidation of HCOO^- on Pd. This is because the desorption of H_{ads} is the rate-determining step (RDS) for the oxidation of HCOO^- on Pd because it blocks an active site of HCOO^- adsorption.^{9,10,12} In general, the adsorption strength of adsorbing species on metal is impacted by its electronic structure. By alloying Pd and other transition metals such as copper (Cu) or gold (Au), the adsorption strength on Pd is weakened because the d-band of Pd is more filled due to electron transfer from other the transition metal to Pd.^{13,14} In addition, the adsorption strength on Pd can also be weakened by the electronic effects caused by filling the d-band of Pd with electrons from heteroatoms such as hydrogen (H) and boron (B) that enter

the Pd lattice.^{12,15}

In a previous study, we synthesized a Pd-H catalyst on a carbon support using sodium borohydride as a reducing agent and observed enhanced catalytic activity for the oxidation of HCOO^- despite the poor morphology compared with that of commercial Pd/C.¹² Many studies have revealed a correlation between morphology and catalytic activity of catalysts in various chemical energy conversion applications such as oxygen reduction^{16,17} and formic acid oxidation^{18,19}. Since the morphology is also closely related to the catalytic activity, we investigated the correlation between changes in morphology and catalytic activity of the catalyst toward HCOO^- oxidation by controlling the synthesis temperature. In this study, we synthesized Pd-H catalysts at various temperatures on the carbon powder (Pd-H/C), taking advantage of a temperature-dependent characteristic of the Pd lattice during synthesis. Through physicochemical and electrochemical analysis, the different prepared catalyst surface morphologies, particle sizes, crystal structures, and catalytic activities toward HCOO^- oxidation were compared.

Experimental

The palladium catalysts (20 wt.%) on a carbon support were prepared via a wet-chemical synthesis method with dimethylamine borane complex (DMAB) as a reducing agent over a range of temperatures. First, 35.4 mg of palladium chloride (PdCl_2 , Sigma-Aldrich, $\geq 99.9\%$) was added into a mixture of 7.5 mL of deionized water (18.2 M Ω cm) and 5 mL of 0.1 M hydrochloric acid (HCl) (Sigma-Aldrich, 37%) and stirred at 50 °C for 20 min. The solution containing the Pd precursor was added to 187.5 mL of deionized water and stirred at 25 °C for 10 min. Then, 2 mL of ammonia (NH_3) solution and 0.973 mL of 0.1 M potassium iodide (KI) were added to adjust the pH to 11 and to act as complexing agents. Next, 84.96 mg of Vulcan XC-72 carbon was added with stirring at 25 °C for 10 min, and the mixture was sonicated for 45 min at various temperatures, namely, 0, 15, 25, and 40 °C. While maintaining the temperature, 20 mL of 0.1 M DMAB was added dropwise to the reaction mixture at 0.4 mL min^{-1} with continuous sonication for 90 min. Finally, each of the catalysts was rinsed with deionized water to remove any residues and subsequently dried in the oven at 60 °C for 180 min.

The particle size and dispersibility of Pd-H/Cs and commercial Pd/C were analyzed by using high-resolution transmission electron microscopy (HR-TEM; Philips TECNA1F20) at the Korea Basic Science Institute (KBSI), Gwangju Center. The crystal structure of the catalysts was analyzed by using X-ray diffraction (XRD; Rigaku, Miniflex II) with Cu $K\alpha$ ($\lambda = 0.15406$ nm). The electronic structure of these catalysts was analyzed with X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific, Theta Probe AR-XPS system) at KBSI, Busan Center. In addition, the oxidation states and lattice structure of these catalysts were analyzed by using X-ray absorption spectroscopy (XAS) with the 7D X-ray absorption fine structure (7D-XAFS) beamline of the Pohang Accelerator Laboratory (PAL). XAS data of the Pd K-edge were measured in transmission mode between 24150 and 25300 eV, employing a double crystal Si (111) monochromator in step-scan mode. A palladium foil was also simultaneously measured as reference.

All electrochemical experiments were performed with a three-electrode system using a potentiostat/galvanostat (Biologic, VSP). The ink consisted of 10 mg of catalyst, 2.5 mL of deionized water (D.I. water 18.2 M Ω), 2.5 mL of dimethyl formamide (DMF, Junsei), and 10 μL of Nafion solution (Sigma-Aldrich, 10 wt.%). For the cell, 40 $\mu\text{g cm}^{-2}$ of Pd metal was used

as a working electrode by drop casting 20 μL of a well-dispersed catalyst ink on a rotating disk electrode (glassy carbon, 0.196 cm^2). A platinum wire and Hg/HgO filled with 1 M potassium hydroxide (KOH) were used as the counter and reference electrode, respectively. To remove impurities on the catalyst surfaces, a cleaning process utilizing cyclic voltammetry (CV) was carried out, scanning from 0.916 to 0.234 V vs. Hg/HgO in 1 M of KOH saturated with N_2 at a scan rate of 100 mV s^{-1} for 0 cycles. Cyclic voltammograms were collected for each catalyst at a scan rate of 20 mV s^{-1} to show the catalyst characteristics. The catalytic activities toward HCOO^- oxidation were also evaluated by CV at a scan rate of 20 mV s^{-1} in 1 M of KOH containing 500 mM HCOOK.

Result and discussion

As in the previous study, the Pd-H/C catalyst was synthesized using NaBH_4 as a reducing agent. NH_3 functioned as a complexing agent; the presence of the complex ($[\text{Pd}(\text{NH}_3)_4]^{2+}$) prevented the formation of $\text{Pd}(\text{OH})_x$. The presence of the iodine ion (I^-) contributed to the reduction of the Pd particle size due to the increased steric hindrance when substituting for the chloride (Cl^-) ligand in the Pd complex.¹² The Pd-H/C prepared using DMAB in this study was compared to that previously prepared using NaBH_4 . As shown in Figure 1, the catalytic activity of Pd-H/C prepared in this study was superior to the previous Pd-H/C catalyst.

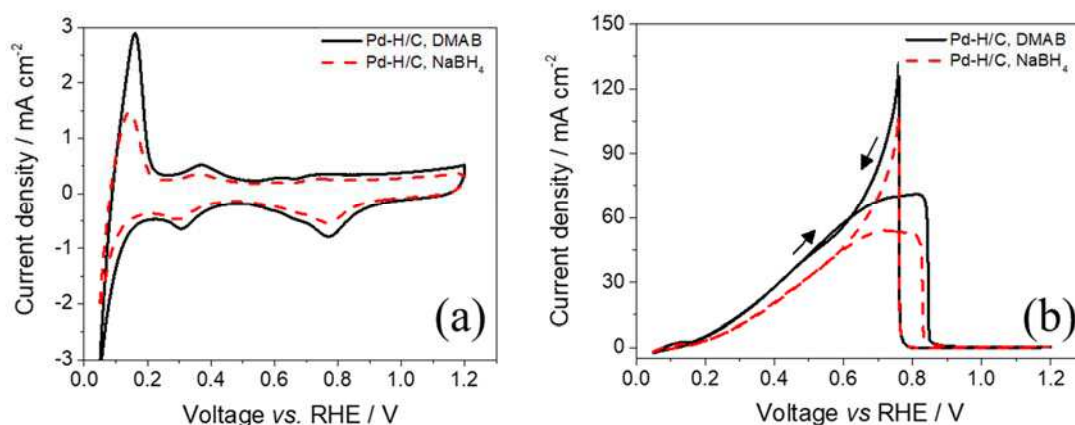


Figure 1. Comparison of Pd-H/C catalyst prepared from DMAB and NaBH_4 ; Cyclic voltammograms at scan rate of 20 mV s^{-1} in (a) 1 M of KOH, and (b) 1 M of KOH containing 500 mM of HCOOK.

Various physicochemical analyses were conducted to compare the structural characteristics of each synthesized Pd-H/C catalyst. TEM analyses for each Pd-H/C synthesized at various temperatures (0, 15, 25, and 40 $^{\circ}\text{C}$) as well as for commercial Pd/C were conducted to evaluate their morphology, including characteristics such as the catalyst particle size and dispersibility on the carbon support (Figure 2). As shown in Figure 2, the particle size increases with increasing synthesis temperature from (a) (4-8 nm), (b) (10-15 nm), (c) (10-15 nm), and (d) (10-20 nm), and the Pd particles were well dispersed at the lower temperatures such as 0 $^{\circ}\text{C}$ and 15 $^{\circ}\text{C}$ (Figure 2a and b). In contrast, at 25 $^{\circ}\text{C}$ and 40 $^{\circ}\text{C}$, the Pd particles showed significant agglomeration (Figure 2c and d), which could be attributed to the high surface energy of Pd.^{20,21} In case of the commercial Pd/C, the particle size was 3-4 nm, and the Pd particles were well dispersed (Figure 2e). As demonstrated in the TEM images shown in Figure 2, the synthesis temperature affects the particle size and their dispersibility.

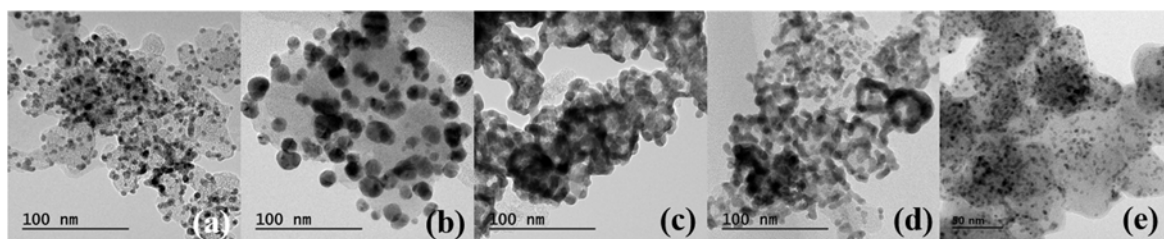


Figure 2. TEM images of Pd-H/C synthesized at various temperatures; (a) 0 °C, (b) 15 °C, (c) 25 °C, (d) 40 °C, and (e) commercial Pd/C.

XRD analysis for each Pd-H/C and the commercial Pd/C was carried out to discern the crystal structure, as shown in Figure 3. The XRD pattern of Pd shows two peaks at 39.4° and 45.8° , which represent the Pd (111) and (200) surfaces. Compared to the peaks of Pd, the XRD patterns of each of the synthesized Pd-H/Cs were negatively shifted to 38.6° and 44.9° , which represent the (111) and (200) surfaces of palladium hydride, respectively (Figure 3a-d). The commercial Pd/C had an XRD pattern very similar to that of Pd, but a small amount of palladium oxide was also observed (Figure 3e). It is also possible to observe a small amount of Pd-H formation in the synthesized Pd catalysts. However, there was no difference among the Pd-H/Cs, so it could be determined that the formation of the Pd-H structure was independent of the synthesis temperature.

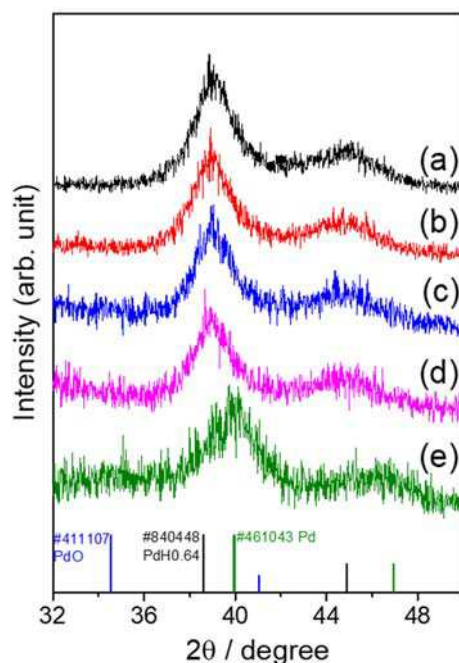


Figure 3. XRD patterns of Pd/C synthesized at various temperatures; (a) 0 °C, (b) 15 °C, (c) 25 °C, (d) 40 °C, and (e) commercial Pd/C.

XPS analysis was also carried out to evaluate the electronic structure of Pd for each Pd-H/C as shown in Figure 4. The Pd 3d binding energy spectra show that electron-enriched states of Pd were dominant in the synthesized Pd catalysts, potentially due to the electron transfer from hydrogen to Pd. (Figure 4a-d) To evaluate the difference in their states, the full width at half maximum (FWHM) was calculated as shown in Table I. Since there was no significant difference between the calculated FWHMs, it was determined that the electronic structure of Pd in each Pd-H/C was nearly identical (Figure 4 and Table I). The Pd 3d spectrum of commercial Pd/C shows mixed states of Pd⁰, Pd²⁺, and Pd^{δ+} attributed to the Pd-C interface.²² As compared to the Pd 3d of the commercial Pd/C, the Pd 3d of the Pd-H/Cs were somewhat positively shifted. As reported in previous studies, this core shift is due to Pd-H formation.^{23–25}

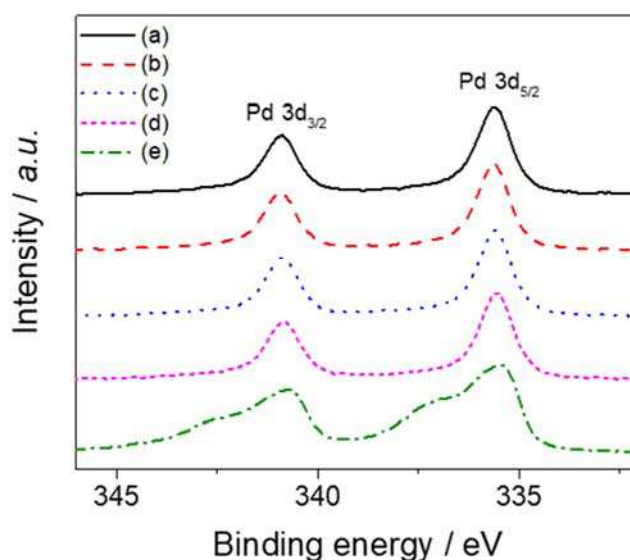


Figure 4. XPS spectra of Pd 3d for Pd/C synthesized at various temperatures; (a) 0 °C, (b) 15 °C, (c) 25 °C, (d) 40 °C, and (e) commercial Pd/C.

Table I. FWHM of Pd 3d for Pd/synthesized at various temperatures; (a) 0 °C, (b) 15 °C, (c) 25 °C, and (d) 40 °C

Name	FWHM of Pd 3d _{3/2} (343–339)	FWHM of Pd 3d _{5/2} (337.5 – 334)
(a)	0.9610	0.9729
(b)	0.9454	0.9213
(c)	0.9608	0.9327
(d)	0.9606	0.9442

The results of the XAS analysis for each Pd-H/C are in accordance with the results of XRD

and XPS analysis as shown in Figures 5 and 6. As shown in the X-ray absorption near-edge structure (XANES) results, the oxidation states of all of the synthesized catalysts were quite similar to the second peak representing metallic Pd (Pd^0) dominant over that represented by oxidized Pd (Pd^{2+}) (Figure 5a-d), while that of commercial Pd/C was Pd^{2+} . (Figure 5e)

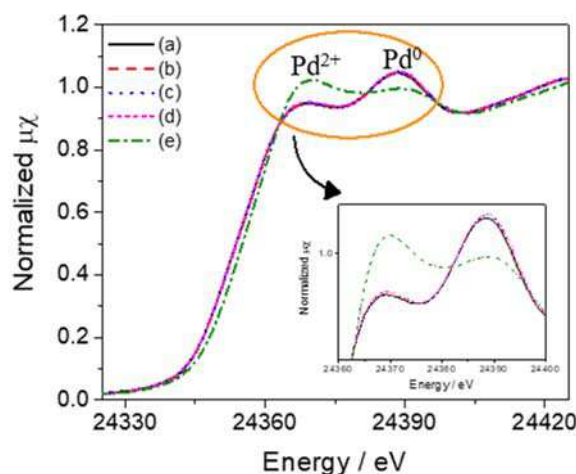


Figure 5. XANES spectra of Pd K-edge for Pd/C synthesized at various temperatures; (a) 0 °C, (b) 15 °C, (c) 25 °C, (d) 40 °C, and (e) commercial Pd/C.

The extended X-ray absorption fine structure (EXAFS) spectra shown in Figure 6 show similarity at peak position and intensity for all Pd-H/Cs, containing two main peaks at approximately 2 and 2.58 Å. The ratio of intensity of two main peaks of each Pd-H/Cs is 1:1.69 (Figure 6a-d); a ratio less than 1:2 between 2 and 2.5 Å is an exemplary value for Pd metal.²⁶ The smaller ratio of two main peaks indicates that both the hydrogen atoms are in contact with Pd and more hydrogen atoms are bound to the Pd. Furthermore, the positive shift of the second peak means indicates an expansion of the Pd-Pd bond distance due to the introduction of hydrogen atoms between the Pd lattice.¹² The ratio of two peaks for commercial Pd/C at approximately 2 and 2.5 Å was less than 1:1.69, possibly due to Pd-O formation (Figures 5e and Figure 6e).

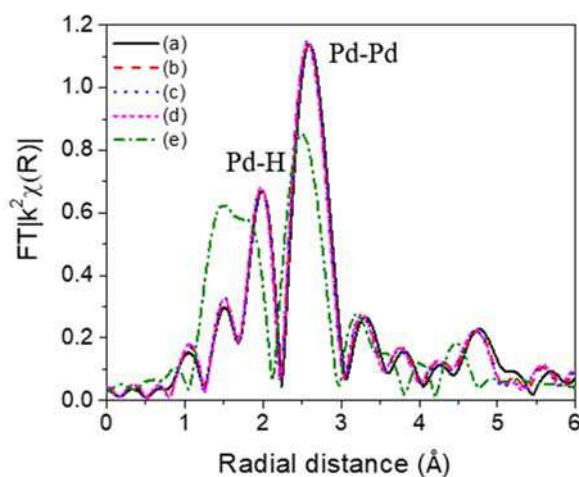


Figure 6. EXAFS spectra of Pd K-edge for Pd/C synthesized at various temperatures; (a) 0 °C, (b) 15 °C, (c) 25 °C, (d) 40 °C, and (e) commercial Pd/C.

The XAS analysis results strongly supports the presence of the Pd-H structural features and the consistency of Pd-H/Cs structures, as inferred from XRD patterns and XPS spectra. Through the physicochemical analysis, we also investigated that the crystal structure and the electronic structure of Pd-H were independent from the synthesizing temperature, but the particle size of Pd-H and its dispersibility were dependent on the temperature.

The electrochemical analysis was performed to check the catalytic activity of each Pd-H/Cs. Figure 7 shows the cyclic voltammograms for each Pd-H/C in a 1 M KOH solution. From the cyclic voltammograms, the electrochemical surface area (ECSA) of each Pd-H/C was calculated as shown in Table II. The ECSA values were (a) 38.15, (b) 27.33, (c) 24.62, and (d) 21.31 m² g⁻¹ and decreased with the synthesis temperature; (a) 0, (b) 15, (c) 25, and (d) 40 °C. These differences were related to the difference of the Pd particle size resulting from the different synthesis temperatures. The ECSA of commercial Pd/C was 62.38 m² g⁻¹ (Figure 7 and Table II). The reduction peak from Pd-O to Pd (405 μC cm⁻²) was used to calculate the ECSA.²⁷

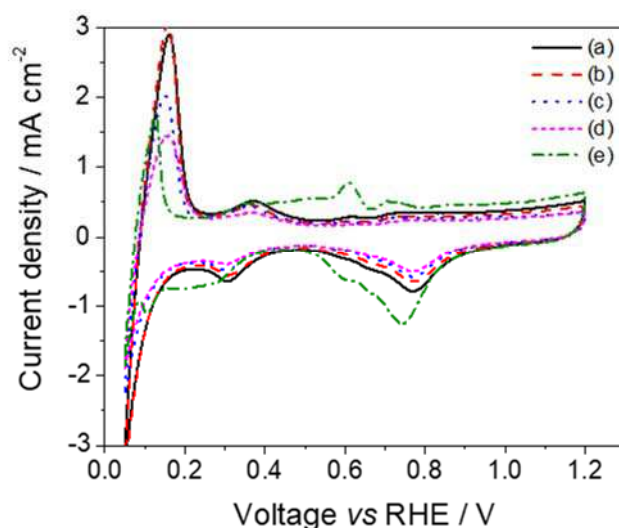


Figure 7. Cyclic voltammograms at a scan rate of 20 mV s⁻¹ for Pd/C in 1 M KOH; (a) 0 °C, (b) 15 °C, (c) 25 °C, (d) 40 °C, and (e) commercial Pd/C.

Table II. ECSA for Pd/C; (a) 0 °C, (b) 15 °C, (c) 25 °C, (d) 40 °C, and (e) commercial Pd/C

Name	ECSA / m ² g ⁻¹
(a)	38.15
(b)	27.33
(c)	24.62
(d)	21.31

(e)

62.38

The cyclic voltammograms in 1 M KOH containing 500 mM HCOOK were recorded to observe the catalytic activity of each Pd-H/C toward HCOO^- oxidation, as shown in Figure 8. The onset potential of each Pd-H/C toward HCOO^- oxidation was similar. In contrast, the peak current density, which can represent the HCOO^- oxidation activity, was different across the catalysts. The peak current densities were (a) 72.5, (b) 67.1, (c) 57.2, (d) 41.1 and (e) 49.0 mA cm^{-2} . Comparing the series of Pd-H/Cs, the catalytic activities represented by the peak current density corresponded to the difference in ECSAs caused by the differences in particle size. As previously mentioned, because the particle size depends on the synthesis temperature, the catalytic activity of each Pd-H/C toward HCOO^- oxidation increased as synthesis temperature decreased (Figure 8a-d). Comparing the commercial Pd/C with Pd-H/C 0 °C, the commercial Pd/C showed less activity in the oxidation of HCOO^- than did Pd-H/C 0 °C despite the larger ECSA of the commercial sample (Figure 8a and e). With similar particle size, the enhanced activity of Pd-H/C can be attributed to the presence of highly metallic and electron-rich Pd due to the electron transfer from H to Pd.¹² However, when comparing Pd-H/C 40 °C with commercial Pd/C, although the Pd-H structure was formed, it could not fully compensate for the difference in ECSA caused by its large particle size and poor dispersibility as compared to that of the commercial catalyst (Table II, Figure 8d and e). In other words, the electronic effect might not fully compensate for the structural difference, so to effectively investigate the electronic effect between catalysts, the particle size should be similar. Therefore, we conclude that the synthesis temperature for the Pd-H/C that showed the best catalytic activity is 0 °C.

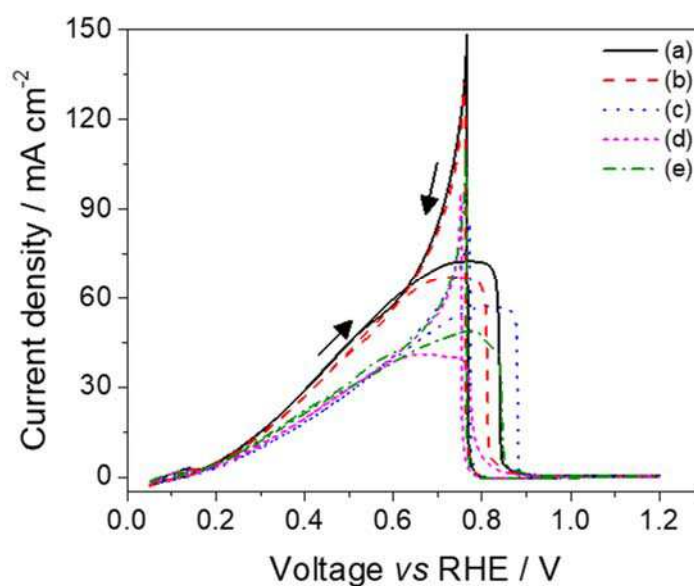


Figure 8. Cyclic voltammograms at scan rate of 20 mV s^{-1} for Pd/C in 1 M KOH containing 500 mM HCOOK; (a) 0 °C, (b) 15 °C, (c) 25 °C, (d) 40 °C, and (e) commercial Pd/C.

Summary

Modifying a catalyst from our previous study,¹² we synthesized Pd-H/C catalysts for the oxidation of HCOO^- using DMAB and multiple synthesis temperatures. The particle size and dispersibility of Pd in the catalysts were different with different synthesis temperatures.

However, through various physicochemical analyses, including XRD, XPS, and XAS, Pd-H formation was consistently observed in each of the catalysts, though other structural changes, such as differences in oxidation states or lattice structures, were not observed. Lower synthesis temperatures resulted in smaller and better-dispersed Pd-H/C catalysts but also larger ECSA values, as shown by the electrochemical analysis. The catalytic activities for the oxidation of HCOO^- correlated with the distribution of ECSA, and Pd-H/C 0 °C showed the best peak current density for the oxidation of HCOO^- . Comparing Pd-H/C with commercial Pd/C, the catalytic activity of Pd-H/C 0 °C was much better than that of the commercial Pd/C, and the ECSA of Pd-H/C 0 °C was smaller than that of the commercial Pd/C. This result is attributed to the more metallic and electron-enriched Pd in Pd-H/C caused by electron transfer from H to Pd. From the experimental results, Pd-H/C 0 °C was determined to be the best Pd/C catalyst for the oxidation of HCOO^- in our investigation. However, as observed with the comparison of Pd-H/C 40 °C to commercial Pd/C, this electronic effect of H does not always compensate for the small ECSA caused by large particle size and severe agglomeration. Therefore, in order to accurately evaluate the electronic effect, size and dispersibility control should first be established.

Acknowledgments

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Chapter 5

Oxidation Reactions

Temperature-Dependent Kinetic Study of Ammonia Oxidation Reaction on Gas Diffusion Electrodes in NH₃-Saturated 1 M KOH Solutions

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Ammonia oxidation reaction (AOR) is sluggish, especially at ambient temperature. To make kinetic study in electrochemical cell more informative and relevant to the catalysts' performance in direct ammonia fuel cells (DAFCs) operating at about 100 °C, it is desirable to study the AOR kinetics at elevated temperatures. However, ammonia evaporation accelerates with increasing temperature causing decrease of ammonia concentration with time. We show here a feasible solution to this issue - let argon gas bubble through concentrated ammonia before entering the electrochemical cell so that the solution can be kept ammonia saturated and oxygen free. Repeatable AOR polarization curves were obtained at temperatures up to 60 °C. The AOR activities are characterized by the average currents at 0.5 V versus RHE measured at 20 mV s⁻¹ in potential cycles below the potential of peak current. For PtIr/C, the PGM mass activities are 25 A g⁻¹ at 25 °C and 225 A g⁻¹ at 60 °C. The results for Pt/C and Ir/C and discussion of the causes for their distinct kinetic behavior will be presented at the meeting.

Introduction

Kinetic characterization of electrocatalysts requires minimization of concentration changes of solution components during the measurements. For the six-electron transfer AOR, $2 \text{NH}_3 + 6 \text{OH}^- = \text{N}_2 + 6 \text{H}_2\text{O} + 6\text{e}^-$, NH₃ and OH⁻ are the reactants. Studies using rotating disk electrode (RDE) have shown the effects of changing ammonia concentration from 1 mM to 2 M at pH 14 and changing KOH concentration from 0.05 to 1 M with 1 M ammonia.¹ It is clear that 1 M KOH is sufficient and convenient for minimizing change of OH⁻ concentration during AOR measurements and for lowering high frequency resistance. An issue is how to keep ammonia concentration constant with time while inert gas flowing through the cell that carries away vaporized ammonia. Here, we show that a feasible solution is to keep ammonia concentration at saturation for any given temperature by a constant gas flow of NH₃-Ar mixed gas in the cell so that the solution remains ammonia-saturated and oxygen-free concurrently.

A second issue for carrying out measurements at elevated temperatures is that catalyst particles may fall off the electrode during the measurements. Since porous surface allows more catalysts and higher ionomer content in a thicker catalyst layer, gas diffusion electrode (GDE) is preferred than a smooth glassy carbon electrode. Previously, we have demonstrated the advantage of GDE in eliminating the gas transport limitation for hydrogen oxidation and evolution reactions.^{2,3} While mass transport is less a limiting factor for the sluggish AOR, the reaction kinetics on GDE may still be affected by ammonia

transport limitation. Even with GDEs, catalyst particles falling off was observed at 65 °C, and thus, we kept most studies at temperature up to 60 °C.

Experimental

Preparation of gas diffusion electrodes

PtIr alloy is known as one of the most active AOR catalysts.⁴⁻⁷ We conducted this study using the commercial PtIr/C catalyst (Premetek, 40 wt%, Pt:Ir molar ratio 1:1, 4.5 nm average particle size). Inks were made by dispersing PtIr/C in mixed solvent of deionized water, ethanol, and isopropanol (volume ratio 1:1:2). Nafion[®] (perfluorinated resin, equivalent weight 1000, Aldrich) was added with about 0.3 ionomer/carbon weight ratio as the binder to make thin catalyst layer smooth and stable. The gas diffusion layer (GDL, Sigracet 25 BC) was cut into 1.4 cm wide and 3 cm long strips and the GDE samples were made by drop casting 10 to 20 μL ink containing 0.1 mg metal on $1.4 \times 0.7 = 1 \text{ cm}^2$ area at one end of the GDL strips. After drying in air, the catalyst-loaded samples were immersed in 1 M KOH before measurements so that less time was needed for getting stabilized polarization curves in alkaline solutions.

Electrochemical measurements

Electrochemical measurements were performed using a Voltalab PGZ 402 potentiostat with an electrochemical cell immersed in a water bath with temperature control (Lauda E100). We held a GDE strip vertically with its catalyst-coated part immersed in solution and faced a Pt-flag counter electrode that was about 1 cm away. A Hg/HgO electrode was used as the reference electrode. The zero potential versus reversible hydrogen electrode (RHE) in 1 M KOH was determined by the open circuit potential on Pt in hydrogen saturated solution. The AOR polarization curves were measured in 1 M KOH solution with argon gas bubbling through concentrated 28% NH_3 solution before entering the cell for keeping the solution oxygen free with NH_3 concentration at saturation, except where is noted otherwise. The iR -free potential was obtained by subtracting the product of measured currents and the high-frequency resistance determined from electrochemical impedance spectra acquired at 500 mV versus RHE.

Results and Discussion

AOR Polarization Measurement with Saturated Ammonia Concentration

Initially, we measured AOR polarization curves in a 1 M KOH solution containing 0.1 M ammonia at 60 °C. The curve measured soon after the solution was deaerated is shown by the blue line in Fig. 1a. After one hour at open circuit, the repeated polarization measurement (green line) exhibited considerably lower AOR currents. We then let argon gas bubble through concentrated ammonia solution before entering the electrochemical cell. With the inlet gas carrying ammonia vapor, the ammonia concentration can be considered at saturation. Under this condition, the third polarization curve was measured (red line), which exhibits the highest currents. This experiment showed the need to avoid ammonia concentration decreasing with time during AOR measurements at elevated temperatures.

Next, we made saturated ammonia solution solely by feeding ammonia-argon mixed gas to the cell containing 1 M KOH. Monitored by repeated potential cycles within low potential region, the AOR polarization curves stabilized within about 30 minutes. Figure 1b shows four AOR polarization curves measured after ammonia reached saturation. The first and fourth curves were obtained at the same 20 mV s^{-1} sweep rate. They overlapped well, demonstrating that adding a bubbler filled with concentrated ammonia in the inert gas line is a feasible method to keep ammonia concentration at saturation and solution free of oxygen concurrently.

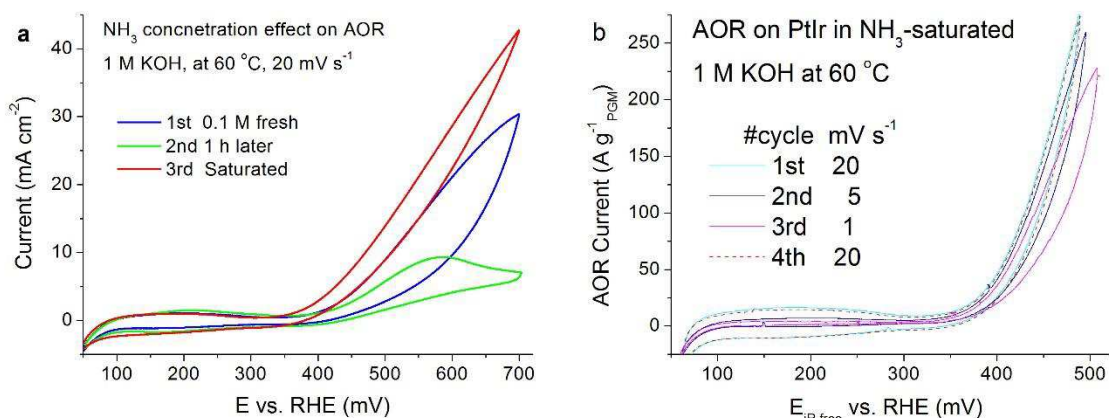


Figure 1. (a) AOR polarization curves for PtIr/C on GDE in 1 M KOH at 60°C measured shortly after the solution containing 0.1 M NH_3 was deaerated with Ar gas (blue), about 1 h later (green), and after feeding Ar- NH_3 mixed gas (red). (b) AOR polarization curves measured in NH_3 -saturated 1 M KOH at different sweep rates. The fourth curve with the same 20 mV s^{-1} sweep rate as the first is for verifying that AOR polarization curves can be reproduced at 60°C invariantly with time.

AOR Current Peak and Increased Irreversibility with Increasing High Potential Limit

In studying the AOR kinetic behavior over a wide potential range at 60°C , we made potential cycles starting at 0.05 V with the high potential limit increased 0.1 V per cycle from 0.5 to 1.2 V. For clarity, only selected curves are shown in Fig. 2a. The current gap between forward and backward potential sweeps increases with higher potential limit. Positive to the AOR current peak potential of 0.65 V, the catalyst surface soon becomes completely deactivated as the currents in the reversed potential sweeps drop to near zero. This behavior has been observed at ambient temperature and attributed to the formation of fully deprotonated N^* intermediate that is inactive for dimerization and blocks the surface sites.^{1,4,6,8}

When temperature is increased from 25 to 60°C , the AOR current increases, especially at low potentials where the activation barriers are higher, resulting in a slightly negative shift of the peak potential as shown in Fig. 2b. In this measurement, the peak current is increased to about sevenfold from 25 to 60°C . This is likely slightly underrepresented the temperature enhancement factor because we used one sample by repeated potential cycles at 25, 40, 50, and 60°C and the current peak commonly decreases slightly with increasing number of potential cycles to high potentials (see the light blue, blue, and green curves in Fig. 2a). Nevertheless, these results show that the temperature effect on the AOR kinetics and comparison of various catalysts can be performed in a consistent manner with reproducible ammonia concentration.

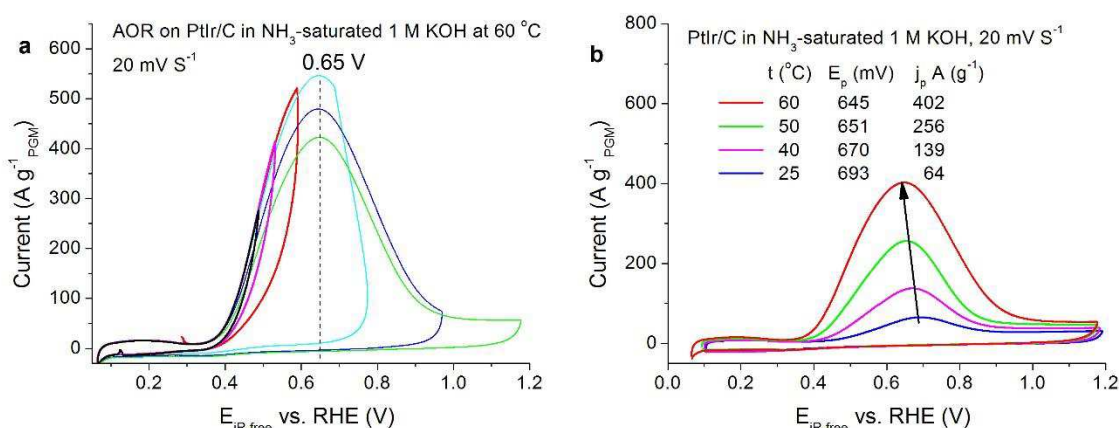


Figure 2. AOR polarization curves measured with sequential increase of the high potential limit at 60 °C (a) and with fixed potential range at various temperatures (b).

Quasi-Steady-State AOR Polarization Curves at Low Potentials

To establish the AOR performance benchmark with commercial PtIr/C catalysts, we measured AOR polarization curves at the potential below 0.6 V versus RHE. A typical example is shown in Fig. 3a using PGM loading of 0.1 mg cm⁻². The mass-normalized AOR current is shown on the right y-axis. After correcting the ohmic (or iR) loss (blue line), we averaged the currents in the forward and backward potential sweeps so that the sweep-rate-dependent capacitance currents can be canceled out. As shown by the red curve, the current is essentially zero below the AOR onset potential. It is considered as a quasi-steady-state polarization curve because such curves still are sweep-rate-dependent due to the deactivation effect of accumulated inactive intermediates. Therefore, the AOR mass activities should be determined using the polarization curves measured at the same sweep rate for quantitative comparison. Figure 3b shows the results for the commercial PtIr/C (1:1 Pt:Ir molar ratio, 4.5 nm average particle size) at various temperatures: the AOR mass activity at 0.5 V increases nearly one order of magnitude from 25 A g⁻¹ at 25 °C to 225 A g⁻¹ at 60 °C.

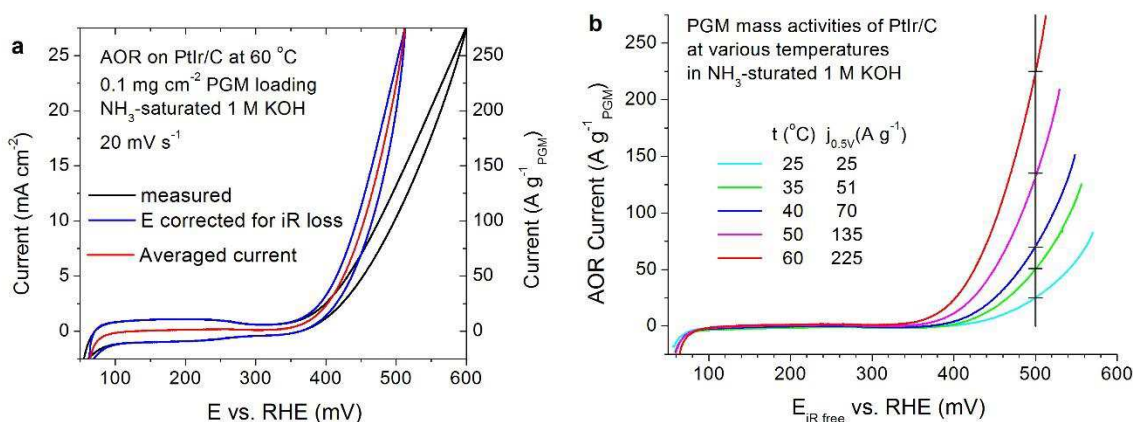


Figure 3. (a) Measured, iR-loss corrected, and steady-state (i.e., currents-averaged) AOR polarization curves for PtIr/C at 60 °C. (b) Steady-state AOR polarization curves for PtIr/C in NH₃-saturated 1 M KOH at various temperatures.

Conclusions

In this study, we showed that AOR kinetic studies can be carried out in solution electrochemical cell up to 60 °C with ammonia concentration at saturation. Using a constant inlet flow of ammonia-argon mixed gas, the solution can be easily kept oxygen free and ammonia saturated for hours. This condition ensures that changes in measured AOR polarization curves are not affected by gradual decrease of ammonia concentration. For temperature dependent measurements, the method resolves the issue of accelerated loss of ammonia with increasing temperature. Using PtIr/C, one of the most active AOR catalysts, we benchmarked the AOR activity at 0.5 V of 25 A g⁻¹ at 25 °C and 225 A g⁻¹ at 60 °C. About tenfold increase in activity by rising temperature to 60 °C can help in studying kinetic behavior in the low potential region that is most relevant to DAFC performance.

Acknowledgments

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Understanding Reaction Mechanisms Using Dynamic Electrochemical Impedance Spectroscopy: Modeling of Cyclic Voltammetry and Impedance Spectra

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The fitting of reaction models consisting of elementary reaction steps to experimental data constitutes a method for verification of the reaction models and the possibility of finding the kinetic parameters of a system. However, due to the complexity that easily arises due to numerous reaction steps, it is notoriously difficult to pose a problem and optimize it to a single solution. Therefore, the successful fitting of a reaction model is not proof since several models can potentially be fit successfully to the same experimental dataset. A possible solution to this problem is to fit the reaction models to one dataset and verify the results by using a complementary experimental technique under the same conditions. Dynamic electrochemical impedance spectroscopy (dEIS) is uniquely suited for such an approach. In this work, a method for fitting and optimizing kinetic parameters in a reaction mechanism to experimental data from cyclic voltammetry is described. Subsequently, the optimized kinetic parameters are used to calculate corresponding dEIS results. Methanol oxidation on Pt at elevated temperatures is used as an example of the application of this method.

Introduction

Electrochemical impedance spectroscopy (EIS) is a suitable tool for mechanistic studies due to the amount of data that is accessible through this technique (1). However, even if the frequency range is wide, the mechanistic information is convoluted making the interpretation complicated. Therefore, data analysis of impedance data is often limited to pattern recognition and fitting of equivalent circuits. Methods for calculating EIS spectra from a stated mechanism are readily available (2, 3). However, the system under study needs to be well understood so that realistic reaction mechanisms can be formulated.

Quantitative analysis using EIS data is a goal as it can utilize information that is readily available experimentally to enhance mechanistic analysis. The use of dEIS is an ideal tool for this purpose because dEIS is collected simultaneously with a pseudo steady-state technique such as slow cyclic voltammetry, allowing for the simultaneous collection of direct current (dc) and alternating current (ac) data. In practical cases, models of different reaction mechanisms have yielded similar results for steady-state techniques making the results ambiguous (4). In our case, with the combination of dEIS and cyclic voltammetry, a reaction mechanism can be fitted to experimental cyclic voltammograms, and the

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calculated dEIS spectra can be used to distinguish between mechanisms that have similar modeled cyclic voltammograms. This combination offers a superior path for performing a mechanistic analysis.

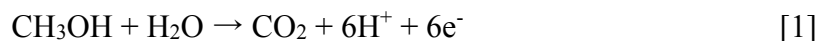
In this work, we present a systematic method to deduce a reaction model from experimental data. The method uses a dc technique, i.e., cyclic voltammetry, to fit kinetic parameters through an iterative optimization process. Subsequently, EIS spectra at any potential can be calculated and compared to the experimental data. This routine makes it possible to use the large amount of information found in dEIS data sets in a mechanistic analysis. Examples from studies of methanol oxidation are used to illustrate the technique.

Problem statement

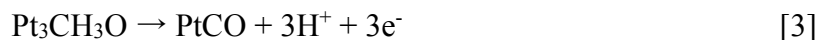
The fitting of a reaction mechanism to experimental data is a general problem in electrochemistry. However, few established methods exist where the kinetic parameters can be quickly optimized. The general statement of the optimization problem is given below for the case of methanol oxidation through adsorbed CO. Experimental data at higher temperatures are used to support the assumption that this reaction pathway dominates the overall mechanism (7). The purpose is to explain the methodology, and show that realistic reaction mechanisms can be proposed.

Methanol oxidation

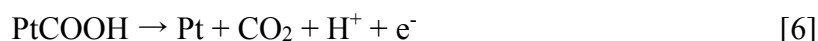
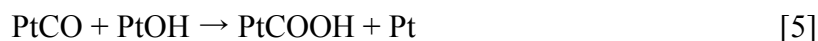
Methanol oxidation in acidic conditions is known to proceed through a dual pathway mechanism, a direct pathway producing formaldehyde, formic acid, and CO₂, and an indirect pathway through adsorbed CO producing CO₂ (8). At temperatures above 100°C, the indirect pathway dominates the current, and the overall reaction mechanism can be simplified (7). The half-cell reaction of methanol to CO₂ is given in Eq. (1).



The total reaction can be separated into two steps in the indirect pathway: CO production and CO oxidation. For the CO production step(s), it is assumed that three Pt sites are necessary to adsorb methanol on Pt in accordance with the literature (9-11). Therefore, the CO production steps can be written as in Eqs. (2)-(3).



Similarly, for the CO oxidation steps, a chemical surface reaction is assumed, i.e., a so-called Kauranen-step (13), giving the steps in Eqs. (4)-(6) as the CO oxidation mechanism.



In addition to all the steps related to methanol oxidation, platinum oxidation will proceed at higher potentials; this reaction is simplified as Eq. (7).



The mechanism consisting of Eqs. (2)-(7) thus constitutes a model for indirect oxidation of methanol on Pt.

Reversible OH/O reactions

The water adsorption step, Eq. (4), is commonly assumed to be reversible. This makes the reaction infinitely fast, and hence, the kinetics of the reaction does not contribute to the shape of the impedance spectra. To simplify the calculation further and to minimize the influence of the platinum oxidation reaction, Eq. (7), this step is assumed to be reversible as well. Following these assumptions, the surface coverages of OH and PtO can be found from Eqs. (8)-(9).

$$\theta_{\text{OH}}/\theta_{\text{Pt}} = K_{\text{OH}} \exp(F\eta/RT) \quad [8]$$

$$\theta_{\text{PtO}}/\theta_{\text{OH}} = K_{\text{PtO}} \exp(F\eta/RT) \quad [9]$$

Here, θ_i is the surface coverage species i defined as $\theta_i = \Gamma_i/\Gamma_{\text{tot}}$, where Γ_i is the surface density of species i (see Eq. (10)), K_{OH} is the equilibrium constant for OH adsorption ($= k_{\text{OH}}/k_{-\text{OH}}$), K_{PtO} is the equilibrium constant of platinum oxidation ($= k_{\text{PtO}}/k_{-\text{PtO}}$), F is the Faraday constant, R is the gas constant, T is the temperature, and η is the overpotential relative to 0 V vs RHE.

System of ordinary differential equations (ODEs)

The mechanism described above has 6 adsorbates (CH_3O , CO , COOH , OH , PtO , and Pt sites), and the total coverage is equal to 1 according to Eq. (11). Note that the CH_3O adsorbate takes up 3 Pt sites.

$$\Gamma_{\text{Pt}} + 3\Gamma_{\text{CH}_3\text{O}} + \Gamma_{\text{CO}} + \Gamma_{\text{COOH}} + \Gamma_{\text{PtOH}} + \Gamma_{\text{PtO}} = \Gamma_{\text{tot}} \quad [10]$$

$$\theta_{\text{Pt}} + 3\theta_{\text{CH}_3\text{O}} + \theta_{\text{CO}} + \theta_{\text{COOH}} + \theta_{\text{PtOH}} + \theta_{\text{PtO}} = 1 \quad [11]$$

The rate of each step is given in Eqs. (12)-(17). The units of the reaction constants, k_i , and the rates, v_i , are s^{-1} and can be turned into flux ($\text{mol cm}^{-2} \text{s}^{-1}$) by dividing by the total surface density of Pt atoms, Γ_{tot} ($2.28 \text{ nmol cm}^{-2}$).

$$v_{\text{CH}_3\text{O}} = k_{\text{CH}_3\text{O}} C_{\text{CH}_3\text{OH}} \theta_{\text{Pt}}^3 \exp((1-\beta_{\text{CH}_3\text{O}})F\eta/RT) \quad [12]$$

$$v_{\text{CO}} = k_{\text{CO}} \theta_{\text{CH}_3\text{O}} \exp((1-\beta_{\text{CO}})F\eta/RT) \quad [13]$$

$$v_{\text{OH}} = k_{\text{OH}} \theta_{\text{Pt}} \exp((1-\beta_{\text{OH}})F\eta/RT) - k_{-\text{OH}} \theta_{\text{OH}} \exp(-\beta_{\text{OH}}F\eta/RT) \quad [14]$$

$$v_{\text{COOH}} = k_{\text{COOH}} \theta_{\text{OH}} \theta_{\text{CO}} \quad [15]$$

$$v_{\text{CO}_2} = k_{\text{CO}_2} \theta_{\text{COOH}} \exp((1-\beta_{\text{CO}_2})F\eta/RT) \quad [16]$$

$$v_{\text{PtO}} = k_{\text{PtO}} \theta_{\text{OH}} \exp((1-\beta_{\text{PtO}})F\eta/RT) - k_{-\text{PtO}} \theta_{\text{PtO}} \exp(-\beta_{\text{PtO}}F\eta/RT) \quad [17]$$

Here, $C_{\text{CH}_3\text{OH}}$ is the concentration of methanol (normalized as a unitless parameter). The differential equations for the model can then be defined for each adsorbate as given in Eqs. (18)-(23).

$$d\theta_{\text{Pt}}/dt = -3\nu_{\text{CH}_3\text{O}} + 2\nu_{\text{CO}} - \nu_{\text{OH}} + \nu_{\text{COOH}} + \nu_{\text{CO}_2} \quad [18]$$

$$d\theta_{\text{CH}_3\text{O}}/dt = \nu_{\text{CH}_3\text{O}} - \nu_{\text{CO}} \quad [19]$$

$$d\theta_{\text{CO}}/dt = \nu_{\text{CO}} - \nu_{\text{COOH}} \quad [20]$$

$$d\theta_{\text{COOH}}/dt = \nu_{\text{COOH}} - \nu_{\text{CO}_2} \quad [21]$$

$$d\theta_{\text{OH}}/dt = \nu_{\text{OH}} - \nu_{\text{COOH}} - \nu_{\text{PtO}} \quad [22]$$

$$d\theta_{\text{PtO}}/dt = \nu_{\text{PtO}} \quad [23]$$

By solving this system of ODEs, with the initial conditions $\theta_{\text{Pt}}(t=0) = \theta_{\text{PtCO}}(t=0) = 0.5$ and other coverages zero, the current density, j , can be calculated at any point in the cyclic voltammogram by using Eq. (24) and the relationship between the potential and the time as given by Eq. (25).

$$j = F\Gamma_{\text{tot}}(\nu_{\text{CH}_3\text{O}} + 3\nu_{\text{CO}} + \nu_{\text{OH}} + \nu_{\text{CO}_2} + \nu_{\text{PtO}}) \quad [24]$$

$$E(t) = E_{\text{init}} + vt \quad [25]$$

The initial potential, E_{init} , is here 0 V vs RHE, and the sweep rate, v , is 5 mV s⁻¹ in all of our experiments.

Experimental

Optimization of kinetic parameters was done using Maple 2017 and a computer with 16 Gb RAM, Intel Core i7-7700T CPU @ 2.90 GHz, and Windows 10 64 bit.

Optimization procedure

Nominally, the problem stated above has 8 rate constants, k_i , and 5 symmetry factors, β_i . To simplify the optimization problem, the symmetry factors were fixed at 0.5 except for $\beta_{\text{CH}_3\text{O}}$, which was fixed at 0.25 (12). This reduced the number of parameters to 8. Due to the exponential relationship inherent in electrochemical systems, the objective function to be minimized was taken as the logarithm of the current, i.e., as given in Eq. (26).

$$RSS = \sum_t (\ln(j_{\text{exp}}(t)) - \ln(j_{\text{mod}}(t)))^2 \quad [26]$$

The optimization of the rate constants was also done in the logarithmic state, i.e., $\log(k_i)$ were the actual optimized parameters. This is important as it simplifies the choice of optimization procedure when the fitted parameters range over values between -20 and 20 instead of the exponential equivalent.

This optimization problem is significantly more complicated than usual because the set of ODEs must be solved numerically every time the optimization routine needs to evaluate the objective function. As the system of differential equations is solved numerically, the gradient is not accessible. Therefore, gradient-free optimization methods are necessary. Built into Maple's NLPSolve command, two methods are especially relevant, the non-linear simplex method and the branch-and-bound method. If successful, the non-linear simplex method is the ideal choice as it does not depend on the initial value and does not need bounds of the solution. On the other hand, the bounds can be given to the branch-and-bound method to ensure that realistic values are obtained. However, this method is slower, increasing the optimization time. To ensure maximum stability, the branch-and-bound

method was used for all single parameter optimizations. For the reversible steps, Eqs. (4) and (7), both the forward and back reaction should be optimized simultaneously. This is only possible with the non-linear simplex method, and therefore, the simplex method was used in those cases.

In summary, the optimization procedure works as follows: Every single parameter is optimized by the branch-and-bound method with the value from the previous iteration as the starting point and bounded by ± 1 in the $\log_{10}$ state, i.e., spanning 3 orders of magnitude. The steps with both forward and back reaction, $k_{\text{OH}}/k_{-\text{OH}}$ and $k_{\text{PtO}}/k_{-\text{PtO}}$, are optimized by the non-linear simplex method with the value from the previous iteration as the starting point. The parameters were fitted in sequence, i.e., $k_{\text{CH}_3\text{O}} - k_{\text{CO}} - k_{\text{OH}}/k_{-\text{OH}} - k_{\text{COOH}} - k_{\text{CO}_2} - k_{\text{PtO}}/k_{-\text{PtO}}$, until convergence was reached. Successful convergence was defined as $(\text{RSS}_{i+1})/\text{RSS}_i < 0.00001$ for the fitting of experimental data, and as $\text{RSS} < 10^{-4}$ for synthetic data, where the subscript i denotes the iteration number.

After posing the problem and choosing the optimization procedure, it remains to determine suitable initial values. Unfortunately, there is, to the authors' knowledge, no appropriate method to determine the initial values except for trial and error. The difficulty is accentuated by the fact that the problem will rarely converge unless the initial values are relatively close to the optimum values. The strategy chosen to find the initial values in this work was to use the experimental data set from cyclic voltammetry and the expected development in coverages from the literature (14), and then manually fit the model until it closely resembled the experimental results. From this coarse result, the optimization procedure was used to find the exact parameter values. As always, there is uncertainty about whether a global minimum is achieved, but getting the correct feature in the dEIS and a close resemblance with experimental IR spectroscopy data of coverages gives confidence that we are not in a local minimum far from the correct solution. In the subsequent section, the method described is used to optimize synthetically-generated data from the given model of methanol oxidation.

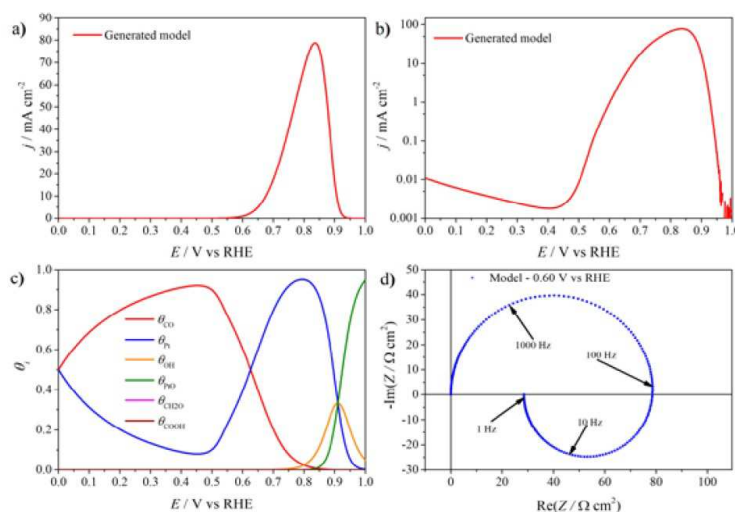


Figure 1. The generated model data from the methanol oxidation model: (a) cyclic voltammogram at 5 mV s^{-1} and 80°C temperature, (b) cyclic voltammogram with logarithmic scale of the current, (c) adsorbate coverage as a function of potential, and (d) representative Nyquist plot of EIS data at 0.60 V vs RHE .

Results and Discussion

Sensitivity analysis

A sensitivity analysis is necessary to estimate the confidence we will have in the fitted parameters. In our case, we generated a synthetic data set with 101 data points between 0.40 and 0.90 V by calculating the cyclic voltammogram at a 5 mV s⁻¹ sweep rate and 80°C temperature from the model of methanol oxidation with known rate constants. The simulated data are shown in Fig. 1 giving the (a)-(b) cyclic voltammogram, (c) the calculated adsorbate coverages as a function of potential, and (d) as a representative Nyquist plot of impedance at 0.60 V vs RHE. Notably, the simulated data is qualitatively similar to reported cyclic voltammograms (15,16), reported coverages from IR spectroscopy data (14), and reported EIS spectra (3,16).

To test the efficiency and sensitivity of the optimization procedure, a single parameter was changed from the known global minimum, and the optimization routine was allowed to run until convergence. This type of study is useful to i) identify the parameters that the model is sensitive towards and which parameters that can be determined confidently, ii) determine if the optimization routine can find the global minimum or will be going towards a local minimum, and iii) understand the convergence of the optimization routine and identify ways to improve this. A total number of 21 tests were run with different initial values to analyze the model. The total time for each iteration was about 7-9 mins. A summary of the different tests is shown in Table 1, and the resulting optimized parameters for each test are shown in Table 2.

TABLE 1. Initial values for rate constants in the sensitivity analysis. All units are in s⁻¹ and the values are given as the base 10 logarithm of the rate constant.

Number	Code	k _{CH3O}	k _{CO}	k _{OH}	k _{COOH}	k _{CO2}	k _{PtO}	k _{OH}	k _{PtO}
Initial		-1	10	-3	5	10	1	10	13
1	000000	-1	10	-3	5	10	1	10	13
2	100000	0	10	-3	5	10	1	10	13
3	010000	-1	11	-3	5	10	1	10	13
4	001000	-1	10	-2	5	10	1	10	13
5	000100	-1	10	-3	6	10	1	10	13
6	000010	-1	10	-3	5	11	1	10	13
7	000001	-1	10	-3	5	10	2	10	13
8	-100000	-2	10	-3	5	10	1	10	13
9	0-10000	-1	9	-3	5	10	1	10	13
10	00-1000	-1	10	-4	5	10	1	10	13
11	000-100	-1	10	-3	4	10	1	10	13
12	0000-10	-1	10	-3	5	9	1	10	13
13	00000-1	-1	10	-3	5	10	0	10	13
14	005000	-1	10	-2.5	5	10	1	10	13
15	000500	-1	10	-3	4.5	10	1	10	13
16	00-5000	-1	10	-3.5	5	10	1	10	13
17	000-500	-1	10	-3	5.5	10	1	10	13
18	00(25)000	-1	10	-2.75	5	10	1	10	13
19	000(25)00	-1	10	-3	4.75	10	1	10	13
20	00(-25)000	-1	10	-3.25	5	10	1	10	13
21	000(-25)00	-1	10	-3	5.25	10	1	10	13

From Table 2, it is evident that the models where the k_{OH} and k_{COOH} parameters were changed did not converge as quickly. To assess the optimization of these parameters, a change of 0.5 or 0.25 (in log form) was made in models 14-21. This was more successful than the fitting of the larger change, i.e., models 4, 5, 10, and 11. However, it is clear that a reasonable estimate of the initial value for these parameters is critical to ensure convergence. The accuracy of the optimized parameters was estimated by taking the average of the optimized parameter values for the models that converged successfully. This is summarized in Table 3. From this result, it is clear that 4 parameters can be reasonably confidently estimated in this model; these are the single parameters $k_{\text{CH}_3\text{O}}$ and k_{COOH} , and the two reversible ratios, $k_{\text{OH}}/k_{-\text{OH}}$ and $k_{\text{PtO}}/k_{-\text{PtO}}$. Notably, this list of parameters indicate that for the reversible steps, the confidence is in the ratios of the forward and back rate constants, $k_{\text{OH}}/k_{-\text{OH}}$ (or $k_{\text{PtO}}/k_{-\text{PtO}}$). Thus, an order of magnitude increase in the k_{OH} parameter is similar to an order of magnitude decrease in the $k_{-\text{OH}}$ parameter, and it is not necessary to have a sensitivity analysis for both of these parameters. The k_{CO} and k_{CO_2} parameters cannot be estimated in this model and this is evident from the assumptions that go into the determination of the initial values, i.e., that these steps are highly irreversible because adsorbed methanol and COOH are not detected in IR spectroscopy studies of methanol oxidation.

TABLE 2. Rate constants after convergence for the different models in the sensitivity analysis. All units are in s^{-1} and the values are given as the base 10 logarithm of the rate constant.

Number	Code	$k_{\text{CH}_3\text{O}}$	k_{CO}	k_{OH}	k_{COOH}	k_{CO_2}	k_{PtO}	$k_{-\text{OH}}$	$k_{-\text{PtO}}$	Number of iterations	Convergence
Initial		-1	10	-3	5	10	1	10	13	n/a	n/a
1	000000	-1.00	6.83	-3.00	5.00	9.26	0.01	10.0	13.0	5	Y
2	100000	-1.00	7.43	-3.00	5.00	5.26	0.01	10.0	13.0	5	Y
3	010000	-1.00	8.80	-3.00	5.00	7.18	0.00	10.0	13.0	3	Y
4	001000	-1.00	6.44	-5.61	5.00	-0.65	2.55	7.38	15.6	345	Y
5	000100	-1.04	14.2	2.40	5.98	9.57	1.45	16.4	13.1	12	N
6	000010	-1.00	6.83	-3.00	5.00	10.5	0.01	10.0	13.0	5	Y
7	000001	-1.01	10.9	-3.14	5.11	6.88	7.38	9.98	20.1	10	N
8	-100000	-1.00	8.80	-3.00	5.00	6.62	0.00	10.0	13.0	4	Y
9	0-10000	-1.00	4.72	-3.00	5.00	4.97	0.01	10.0	13.0	7	Y
10	00-1000	-1.00	6.44	-6.29	5.00	-0.54	-1.32	6.71	11.7	317	Y
11	000-100	-0.88	-1.50	-6.10	4.78	-2.54	-5.95	6.65	60.5	80	N
12	0000-10	-1.00	4.72	-3.00	5.00	2.88	0.01	10.0	13.0	10	Y
13	00000-1	-1.00	6.83	-3.00	5.00	7.06	0.01	10.0	13.0	5	Y
14	005000	-1.00	5.28	-3.47	5.00	-0.47	2.31	9.53	15.3	288	Y
15	000500	-1.03	14.0	-3.83	5.39	8.89	4.86	9.56	17.2	80	N
16	00-5000	-1.00	10.4	-5.36	5.00	11.0	-0.74	7.64	12.3	256	Y
17	000-500	-0.96	4.56	-8.70	4.81	-2.16	-6.80	4.10	49.5	72	N
18	00(25)000	-1.00	6.42	-4.65	5.00	-0.22	1.92	8.35	14.9	274	Y
19	000(25)00	-1.02	7.89	-4.47	5.17	8.36	7.22	8.70	19.9	80	N
20	00(-25)000	-1.00	10.4	-4.65	5.00	9.56	1.58	8.35	14.6	213	Y
21	000(-25)00	-0.96	4.61	-4.14	4.81	-2.14	7.92	8.66	50.4	71	N

TABLE 3. The average value and the standard deviation of the optimized values for the models that converged successfully ($RSS < 10^{-6}$). All units are in s^{-1} and are given as the base 10 logarithm of the rate constant.

Number	k_{CH_3O}	k_{CO}	k_{OH}	k_{COOH}	k_{CO_2}	k_{PtO}	k_{-OH}	k_{-PtO}	k_{OH}/k_{-OH}	k_{PtO}/k_{-PtO}
Average value	-1.00	7.17	-3.86	5.00	5.17	0.45	9.14	13.5	-13.0	-13.0
Standard deviation	$4.3 \cdot 10^{-4}$	>1	>1	$1.7 \cdot 10^{-3}$	>1	>1	>1	>1	$1.8 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$

The observations from the converged results are further supported by plotting the error function, RSS , as a function of iteration number in Fig. 2. Here, the models with changes in the k_{OH} and k_{COOH} parameters use more iterations to converge successfully (if ever). This indicates that these parameters are dependent on each other, and that a wrong parameter can be compensated by the other parameters to reach lower RSS without necessarily reaching the global minimum (or very slowly going towards the global minimum). Complementary methods to estimate these values would be useful to improve the stability of the optimization procedure.

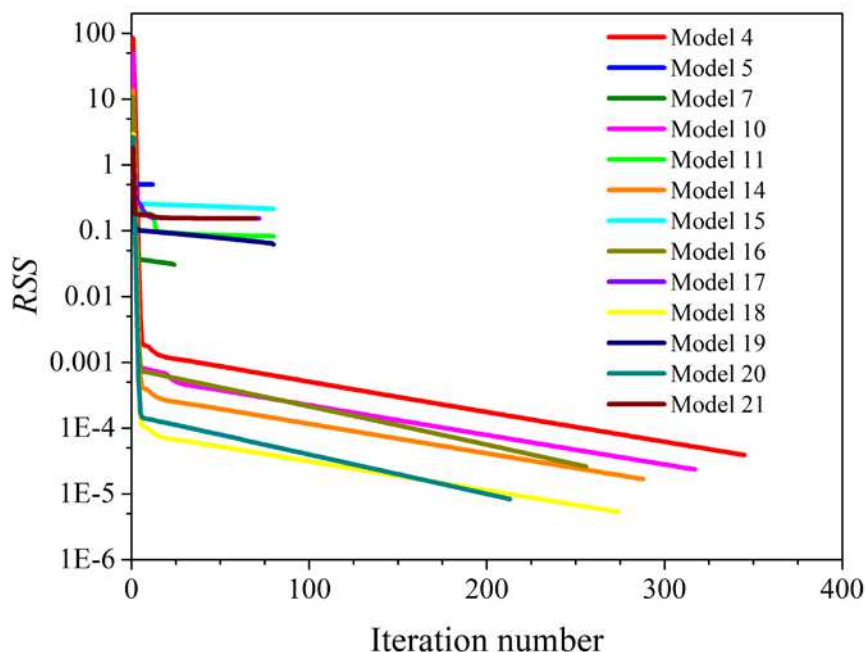


Figure 2. Error function vs number of iterations for the models used in this work. The models that converged very quickly (1, 2, 3, 6, 8, 9, and 13) were omitted for clarity.

Improvement of the method

The method to optimize the parameters here to an experimental cyclic voltammogram is suitable for many important electrochemical reactions. The method converges relatively slowly, so it is important to have a reasonable estimate of the initial values to ensure economic calculation. Complementary methods to estimate the initial values would be desirable, and at the very least, a qualitative estimate of the adsorbate coverages from IR spectroscopy is a necessity. This data is available in the literature for commonly studied oxidation reactions. Another approach is to use the dEIS data in the optimization. For example, the low-frequency intercept has been suggested as an additional parameter in the optimization (17). However, in many cases, the low-frequency intercept is not necessarily

available experimentally within a reasonable frequency range for dEIS (1 Hz – 100 kHz) making this only useful in some cases.

To ensure faster convergence, the simultaneous optimization of several parameters would be useful. To identify the more important parameters, a sensitivity analysis can be used to identify the critical parameters, i.e., $k_{\text{CH}_3\text{O}}$, k_{COOH} , $k_{\text{OH}}/k_{-\text{OH}}$, and $k_{\text{PtO}}/k_{-\text{PtO}}$ in our case. Subsequently, multi-parameter optimization can be used on this subset of parameters. We briefly attempted this with some success. The main challenge with doing this is to ensure that the optimization procedure is able to explore the parameter space successfully. As this type of optimization can only be done using the non-linear simplex method in Maple, it would be useful to limit the parameter space explored to ensure some stability.

The method described in this paper was used to model experimental data of methanol and formic acid oxidation on Pt with 6 and 8 different models, respectively. The reader is referred to these publications (18,19) for further demonstration of this method.

Conclusions

A method was developed for numerical optimization of kinetic parameters and calculation of EIS spectra. Synthetic data appropriate for methanol oxidation on platinum at 80°C were used as an example. A reasonable mechanism of methanol oxidation was suggested, and the sensitivity of the relevant parameters was assessed. The method is uniquely suited to help in the interpretation of experimental data when dEIS is measured simultaneously with a pseudo steady-state dc technique, here: cyclic voltammetry. The procedure described in this work is an improvement to existing methods of parameter optimization in electrochemical problems both in terms of the type of data optimized and the amount of information that can be extracted from the optimized models.

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CuPt and CuPtRu Nanostructures for Ammonia Oxidation Reaction

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Liquid fuels, such as methanol, ethanol, and ammonia, are attractive alternative to hydrogen for fuel cells due to their lower costs for storage and distribution. Lack of sufficiently active catalysts for their oxidation reactions is a roadblock. Our previous study found that Pt₃Cu nanodendrites yielded higher activity and durability than Pt nanoparticles for methanol oxidation reaction (MOR) in acid. In this study, we synthesized two types of nanostructures of CuPt and CuPtRu catalysts *via* seed-mediated growth of Pt and Ru on Cu and tested their performance for ammonia oxidation reaction (AOR) in alkaline solution. Unlike for MOR, the nanodendrites do not promote AOR activity - CuPt performs similar to Pt and CuPtRu is less active than Pt. Interestingly, the AOR peak current is increased by 64% on CuPt nanowires and 330% on CuPtRu nanowires as compared to Pt nanoparticles. These results suggest that AOR prefers extended surface on long nanowires, distinctly differing from MOR. This can be contributed to two factors: NH₃ oxidization to N₂ involves dimerization of two N-containing intermediates to form the N-N bond and diffusion barriers for adsorbed intermediates are generally lower on terrace than at low-coordination sites. This demonstrated strong effect of surface morphology will be further studied and utilized in developing advanced AOR nanocatalysts.

Introduction

Previous studies have shown that Pt is active for AOR in alkaline media, $2\text{NH}_3 + 6\text{OH}^- = \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^-$, in a narrow potential window.¹⁻³ The onset potential above 0.4 V versus RHE is due to the activation barrier for deprotonation of NH₃ to NH₂^{*}, and the AOR current peaks about 0.65 V is because fully deprotonated N^{*} intermediate formed at high potentials is inactive for dimerization and blocks surface sites.⁴ Cu is inactive over the entire potential region because its binding to N species is too weak and thus the potential for deprotonation is too high. Ru is at the other extreme. Strong adsorption of N species on Ru facilitates deprotonation, but causes difficult for dimerization of two partially deprotonated intermediates, resulting in a quick deactivation by inactive reaction intermediates. Studies of metal alloys with Pt also found that the AOR peak current on Pt was reduced by alloying with Cu⁵ or Ru¹.

In this study, our goal is to explore the effects of core-shell metal distribution and surface morphology on the AOR activity of Pt. Using Cu seed-mediated growth of Pt

followed by acid treatment, a lattice contraction of Pt surface layer can be induced by the Cu core with or without its hollowing out. For studying surface morphology effects, nanodendrites represent the surface rich in low coordination sites and nanowires with micrometer length provide extended surface in one dimension, both with high surface area per Pt mass. We further include Ru in the shell on Cu to study whether the presence of Ru at the surface can promote ammonia deprotonation for lowering the AOR onset potential. Our initial results are presented here.

Experimental Methods

Synthesis of CuPt and CuPtRu Nanoendrites and Nanowires

The core-shell type nanostructures were synthesized using our previously-established, seed-mediated methods.⁶⁻⁸ Briefly, Cu seeds were prepared by adding specific amounts of copper acetylacetonate ($\text{Cu}(\text{acac})_2$), copper chloride (CuCl_2), and dodecylamine (DDA) to a 3-neck 25-mL round-bottom flask equipped with a temperature-controlled, heating mantle and a magnetic stirring plate. The flask was connected to a condenser for cooling and a Schlenk line to maintain air-free conditions. For synthesis of nanodendrites, $\text{Cu}(\text{acac})_2$ (52.4 mg, 0.20 mmol), CuCl_2 (13.4 mg, 0.010 mmol), and DDA (5 g) were used; for synthesis of nanowires, $\text{Cu}(\text{acac})_2$ (52.4 mg, 0.20 mmol), CuCl_2 (26.8 mg, 0.020 mmol), and DDA (5 g) were used.

The synthesis of Cu seeds was allowed to proceed at 220 °C for 50 min under the protection of argon prior to the addition of the noble metal precursors. For synthesis of CuPt catalysts, platinum acetylacetonate ($\text{Pt}(\text{acac})_2$, 30 mg, 0.076 mmol) in 1 mL of oleylamine (OLAM) was added to the reaction solution. In synthesis of CuPtRu catalysts, $\text{Pt}(\text{acac})_2$ (30 mg, 0.076 mmol) in 1 mL of OLAM and ruthenium chloride (RuCl_3 , 15.8 mg, 0.076 mmol) in 1 mL of OLAM were simultaneously added to the reaction solution. The reaction was allowed to proceed additional 90 min at 220 °C. After the reaction, the product was purified by ethanol to remove excess reactants and resuspended in toluene for further ligand removal procedure.

To remove the DDA and OLAM ligands on the surface of the nanostructures, the resulting product was dried in a 2 dr. vial by evaporating the solvent toluene. Then, 1 mL of polyvinylpyrrolidone (PVP, MW 55,000) aqueous solution (2 mg/mL) was add to the vial, followed by adding 2 mL of water. The nanostructures were resuspended in the PVP aqueous solution. Following this step, 2 mL of glacial acetic acid was added to the vial. The reaction vial was placed in a 60 °C oil bath and the reaction was allowed to proceed for 30 h. The product was purified by water and re-dispersed in water for electrochemical characterization.

Electrochemical Measurements for Ammonium Oxidation

The catalyst samples stored in water were sonicated for 1 min to obtain uniform dispersion. Then certain volumes of the dispersed inks were placed onto glassy carbon electrodes (GCE) and dried in air. The platinum group metal (PGM) loadings, i.e. Pt and Ru, for all four samples were controlled to be $40 \mu\text{g cm}^{-2}$ on the GCE. We also made electrodes with $40 \mu\text{g cm}^{-2}$ Pt loading using commercial Pt nanoparticles on carbon support (2.6 nm in diameter, 46 wt% Pt from TKK) as a reference for comparison.

Electrochemical measurements were carried out by using a Voltalab PGZ 402 potentiostat. The catalyst-coated GCE was immersed in solution and faced a Pt-flag

counter electrode. A Hg/HgO electrode in 1 M KOH solution was used as the reference electrode, and the zero potential versus RHE was determined by the open circuit potential on Pt in hydrogen-saturated 1 M KOH solution, which was about -921 mV versus Hg/HgO at ambient temperature. Correction of ohmic loss was made by subtracting the product of measured currents and the high-frequency resistance determined from electrochemical impedance spectra acquired at 450 mV versus RHE. The cyclic voltammetry curves were recorded in argon-purged 1 M KOH solution. The AOR polarization curves were measured in 1 M KOH solution saturated with NH₃ by letting argon gas bubble through 28% NH₃ solution before entering the cell, which also kept the solution oxygen-free. At ambient temperature about 23 °C, the polarization curves obtained were similar to those in 0.1 M NH₃. The main advantage of using an NH₃ bubbler is to ensure constant NH₃ concentration over hours during measurements of different samples because loss of vaporized NH₃ occurs with inert gas flowing through the cell, which is needed for keeping solution free of oxygen.

Results and Discussion

Composition of the CuPt and CuPtRu Nanostructures

The compositions of the CuPt and CuPtRu nanostructures were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS). Table 1 lists the mass concentration (mg/mL) and the atomic percentage (at.%) of each sample. We prepared electrodes with the same PGM loading of 40 $\mu\text{g cm}^{-2}$ for each of the four catalysts using the mass concentrations of Pt and Ru listed here. Compared to the Cu:Pt atomic ratios of about 2.7 in the metal precursors, the Cu contents relative to Pt were lowered to about 0.65 in these catalysts. This is in part due to the acid treatment, in which Cu dissolution results in hollow structures. Even though Ru:Pt ratios in the precursors were 1.0, actually deposited Ru in making nanodendrites and nanowires was considerably less as indicated by the atomic percentages of Pt are 5 to 8 fold higher than those for Ru. Compared to Pt, less Ru being reduced during the chemical reactions could be attributed to the lower redox potential of Ru³⁺ to Ru. The high Pt:Ru atomic ratio in the final products is desirable since Ru is expected to act as a deprotonation promoter for AOR on Pt.

TABLE I. Composition of CuPt and CuPtRu nanostructures analyzed by ICP-MS.

Sample #	Sample Name	Cu (mg/mL)	Pt (mg/mL)	Ru (mg/mL)	Cu (at.%)	Pt (at.%)	Ru (at.%)
1	CuPtRu ND	0.139	0.745	0.075	32.4	56.6	11.0
2	CuPt ND	0.139	0.660	-	39.3	60.7	-
3	CuPtRu NW	0.122	0.515	0.037	39.0	53.7	7.3
4	CuPt NW	0.180	0.678	-	44.9	55.1	-

ND stands for nanodendrites and NW stands for nanowires.

Morphology of the CuPt and CuPtRu Nanostructures

Figure 1 shows the transmission electron microscopy (TEM) images of nanodendrites of CuPt and CuPtRu and nanowires of CuPt and CuPtRu. The nanodendrites are ~25 nm in size with branches of connected smaller solid or hollow particles. The nanowires were several micrometers long with a diameter of tens nanometers. Both nanowire samples contained some nanoparticles as by-products. Compared to CuPt nanowires, the CuPtRu

nanowires were thicker. These images support that the nanodendrites are rich in low-coordination sites while nanowires provide one-dimension extended surface.

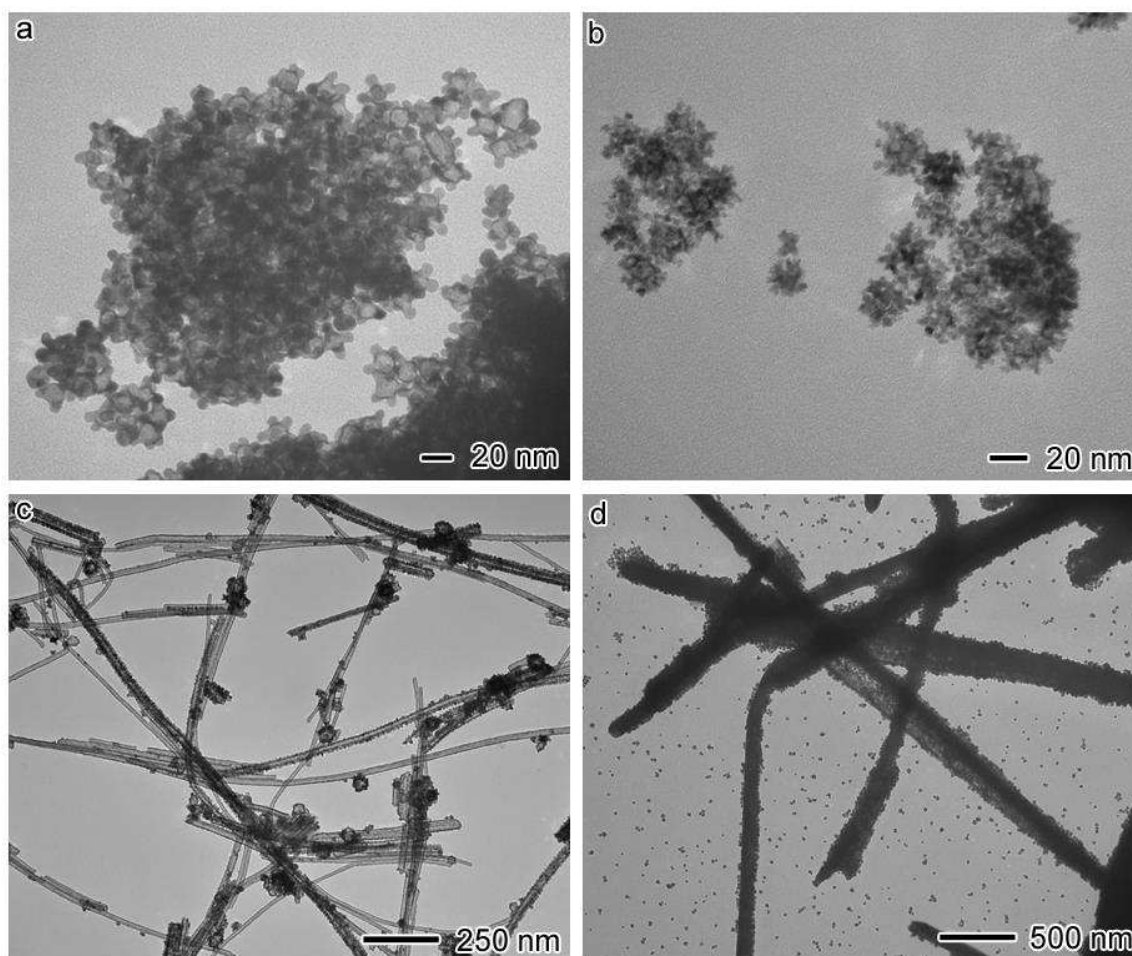


Figure 1. TEM images of CuPt nanodendrites (a), CuPtRu nanodendrites (b), CuPt nanowires (c), and CuPtRu nanowires (d).

Voltammetry and AOR polarization results

In Fig. 2a, we compared the voltammetry curves of CuPt and CuPtRu nanodendrites with that carbon supported Pt nanoparticles. The black curve shows the characteristic voltammetry feature of Pt, i.e., H adsorption/desorption current peaks at low potentials and OH adsorption/desorption current peaks at high potentials. These features are considerably altered on CuPt nanodendrites (blue curve), suggesting that Cu is partly exposed and involved in the surface electrochemical reactions. In contrast, the voltammetry curve for CuPt nanowires (green curve in Fig. 2b) is similar to that of for Pt/C (black curve), indicating there is less exposed Cu. For the CuPtRu samples, large capacitance-like currents were observed for both nanodendrites (pink curve in Fig. 2a) and nanowires (red curve in Fig. 2b), which were consistent with having Ru at the surface. The higher currents for the CuPtRu nanowires (red curve in Fig. 2b) than CuPt nanowires (green curve in Fig. 2b) may result from more attached small particulates on the nanowire surface (Fig. 1c and 1d).

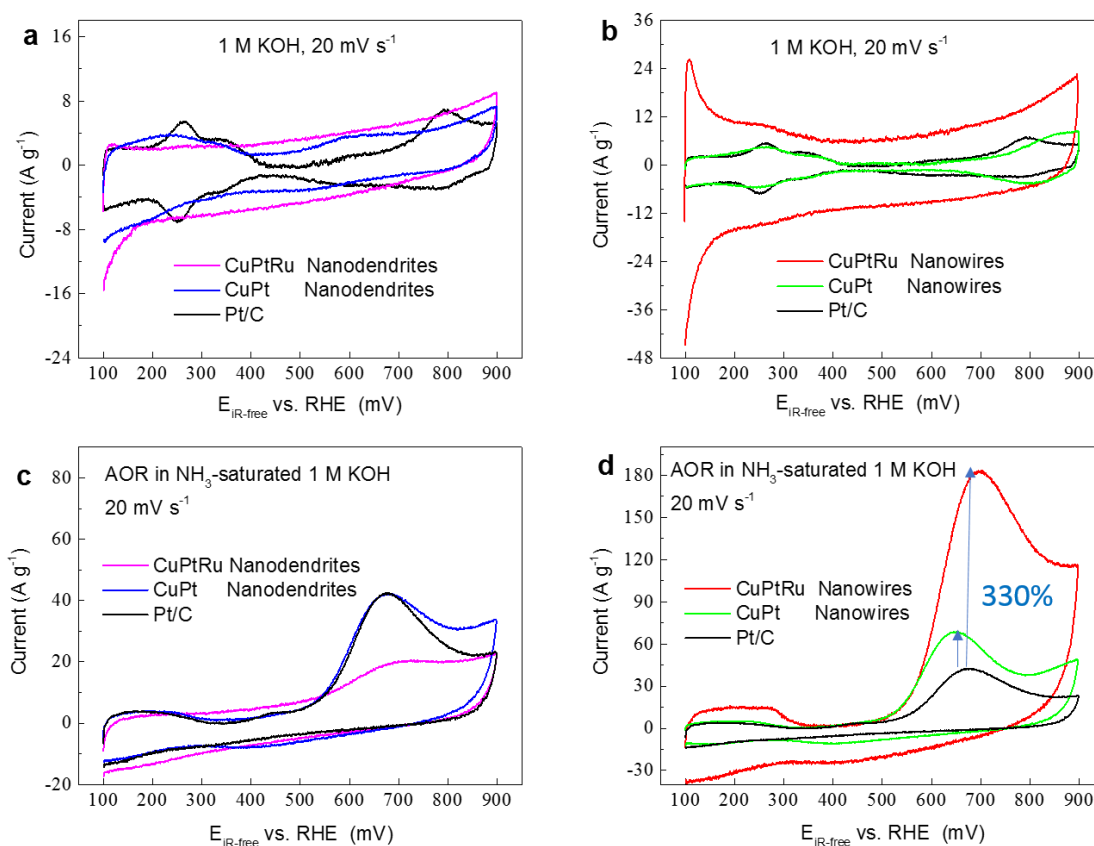


Figure 2. Voltammetry curves measured at ambient temperature about 23 °C in 1 M KOH (a,b) and AOR polarization curves measured in ammonia-saturated 1 M KOH (c,d) for nanostructured catalysts (color lines) compared to Pt nanoparticles on carbon support (black lines). Currents are normalized to the PGM loading.

The AOR polarization measured in NH₃-saturated 1 M KOH solution are shown in Fig. 2c and 2d for the samples of nanodendrites and nanowires, respectively. The CuPt nanodendrites (blue curve in Fig. 2c) exhibit an AOR activity similar to that of Pt/C (black curve), suggesting that lattice contraction of Pt induced by Cu core or hollow structure has little effect on the AOR activity. The CuPtRu nanodendrites are less active than Pt/C for the AOR (pink curve). The negative impact of Ru is similar to that found with Pt-Ru alloy.⁵

Interestingly, situation differs completely for the nanowire samples. As shown in Fig. 2d, the AOR peak current is increased by 330% on CuPtRu nanowires (red curve) and 64% on CuPt nanowires (green curve) compared to that obtained on Pt/C (black curve). Since both nanowire samples enhance the AOR activity and the two nanodendrites performed poorly, extended surface is demonstrated to be more beneficial than low coordination sites for AOR. This is understandable because NH₃ oxidation to N₂ involves dimerization of two N-containing intermediates in the formation of N-N bond and low diffusion barrier on terrace facilitates the reactions among adsorbed intermediates. In contrast, oxidation of CH₃OH or C₂H₅OH to CO₂ does not involve combination of two adsorbed intermediates, and thus, nanodendrites have been found promoting the activity for methanol oxidation.⁸ It is particularly intriguing that the presence of Ru in nanowires positively impact on the AOR activity. Further studies are required to understand the role of surface Ru, either on the surface of nanowires or on the attached small particulates.

Conclusions

We synthesized CuPt and CuPtRu nanodendrites and nanowires with a seed-mediated method to explore the effects of core-shell metal distribution and surface morphology on the AOR activity of Pt. The most interesting finding is a high AOR peak current of 180 A g⁻¹ on CuPtRu nanowires, which is four times of that on Pt/C. With Cu and Ru both are AOR-inactive metals, the result illustrates that AOR kinetic is sensitive to surface morphology. While it is understandable for extended surface being beneficial for AOR, the role of attached small particulates opens many possibilities. The results warrant us to further explore and rationally design one-dimensional structures for enhancing the AOR performance.

Acknowledgments

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Chapter 6

HER, OER and CO₂ Reduction

Structural Effect of Gold Single Crystal Orientation on the Spontaneous Deposition of Rh nanoislands: Hydrogen Evolution in Acid Solution

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Rh/Au(100) and Rh/Au(111) electrodes with Rh coverage below a monolayer are prepared by a spontaneous deposition method. Electrodes are characterized by AFM and XPS. Hydrogen evolution reaction (HER) is studied by linear sweep voltammetry in 0.1 M HClO₄ solution. Results for gold single crystals with 50% Rh coverage, which have shown the best catalytic activity for HER are presented in this work. Enhanced catalytic activity of such bimetallic electrodes compared to the ones with higher Rh coverage is ascribed to the presence of smaller Rh islands, which provide suitable active surface sites. Rather strong electronic interaction between Rh deposit and gold substrates, which is manifested by the upshift of Rh3d_{5/2} photoelectron line, also contributes to their activity. Structural effect is manifested through a higher activity of 50% Rh/Au(111) than 50% Rh/Au(100), which is consistent with the difference in activity of respective bare gold single crystals.

Introduction

Hydrogen evolution reaction (HER) is one of the most extensively studied electrochemical processes due to its global importance in both applicable and fundamental scientific aspects related not only to the production of hydrogen as the sustainable energy resource, but also to the understanding of the electrochemical kinetics. HER is strongly dependent on the nature of cathodic electrode material since just in the group of precious metals reaction rate varies by several orders of magnitude between the most active (Pt, Ir, Rh, Pd), and the most inert ones (Au) (1-3). HER is also structure sensitive, so the crystallographic orientation of the electrocatalyst must be taken into account (4-7). For the fundamental studies on HER catalysis, various electrode materials are widely used (8), among which noble metal single crystals modified by foreign metal overlayers are continuously being devoted a lot of attention (9,10). In this field, Au single crystals offer certain convenience as substrates. Gold is rather inert for this reaction, so the main contribution to the HER reactivity comes from a foreign metal, although Au as a support contributes indirectly through the strong electronic interaction with the deposited foreign metal overlayer. Rh stands out as a desirable candidate to be applied as thin layer in HER electrocatalysis, since it is very active for this reaction (1-3), yet very expensive and scarce. Electrochemically deposited Rh on gold single crystals has been studied in detail using electrochemical techniques (11) and *in situ* Scanning tunneling microscopy

(12), where in both cases Stranski-Krastanov or layer-by layer growth followed by island growth mode was reported. Island growth of Rh evaporated on Au in ultra-high vacuum chamber without intermixing at room temperature has also been reported, which was attributed to a large lattice mismatch (0.288 nm for Au versus 0.269 nm for Rh) (13). Recently the focus has been given on theoretical and experimental investigations of HER electrocatalysis on Rh overlayers on Au(111) substrate (14-16). These studies have yielded significant results, showing that Rh/Au(111) electrodes prepared by the facile and fast spontaneous deposition method are very active for HER in sulfuric acid solution (15,16). High activity of Rh/Au(111) system for HER was explained by rather strong electronic effect induced between Au(111) substrate and Rh nanoislands which facilitated different steps in HER mechanism and thus improved the overall reaction rate. Indeed, this electronic interaction has been experimentally evidenced by XPS analysis (16). Having in mind that hydrogen evolution is structure sensitive reaction, further studies on Rh overlayers supported on other gold single crystals besides Au(111) imposes as a logical task.

In this work, both Au(100) and Au(111) single crystals were used as substrates for the spontaneous deposition of Rh. Physical characterization of all electrodes was performed *ex situ* by Atomic force microscopy (AFM) and by X-ray photoelectron spectroscopy (XPS), which provided rather comprehensive insight into the surface structure and into the electronic interaction between gold substrates and Rh deposited. Catalytic activities of Rh/Au(100) and Rh/Au(111) bimetallic electrodes for HER in perchloric acid solution were compared and discussed in terms of the observed differences in the surface properties.

Experimental

Preparation of bimetallic Rh/Au electrodes

Au(100) and Au(111) single crystal electrodes, 12 mm in diameter, (MaTeck, Julich, Germany), with miscut lower than 0.1° , were used as substrates. Maintenance of the purity and orientation of gold single crystals was accomplished by electrochemical polishing and annealing in butane flame before each experiment, as described elsewhere [14]. Polycrystalline Rh, 5 mm in diameter, mirror polished (MaTeck, Julich, Germany), was prepared by potential cycling in 0.5 M H_2SO_4 before electrochemical measurements in acid solution. Spontaneous deposition of Rh was performed by immersion of the Au(100) or Au(111) electrodes at the open circuit potential (OCP) into (1mM $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ + 0.05 M H_2SO_4) solution for chosen times of 0.5, 1, 3, and 30 min. Careful rinsing with the excess of Milli-pure water was done instantly after the substrate electrode was removed from Rh solution in order to prevent continuation of the deposition beyond desired time. According to the comprehensive preliminary investigation of the activity of prepared bimetallic Rh/Au electrodes for HER in perchloric acid solution, it has been observed that the ones with 50% Rh coverage have shown the highest activity. Such coverage was achieved after 1 min Rh deposition on both Au(100) and Au(111) substrates. Only results for these electrodes will be presented in this work.

Physical characterization

Ex situ characterization of the surface features of as prepared Rh/Au(100) and Rh/Au(111) electrodes was performed by AFM. Imaging of the surfaces of bare gold

substrates and bimetallic electrodes was performed by Multimode Quadrex SPM with Nanoscope IIIe controller (Veeco Instruments, Inc.) operating in a tapping mode. Height and phase AFM images were recorded simultaneously from various surface sites. Lateral size and height of the deposited Rh islands was estimated from height images. The overall coverage, taken as a percentage of the Au single crystal surface covered with Rh deposit, was estimated from phase AFM images.

XPS analysis of as prepared 50% Rh/Au(100) and 50% Rh/Au(111) bimetallic electrodes was carried out using SPECS System with XP50M X-ray source for Focus 500 and PHOIBOS 100/150 analyzer. AlK α source (1486.74 eV) at a 12.5 kV and 32 mA was used for this study. High resolution spectra of Rh 3d photoelectron line included 6 collected scans, which were recorded with the energy step of 0.1 eV and dwell time 2.0 s and pass energy of 40 eV in the FAT mode.

Electrochemical measurements

All electrochemical measurements were performed in the hanging meniscus arrangement in the three electrode cell, with Pt wire as counter electrode and Ag/AgCl, 3M KCl as the reference electrode. Linear sweep voltammetry was used for the electrochemical characterization and HER investigations on bare Au(100) and Au(111), Rh(poly) and obtained Rh/Au(100) and Rh/Au(111) electrodes in deaerated 0.1 M HClO₄ solution. The initial potential for HER studies was chosen according to the well-known electrochemical features of bare Au(100) and Au(111) electrodes in perchloric acid solution (17) and preliminary electrochemical characterization of Rh/Au(100) and Rh/Au(111) using cyclic voltammetry (CV). Before each experiment, bimetallic electrodes were held for 15 minutes at the potential of 0.0 V in order to ensure the reduction of any amount of Rh oxides possibly formed during spontaneous deposition. Thorough electrochemical polishing of Rh/Au(100) and Rh/Au(111) electrodes was performed after each measurement in order to completely remove Rh deposit and to prepare clean gold surfaces for further work.

Chemicals

Depositing Rh solution was prepared using RhCl₃·xH₂O (MaTeck) and suprapure H₂SO₄ (Merck), while carrying electrolyte for electrochemical measurements was prepared using supra pure HClO₄ (Merck). All solutions were diluted with Milli-Pure water. Constant flow of the 99.999 % N₂ (Messer) in or over the working solution was ensured before and during each electrochemical experiment in order to maintain electrolyte well de-oxygenated. All measurements were performed at room temperature.

Results and Discussion

Spontaneous Deposition of Rh on Au(100) and Au(111)

Open circuit potential (OCP) monitoring during spontaneous deposition can provide information about the change of the deposition rate over time. Chronopotentiometry curves recorded over 30 minutes during the immersion of the Au(100) or Au(111) electrodes into 1mM RhCl₃·xH₂O + 0.05 M H₂SO₄ solution, are given in **Figure 1**. The same OCP value of 0.656 V is established during the contact of the carrying 0.05 M

H₂SO₄ solution free of Rh ions with either Au(100) or Au(111), which is marked in **Figure 1** as $E_{\text{ocp}}[\text{Au}/0.05 \text{ M H}_2\text{SO}_4]$.

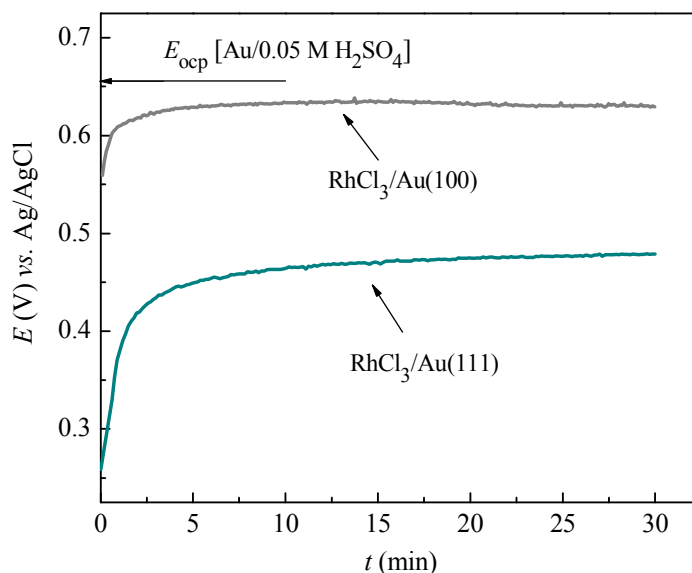


Figure 1. OCP change during spontaneous deposition of Rh on Au(100) and Au(111) electrodes from 1 mM RhCl₃·xH₂O+0.05 M H₂SO₄.

During the first few minutes of the spontaneous deposition of Rh on either Au(100) or Au(111), OCP rapidly increases and afterwards slows down up achieving a plateau. In the case of Au(100) substrate, OCP value increase from 0.560 V to 0.625 V during the first three minutes of the deposition, indicating a rather fast deposition, and after that reaches the plateau at 0.631 V, indicating a pronounced slowdown in the deposition process and achieved saturation coverage. In a similar manner, during Rh deposition on Au(111), OCP value increase from 0.260 V to 0.480 V at saturation. According to the CVs of bare Rh (18) and of Rh/Au(111) in sulfuric acid solution (15), one can see that high OCP values during Rh deposition on Au(100) correspond to the partial formation of Rh oxide (18), while lower OCP values established during Rh deposition on Au(111) correspond only to the not oxidized (metallic) Rh deposit (15, 18). The oxidation state of the deposited Rh on different Au single crystals will be discussed below on the basis of XPS data. Reactions on the gold electrode during spontaneous Rh deposition responsible for the established OCP values were discussed in detail in ref. (16).

AFM imaging of Rh/Au(100) and Rh/Au(111)

Height and phase AFM images of 50% Rh/ Au(100) and 50% Rh/Au(111) bimetallic surfaces and corresponding cross-sections are given in **Figure 2**. Surface topography images and cross section analysis of Rh/Au(100), **Figure 3a and b**, and Rh/Au(111) obtained after 1 min Rh deposition, **Figure 3e and f**, reveal that on both gold substrates, Rh islands are deposited, the height of which ranged from mainly 0.25 to even 0.75 nm, indicating that the deposit is mostly one monolayer (ML) high, with a few two or three ML high islands. Lateral sizes of the individual Rh islands can be estimated from phase AFM images, **Figure 3c and g**, when the threshold is set at the height corresponding to gold substrate as the background, and cross-section analysis, **Figure d and h**. Lateral sizes ranged from 20-40 nm for Rh/Au(100) and from 5-20 nm for Rh/Au(111).

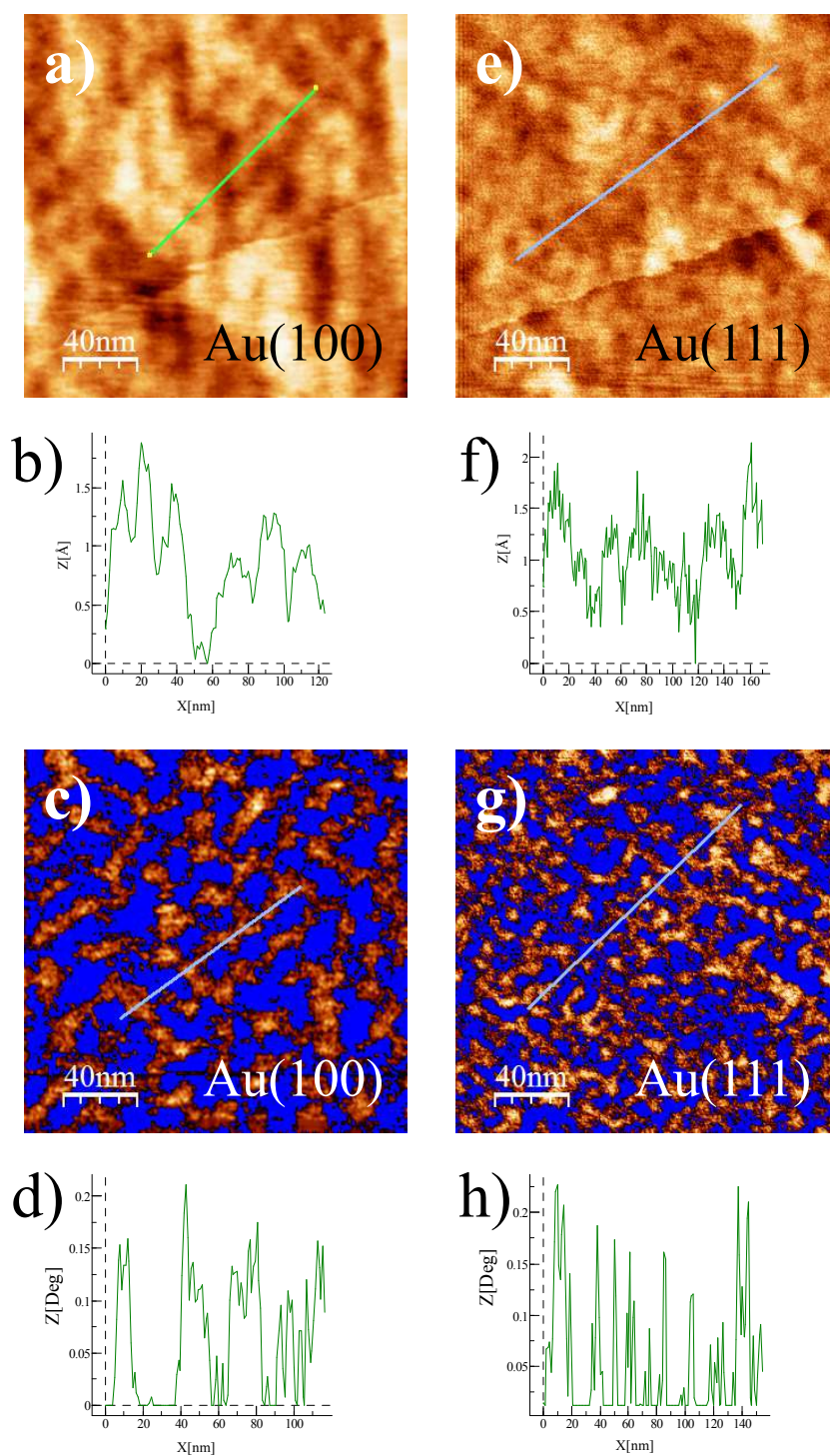


Figure 2. AFM images (200 x 200) nm², of 50% Rh/Au(100) (left column) and 50% Rh/Au(111) (right column): a) surface topography, z-range 0.4 nm; b) cross-section along the line indicated in the image; c) and d) phase image and corresponding cross-section, z-range 0.38°; e) and f) surface topography and corresponding cross-section, z-range 0.3 nm; g) and h) phase image and corresponding cross-section, z-range 0.28°.

Generally, much larger (highly agglomerated) Rh islands are deposited on the Au(100) than on gold Au(111), where a higher number of smaller Rh islands are deposited. The arrangement of the deposited Rh islands over the Au single crystal substrate, as well as their geometry resembles the symmetry of the underlying Au(100) and Au(111) substrates. Despite the difference in number and size of the deposited Rh islands, the overall Rh coverage is estimated to be $(50 \pm 5)\%$ in both cases.

XPS analysis of Rh/Au(100) and Rh/Au(111)

XPS spectra of the 50% Rh/Au(100) and 50% Rh/Au(111) surfaces, presented in **Figure 3**, are taken immediately after the electrodes were prepared and rinsed with water, before being subjected to the electrochemical reduction of deposited Rh and subsequent electrochemical measurements.

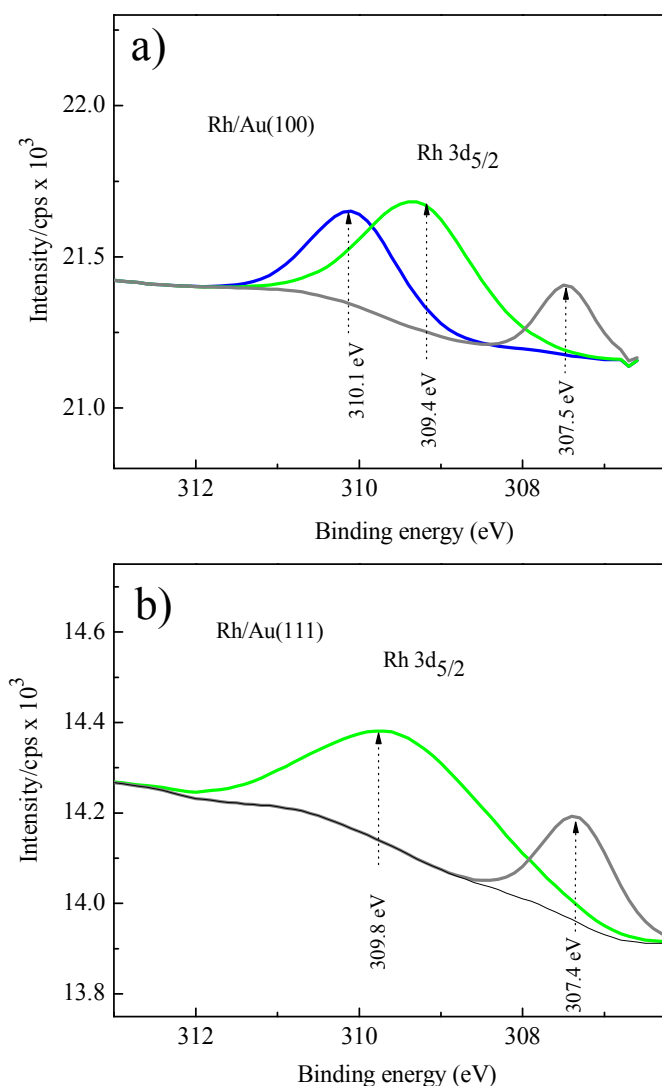


Figure 3. High resolution XPS spectra showing the fitted binding energies of Rh 3d_{5/2} photoelectron line taken from: a) Rh/Au(100); b) Rh/Au(111).

High resolution spectra of Rh 3d were deconvoluted in order to define precisely the oxidation states of the deposited Rh islands. Rh3d_{5/2} photoelectron line was deconvoluted

into three lines: one at 307.5 eV for metallic Rh (19), one at 309.3 eV, and assigned to Rh_2O_3 oxide species (20), and one at 310.1 eV assigned to $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (21). For Rh/Au(111), $\text{Rh}3d_{5/2}$ photoelectron line was deconvoluted into two lines: one at 307.4 eV corresponding to metallic Rh, whose recommended binding energy is 307.16 eV (19), and the other one at 309.8 eV corresponding also to $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (21).

An upward shift of 0.25 eV and 0.24 eV for metallic rhodium for Rh/Au(100) and Rh/Au(111), respectively, indicate the influence of both substrates on the electronic state of the deposited Rh, which can be regarded as a direct evidence of the electronic interaction between substrate and the deposit, as already reported for Rh/Au(111) (16).

Hydrogen Evolution on Rh/Au(100) and Rh/Au(111)

Polarization curves for HER on obtained Rh/Au(100) and bare Au(100) electrodes recorded in 0.1 M HClO_4 and Tafel analysis are presented in **Figure 4**. For comparison, corresponding results for bare Rh(poly) recorded under the same conditions are also given.

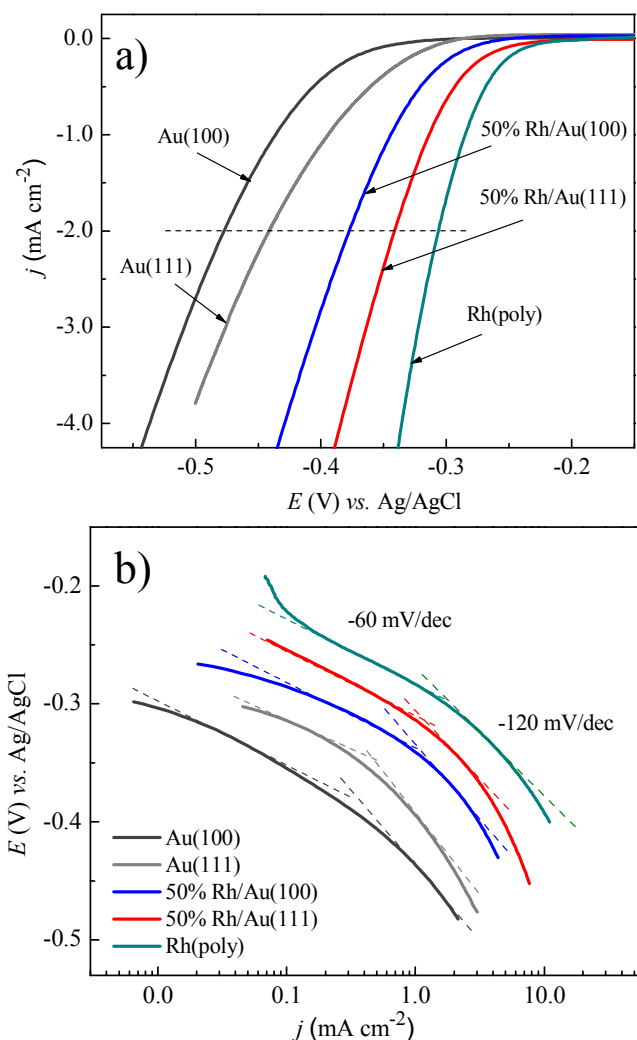


Figure 4. a) Polarization curves for hydrogen evolution recorded in 0.1 M HClO_4 on bimetallic 50% Rh/Au(100) and 50% Rh/Au(111), compared with the ones for HER on bare Au(100), Au(111) and Rh(poly). Sweep rate was 10 mV/s. b) Corresponding Tafel plots.

Figure 4a shows that bare Au(100) substrate is fairly inactive for HER, and high overpotentials are needed for appreciable reaction rate, while bare Rh(poly) shows clear difference in the activity for HER, which is shifted to the more positive potentials for 180 mV at the current density of -2.0 mA cm^{-2} . The presence of spontaneously deposited Rh islands led to the notable enhancement of HER catalysis with respect to bare Au(100). The potential for HER on 50% Rh/Au(100) electrode is shifted positively for 110 mV with respect to Au(100) substrate at the same current density of -2.0 mA cm^{-2} . Notable approach to the activity of Rh(poly) is achieved since the starting difference of 180 mV between Au(100) and Rh(poly) is lowered to about 70 mV.

In the case of Au(111) as a substrate, the difference between the activities of bare Au(111) and Rh(poly) at the same current density of -2.0 mA cm^{-2} , is around 140 mV. Spontaneous deposition of Rh contributed to the notable enhancement of the HER catalysis with respect to bare Au(111). The potential for HER on 50% Rh/Au(111) is shifted positively for 100 mV with respect to bare Au(111). Although Rh(poly) is still more active for HER than any of the investigated Rh modified gold single crystals, it should be noted that the significant lowering of the difference to only 40 mV is achieved for 50% Rh/Au(111).

Tafel analysis of the above given polarization curves, **Figure 4b**, reveal that for all examined electrodes the same Tafel slope value of -60 mV/dec is obtained at lower overpotentials, which changes to -120 mV/dec at higher overpotentials. For Au(100) and Au(111), these Tafel slopes were already observed for HER in acidic medium (5), but their interpretations are still unambiguous. Several possible mechanisms were proposed earlier (22), while one of the most recent studies of HER on gold electrodes suggests that barrierless discharge occurs at lower overpotentials followed by the ordinary discharge at higher overpotentials (23), which means that the discharge step is the rate determining in the whole potential range. In the case of Rh(poly), similarly as for Pt (24), the Tafel slope of -60 mV/dec can be assigned to either Volmer-Tafel or Volmer-Heyrowsky mechanism under Temkin conditions at lower overpotentials, while at higher overpotentials Volmer-Heyrowsky sequences are operative (25). For bimetallic Rh/Au(100) and Rh/Au(111) electrodes, Tafel slope of -60 mV/dec is most likely linked with Volmer-Tafel mechanism since previous theoretical work have shown that these steps in HER mechanism should be very fast on Rh/Au electrodes (14). At higher overpotentials, the occurrence of the Heyrowsky step is also possible.

Conclusions

Structural effect on the spontaneous deposition of Rh has been investigated using Au(100) and Au(111) electrodes as substrates. AFM images of Rh/Au(100) and Rh/Au(111), both with 50% Rh coverage, reveal the structural difference of the deposited Rh islands with respect to the orientation of the underlayng gold substrate. While a small number of large Rh islands are deposited on the Au(100), a number of smaller islands are deposited on the Au(111) substrate. XPS analysis of the oxidation state of the deposited Rh islands have shown that on as prepared 50% Rh/Au(100), Rh-oxide, metallic Rh and RhCl_3 species are detected, while on 50% Rh/Au(111), only metallic Rh and RhCl_3 species are formed during deposition. Therefore, before HER measurements the electrodes were held at potential negative enough to reduce higher valence Rh species to metallic Rh. It is shown that HER in perchloric acid solution occur following the same reaction mechanism on both electrodes, but that at the same current density of -2.0 mA cm^{-2} , 50% Rh/Au(111) is for 40 mV more active than 50% Rh/Au(100), which can be

directly linked with the orientation of the underlying Au single crystal as an determining factor for the HER activity. This is consistent with structural sensitivity of bare Au(100) and Au(111) electrodes in perchloric acid solution.

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Electrochemical CO₂ reduction on oxide-derived Cu surface with various oxide thicknesses

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Cuprous oxide on copper foil electrodes prepared via electrochemical deposition and thermal annealing are investigated towards CO₂ electrochemical reduction at low overpotential. The thickness of the electrochemical deposited Cu₂O was controlled by varying the constant-current deposition time. The surface morphology and roughness were examined with SEM and CV respectively. The electrode fabricated by cuprous oxide deposited for 20 min demonstrated the best faradic efficiency (7.02%) and specific activity (0.123 mA/cm²) towards formate/formic acid formation at -0.5 V vs. RHE in CO₂ saturated 0.5 M K₂CO₃ among studied samples.

Introduction

A steadily raising amount of carbon dioxide (CO₂) released in atmosphere due to increased consumption of fossil-fuel causes harmful climate change. Additionally, limited reserves of fossil-fuel put a pressure on their future availability thus setting a stage for increased interest in utilizing renewable energy. Electrochemical reduction of CO₂ (CO₂RR) is a promising way to reduce amount of CO₂ as well as generate 'carbon neutral fuels(1, 2). Among various products of CO₂RR, formate/formic acid is the promising one for it is the fuel for direct formic acid fuel cell as well as an important C₁ building block for the chemical industry and an efficient hydrogen storage material(3, 4). Metals, such as Hg, Cd, Pb, Tl, In and Sn, with high overpotential for hydrogen evolution reaction and negligible CO adsorption could be used as catalysts for CO₂RR to create formate/formic acid with high selectivity but high overpotential is required(5). Cu and Cu₂O based materials have been the focus of a CO₂RR research because it is one of the most promising catalysts materials capable of producing hydrocarbons(6-9). Kanan's group reported that reducible metal composites based on oxide-derived Cu and Sn/SnO_x thin film have remarkable catalytic properties for CO₂RR due to the higher level of surface defects and residual oxygen(10). Boon Siang's group reported CO₂RR to ethylene and ethanol on electrochemically deposited Cu₂O and demonstrated that the faradic yields for C₂ product can be systematically tuned by varying the thickness of the Cu₂O overlayer(11).

In this study, thermally annealing induced Cu₂O on Cu electrode and various thicknesses electrochemically deposited Cu₂O on Cu electrodes were prepared. Their morphology as well as the performance of CO₂RR at lower overpotential towards formate generation were tested and discussed.

Experiment

Copper foil strip electrodes (noted as Cu-clean) were cut from large piece of copper foil (0.25mm thickness, 99.8% Fisher) and cleaned by immersing them in 6M HCl (ACS reagent, Sigma) solution for 2min and then rinsed thoroughly with di-ionized water. To coat the Cu-clean electrode with Cu_2O , thermal or electrochemical (constant current) treatment was performed. Thermal annealing was done at 400°C for 10min (noted as Cu-400) in N_2O (99.99% Matheson) flow. For Cu_2O electrochemical deposition, an aqueous electrolyte consisting of 0.3 M CuSO_4 (99%, Sigma), 2.3M Lactic Acid (USP/FCC, Fisher), and $\sim 3\text{M}$ NaOH (99.99%, Sigma) was used as plating solution(6). It was prepared by first diluting lactic acid with water ($18.2\text{ M}\Omega$, Millipore) to the concentration of 2.3M and then adding appropriate amount of CuSO_4 . Once the CuSO_4 was dissolved, the solution was cooled with ice bath and NaOH concentrated solution (12M) was added dropwise until the pH of the solution reaches 9.3. Cu_2O deposition was performed at 60°C with constant current density of $0.6\text{mA}/\text{cm}^2$. The deposition time was 10min, 20min, 30min and 40min noted as Cu-10min, Cu-20min, Cu-30min and Cu-40min respectively. The as-prepared electrodes were washed thoroughly with di-ionized water and dried with N_2 flow.

A H-shaped, two compartment electrochemical cell separated with Nafion membrane (117, Dupont) was used for CO_2RR experiments. The working compartment contained an Ag/AgCl reference electrode with a salt bridge and the working electrode. The counter compartment contains a Pt foil as counter electrode. The electrolyte contains 0.5M KHCO_3 (99.95% trace metal basis, Sigma) and 0.01M disodium ethylenediaminetetraacetate (ACS reagent, Sigma) saturated with CO_2 (Ultra-Pure, Air-gas).

The liquid product, formate/formic acid, was quantified via Nuclear Magnetic Resonance spectroscopy (NMR) (400 M Hz, Bruker) while electrode surface morphology was characterized with Scanning Electron Microscope (SEM) (S-4800, Hitachi) at 5 kV, $10\text{ }\mu\text{A}$.

Results and discuss

SEM images of thermally and electrochemically prepared Cu_2O electrode surfaces as well as Cu-clean electrode for comparison are shown in Figure 1 (a)-(f). The Cu-clean electrode surface exhibits smoother surface compared to Cu_2O coated electrodes. The surface of thermally annealed Cu electrode, Cu-400, was smooth and the morphology was similar compared to the Cu-clean electrode surface. This indicates thin and tightly-bonded Cu_2O layer. All of the electrochemically deposited Cu_2O layers consist of agglomerates of angular-shaped crystallites. Also, it can be noticed that the Cu_2O coverage increases with the deposition time. The Cu-10min surface showed low coverage and smaller gains size of Cu_2O than other electrochemically prepared samples and some of the area is similar to Cu-clean surface, indicating a thin layer of Cu_2O . Cu-20min is almost fully covered with angular-shaped Cu_2O while Cu-30min is fully covered. Cu-40min electrode surface was fully covered with angular-shaped Cu_2O , and the gain size of Cu_2O was significantly larger than the other samples.

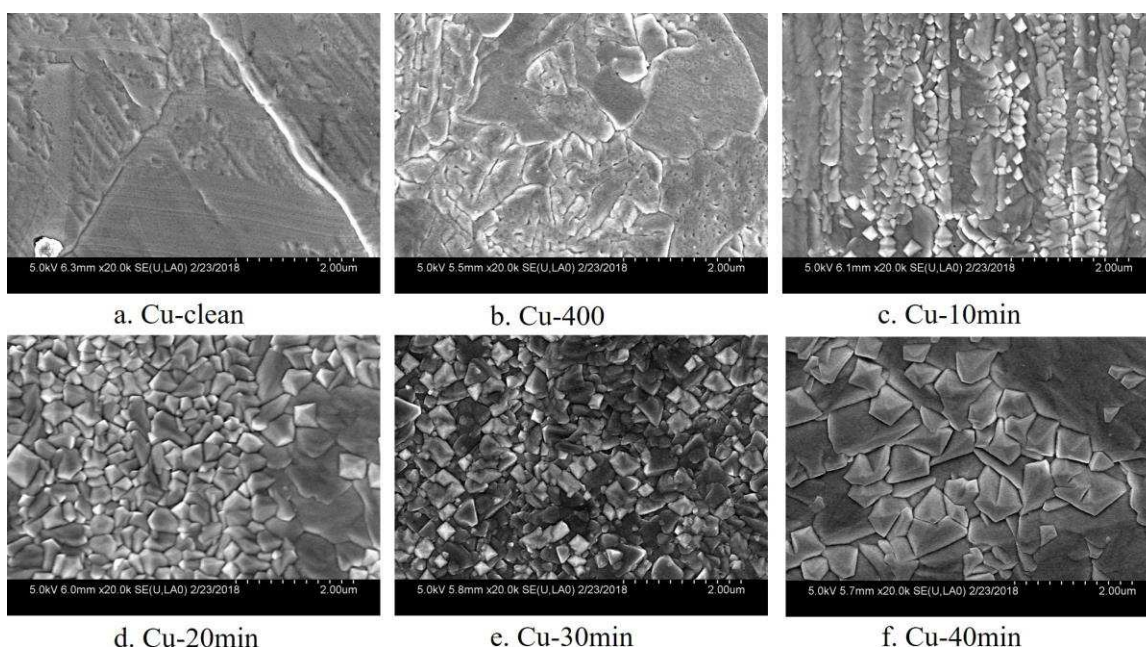


FIGURE 1. SEM images of the thermally and electrochemically prepared Cu_2O electrode surfaces. The Cu-clean electrode is shown for comparison.

The electrochemically active surface area (ECSA) of the electrodes was estimated through a double layer capacitance measurement. The double layer capacitances of each electrode were measured via cyclic voltammetry in deaerated 0.1 M phosphate buffer solution at pH=7.35. The surface roughness of the Cu-clean was defined as 1, and then, the ratio between corresponding double layer capacitance of the electrode and the double layer capacitance of Cu-clean electrode is the roughness factor of the electrode(10). Before ESCA measurement, the as-prepared electrodes were held at -0.5V vs. RHE until stable. The roughness factors of the electrodes are presented in Table 1.

TABLE 1. Double layer capacitance and the roughness factors of the thermally and electrochemically prepared Cu_2O electrode surfaces. The Cu-clean electrode is shown for comparison.

Electrode	Capacitance	Roughness factor
Cu-clean	0.154mF/cm ²	1.00
Cu-400	0.274mF/cm ²	1.78
Cu-10min	2.56mF/cm ²	16.6
Cu-20min	4.23mF/cm ²	27.47
Cu-30min	5.91mF/cm ²	38.4
Cu-40min	8.63mF/cm ²	56.0

It can be noticed that all Cu_2O covered electrodes have larger surface roughness factor compared to the Cu-clean. Also, the surface roughness of electrochemically deposited Cu_2O electrodes is larger than that for thermally annealed electrodes and that as deposition time increases, the roughness factor of the electrodes increases.

CO_2RR experiments were performed in solution containing 0.5 M KHCO_3 and 0.01 M disodium ethylenediaminetetraacetate saturated with CO_2 at -0.5 V vs RHE for 15min. Figure 2 shows chronoamperometry curves for Cu_2O covered electrodes as well as Cu-clean electrode for comparison. During the initial phase of CO_2RR , reduction peaks were observed for all electrochemically deposited Cu_2O electrodes. This feature, already observed in literature, indicates partial reduction of the surface cuprous oxide.

The Cu-clean and Cu-400 showed almost identical electrochemical response. The absence of Cu_2O reduction peak for Cu-400 indicates very thin Cu_2O layer which is supported by SEM pictures and roughness factor close to 1. Among studied samples, Cu-20min showed the largest current density towards CO_2RR indicating that it is the most active electrode.

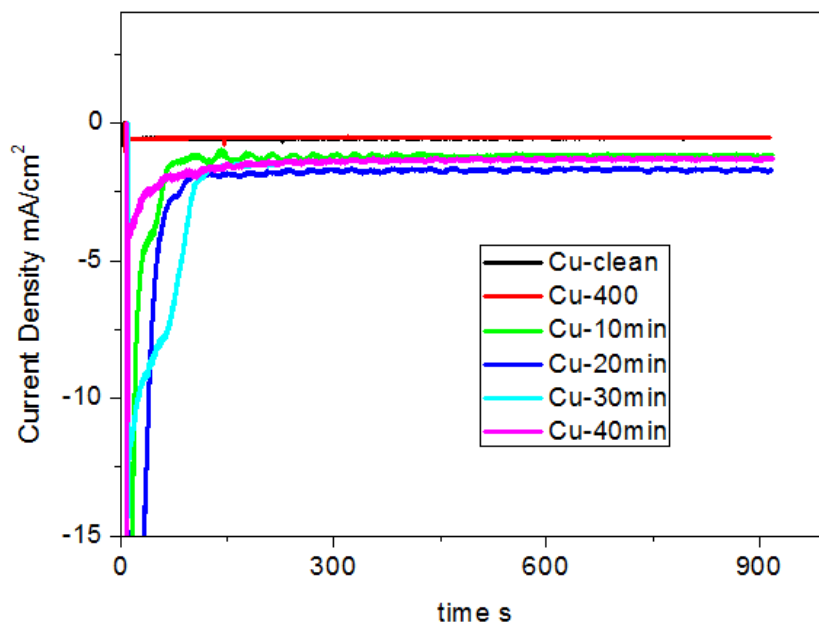


FIGURE 2. Chronoamperometry curves for the thermally and electrochemically prepared Cu_2O electrode surfaces as well as Cu-clean electrode for comparison recorded in 0.5 M KHCO_3 and 0.01 M disodium ethylenediaminetetraacetate saturated with CO_2 at -0.5 V vs RHE for 15min. Current density normalized to geometric area of the electrode.

The electrolyte was analyzed with NMR and presence of formate is observed. The NMR data was used to quantify the faradic efficiency and formate formation current density for studied samples and results are presented in Figure 3.

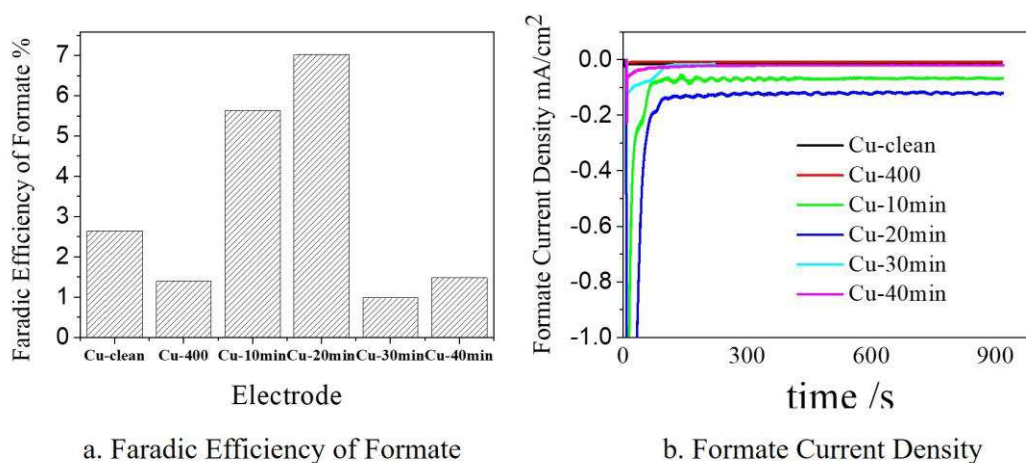


FIGURE 3. Faradic efficiency of formate generation (a) and formate generation current density (b) of the thermally and electrochemically prepared Cu_2O electrode surfaces as well as Cu-clean electrode for comparison. Current density normalized to geometric area of the electrode.

The results showed that only Cu-10min and Cu-20min have substantial activity for formate production. The Cu-20min showed the highest faradic efficiency for formic acid production (7.02%) and formate formation current density (0.123 mA/cm²) at 0.5 V vs RHE in 0.5 M KHCO₃ among studied samples. The samples with too thick (Cu-30min and Cu-40min) or too thin (Cu-400 and Cu-10min) layers will hinder CO₂RR. The electrode with thin Cu₂O layer has low number of active site for CO₂RR due to small amount of Cu₂O whilst the electrode with thick layer of Cu₂O is not conductive enough for efficient charge transfer since it is a semiconductor(6).

Conclusion

Cu₂O/Cu electrodes were thermally and electrochemically prepared and their activity for CO₂RR towards formate generation at lower overpotential (-0.5 V vs RHE) was examined and compared to the performance of the Cu clean electrode. Cu-20min has the highest faradic efficiency (7.02%) and formate generation current density (0.123 mA/cm²) among studied samples. This study revealed that Cu₂O was active towards CO₂RR and that appropriate thickness and morphology was necessary for such a high CO₂RR activity.

Acknowledgments

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Modulating Selectivity in CER and OER through Doped RuO₂

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Electrochemical chlorine evolution reaction (CER) is one of the most important electrochemical reactions due to importance of Cl₂ as an industrial chemical. However, electrochemical CER is bridled with parallel oxygen evolution reaction (OER) reducing the performance of anodic CER. In this context, guiding principles behind enhancing the selectivity of CER is investigated experimentally and computationally in RuO₂ doped with earth-abundant first-row-transition-metals (i.e. Ti, Fe, Mn, Co, Ni, Cu, Zn). Computational studies suggest that doping of metals having higher d-electrons than Ru in RuO₂ tend to lower the binding strength of OER intermediates thereby increasing its overpotential. However, doping has less effect on the binding strength of monovalent CER intermediates resulting in higher CER selectivity. Computational studies suggest that Cu (d⁹)-doped RuO₂ would show maximum CER selectivity and this is corroborated by experiments in acidic medium with electrodeposited Cu-doped RuO₂ where 95% selectivity was obtained at a dopant concentration of 2%.

Introduction

The importance of electrochemical chlorine evolution reaction (CER) as an anodic reaction lies in both chlor-alkali industries and brine electrolysis, which involves annual production of molecular Cl₂ around 70 million tonne with widespread usage in pesticide, insecticide, water treatment and bleaching etc(1, 2). While the thermodynamics favors oxygen evolution reaction (OER), the overpotential associated with chlorine evolution reaction (CER) is less than that for OER and hence, co-evolution of both gases is observed (3).

Desired Reaction: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ E⁰=1.36V vs SHE
 Undesired Parallel Reaction: $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$ E⁰=1.23V vs SHE

The parallel electrochemical co-evolution of O₂ creates major issues in obtaining pure Cl₂ gases. An acidic pH of the electrolyte favors molecular Cl₂ generation and with increase of pH of the electrolyte the selectivity of generation of molecular O₂, ClO⁻ and ClO₃⁻ increases (3). Also, presence of oxidizing acids such as sulphuric acid, nitric acid and phosphoric acid in the electrolyte lowers the CER selectivity even at lower pH (3). Generally, RuO₂-based anodes are used in industry and are good electrocatalyst for both OER and CER (3-5). However, in addition to being expensive, RuO₂-based anodes face

dissolution under acidic medium which makes the whole process capital-intensive. This demands for designing of doped RuO_2 electrocatalysts with earth-abundant elements which can make the whole process more selective towards CER than OER without involving increase in the cost of the catalyst.

To address the issue of selectivity towards CER and catalyst cost simultaneously, a mixture of RuO_2 with other rutile oxides such as IrO_2 , TiO_2 or SnO_2 in a particular composition of $\text{Ru}_{0.3}\text{M}_{0.7}\text{O}_2$ (e.g. $\text{M}=\text{Ir}$, Ti , Sn) better known as dimensionally stable anode (DSA), are used for CER in acidic condition since 1970's in chlor-alkali industries (3, 6-8). In these DSA rutile oxide structures, Ru act as a dopant and activates the host sites towards CER while retaining its own CER selectivity(9). However, the reason for this success with understanding of its underlying surface chemistry of these DSA structures is far from complete and subject for much discussion and debate still today. Among other dopants, Ni(10), Co(11), Fe(12), Zn(13, 14), Nb(15), Ce(15), Sb(16, 17), Mg(18) in RuO_2 or DSA electrodes have been explored experimentally. With advent of density functional theory (DFT) and ab-initio thermodynamics, the search of better catalyst has become less arduous experimentally due to increased understanding of the surface chemistry of the electrocatalyst (19, 20).

In the present study, CER selectivity of earth-abundant first-row-transition-metal (i.e. Ti, Fe, Mn, Co, Ni, Cu, Zn) doped RuO_2 is investigated through combining both DFT-based computational and experimental studies. The experiments are carried out in acidic medium since CER shows higher selectivity in lower pH (3) and the predictive computations take into account of acidic conditions. Computational studies suggest that surface Cu-doped RuO_2 (110) should show highest CER selectivity among the investigated doped RuO_2 structures which is indeed found experimentally with a dopant concentration of 2%. However, Cu-dopant can also activate *lattice-oxygen-vacancy aided water dissociation pathway* due to its low-valent characteristics and enhances the selectivity of OER at higher dopant concentration. Similarly, Zn-doped RuO_2 shows higher CER selectivity in surface -5c sites which is a preferred configuration and shows a lower CER selectivity when dopants occupy -br sites due to *lattice-oxygen-vacancy aided water dissociation pathway*. The present work offers new design insight of electrocatalyst for enhancing CER selectivity during electrochemical Cl_2 production.

Reaction Mechanism of OER and CER

The recent advancement in these theoretical studies has led to greater insight in to the underlying OER and CER mechanisms on RuO_2 (110) surface (4, 21, 22). Contrary to previous understanding that under co-ordinated (cus) metal sites acting as an active site and taking part in reaction with chloride ions, the present DFT studies indicate that it is the adsorbed oxygen on under co-ordinated metal sites that is responsible for interaction with chloride ions 2 (4) (Figure 1). This makes both OER and CER are having common reaction intermediates of having a structure of $\text{M}_{\text{cus}}\text{-O}_{\text{ads}}$ (half covered -O regime and fully covered -O regime in Figure 1). There is a competition between H_2O and chloride ions to form subsequent adsorbate structures of $\text{M}_{\text{cus}}\text{-OOH}_{\text{ads}}$ and $\text{M}_{\text{cus}}\text{-OCl}_{\text{ads}}$ which are precursors to OER and CER respectively. It is to be noted that both CER and OER proceeds through a coupled electron transfer (CET) pathway mirroring an Eley-Rideal (ER) process. The schematic diagrams of OER and CER reaction pathways are given in Figure 1.

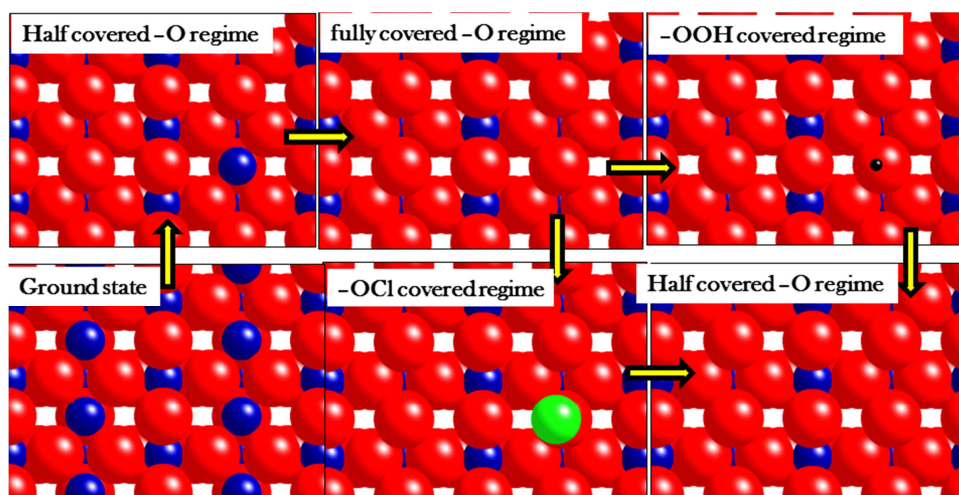


Figure 1: Reaction mechanism of OER and CER on RuO_2 (110). The arrows describe the progress of the reaction pathway. Blue, red, green and black balls correspond to Ru, O, Cl and H atoms.

Density Functional Theory (DFT)-based Computational Details

All the computations regarding adsorption energies of reactants have been carried out with the Density Functional Theory (DFT) approach, utilizing the Vienna Ab Initio Simulation package (VASP) and PBE pseudo-potential (23-25). The bulk lattice constants of RuO_2 are optimized using the $8 \times 8 \times 12$ Monkhorst-Pack type of k -point sampling(26). An energy cut-off of 400 eV is used during calculation.

The bulk lattice constants of RuO_2 are found to be $a = 4.55 \text{ \AA}$ and $c = 3.14 \text{ \AA}$ as against experimentally found $a = 4.49 \text{ \AA}$ and $c = 3.10 \text{ \AA}$ (27). The RuO_2 (110) surface is modelled by a periodic stack of asymmetric slabs containing five O-Ru-O layers with adsorption of reactants are carried out only on one side of the slab. The structure of the topmost three O-Ru-O trilayers including the adsorbates is allowed to freely relax, while the bottom two O-Ru-O trilayers are kept fixed. A vacuum region of $15 \text{ \AA}$ separates consecutive slabs in the vertical direction. The DFT surface calculations were restricted to 2×1 unit cells using a 4×4 Monkhorst Pack k -point mesh for slab calculations. Solvent interaction related corrections are not carried out as they are not too large to be considered ($\sim 20 \text{ meV}$) (21). A Fermi smearing of 0.1 eV and Pulay mixing is used to ensure the fast convergence of the self-consistent electron density. Atomic positions are relaxed until the sum of the absolute forces is less than $0.05 \text{ eV/\AA}$.

The 2×1 surface unit cell of the stoichiometric RuO_2 (110) contains two bridge ($\text{Ru}_{2\text{br}}$) and two cus sites (Ru_{cus}) (Figure 2). We consider adsorption of O_{br} , OH_{br} , OCl_{br} , and Cl_{br} at bridge sites ($\text{Ru}_{2\text{br}}$) and adsorption of O_{cus} , OH_{cus} , OCl_{cus} , Cl_{cus} , $(\text{O}_2)_{\text{cus}}$ and OOH_{cus} at cus sites (Ru_{cus}). We have considered Volmer-Heyrovsky mechanism of CER as it is reported to be the most favourable CER pathways among the all known CER pathways(5).

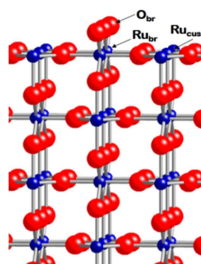


Figure 2. Side view of the $\text{Ru}_{20}\text{O}_{40}$ (110) surface used in the DFT calculations. The bridging oxygen atoms (O_{br}), the five-coordinated Ru-atoms (Ru_{cus}), and the six-coordinated Ru atoms (Ru_{br}) co-ordinated with O_{br} are indicated in the figure. Red and blue balls correspond to O and Ru and dopant atoms respectively

The entropy correction of the adsorption energies are done by relations as in used previous literatures (28),

$$S = k_B \ln \prod_{i=1}^N \frac{1}{1 - \exp\left(\frac{h\omega_{X,i}}{2\pi k_B T}\right)}$$

where i is the specific vibrational mode, N is the total number of vibrational modes for reaction intermediate X , k_B is the Boltzmann constant and T is the absolute temperature. All the gases and vapors are assumed to behave ideally and are summarized in Table 1.

Table 1. Zero-point energy (ZPE) and entropies of the water vapor and diatomic gases involved in electrochemical conditions.

Gas	ZPE (eV)	TS (eV)
H_2O (l)	0.57	0.67 (at 0.035 bar)
H_2	0.35	0.40
Cl_2	0.06	0.69

The relation between free energy change of reaction (ΔG), pH and applied electrochemical potential U is derived using the first principle thermodynamical methodology explained by Norskov et al. (21, 29, 30) and Over et al.(4, 5)

Experimental Details

Electrocatalysts were prepared using electrodeposition technique on titanium plate in an acidic medium containing 0.1 M boric acid (Fisher-Scientific, ACS grade, purity $\geq 99.5\%$). Salts $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (99.9% pure), TiCl_4 (99.0%), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (96%), FeCl_3 , CoCl_2 (99.0%), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (98%), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.0 %) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (99.1%) were used as a precursor for Ru, Ti, Mn, Fe, Co, Ni, Cu and Zn respectively. To increase the ionic conductivity during electrodeposition, 1.0 M of NaCl (Fischer-Scientific) salt was used as a supporting electrolyte. All aqueous solutions were prepared with DI water.

Metallic Ru and first row transition metals are co-electrodeposited on Ti-support under electrochemically reducing (-0.8 V vs. Ag/AgCl) and acidic conditions. Before starting the electrodeposition process, Ti plate was scrubbed by emery paper, sonicated for 30 minutes in acetone, cured with oxalic acid at 100°C to remove any oxide layer from its surface and rinsed with DI water. The intricate details of electrodeposition are given in our previous paper (31). The electrodeposition results in deposition of doped metals on Ti-plate which are further heated to oxides at an elevated temperature. The concentration of transition metal dopants in RuO_2 are varied through changing the

concentration of precursor solution (550°C for 5 hrs.). The compositions of electrodes are investigated by X-ray Fluorescence (XRF).

(0.5 M NaCl + 1 M HCl) solution was used to perform all the electrochemical characterizations at room temperature. Pt mesh as counter electrode and Ag/AgCl (saturated KCl) as reference electrode were used to measure all potentials reported. Potentiostat (Auto Lab PGSTAT302N) was used to perform linear sweep voltammetry (LSV) and CV of the electrodes in a single-compartment cell. The scan rate for CV measurements was kept at 10 mV/s. The potential window of 0-1.6 V (vs Ag/AgCl) was maintained while performing the electrochemical characterizations.

Measurement of Chlorine Evolution: Gas Chromatography (GC) experiments were carried out to detect CER selectivity using a Thermo-Scientific Trace GC 800 gas chromatograph instrument with a thermal conductivity detector (TCD) and flame ionization detector (FID). The evolved gases are collected and quantified via GC. The gas evolved from anode corresponds to a mixture of Cl₂ and O₂ gas. In addition to the gas-chromatography results, we have correlated the GC data with current densities at Cl₂ reduction (CRR) peak at around ~ 1 V (vs Ag/AgCl) found from electrochemical CV data. The evolved chlorine during oxidation cycle gets soluble in water (solubility of chlorine in water = 0.995 g/100 g of H₂O) which gets reduced during reduction cycle of CV(32, 33). The concentration of dissolved chlorine in water would be proportional to the CRR current density obtained from CV. Using this hypothesis, it is assumed that the reducing current density of chlorine would be proportional to chlorine in the gas-mixture obtained from GC experiment. The calibration curve of both sets of experiments are plotted and shown in Figure 3.

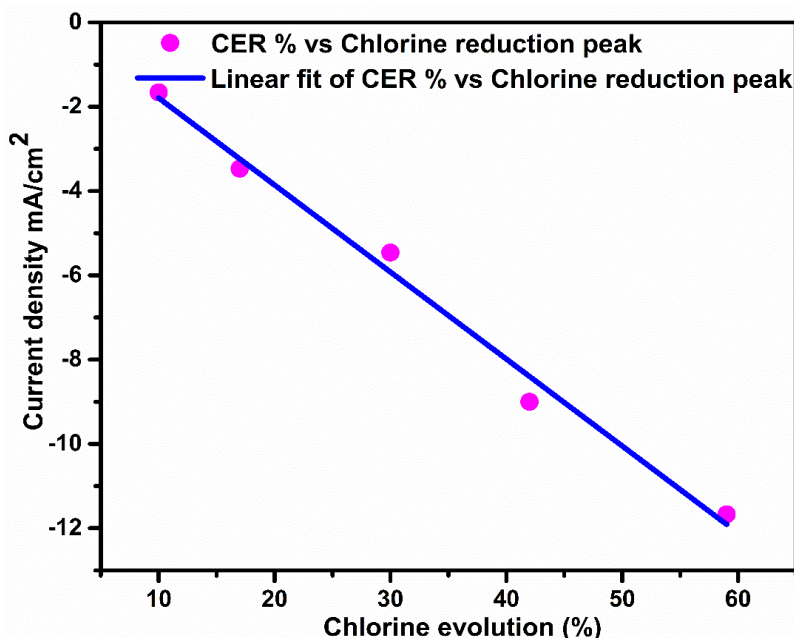


Figure 3. Linear fit of chlorine reduction current density vs chlorine evolution data extracted from gas chromatography.

The calibration curve shows a linear dependence of both sets of data (Regression = 0.98). The calibration equation is found to be

$$y = -0.2064x + 0.27$$

where y is CRR current density (mA/cm^2) at 1 V and x is chlorine evolution percentage at (1.4 V) obtained from GC analysis. Using this calibration curve, the chlorine selectivity can be easily calculated using electrochemical analysis in addition to GC techniques.

Result and Discussion

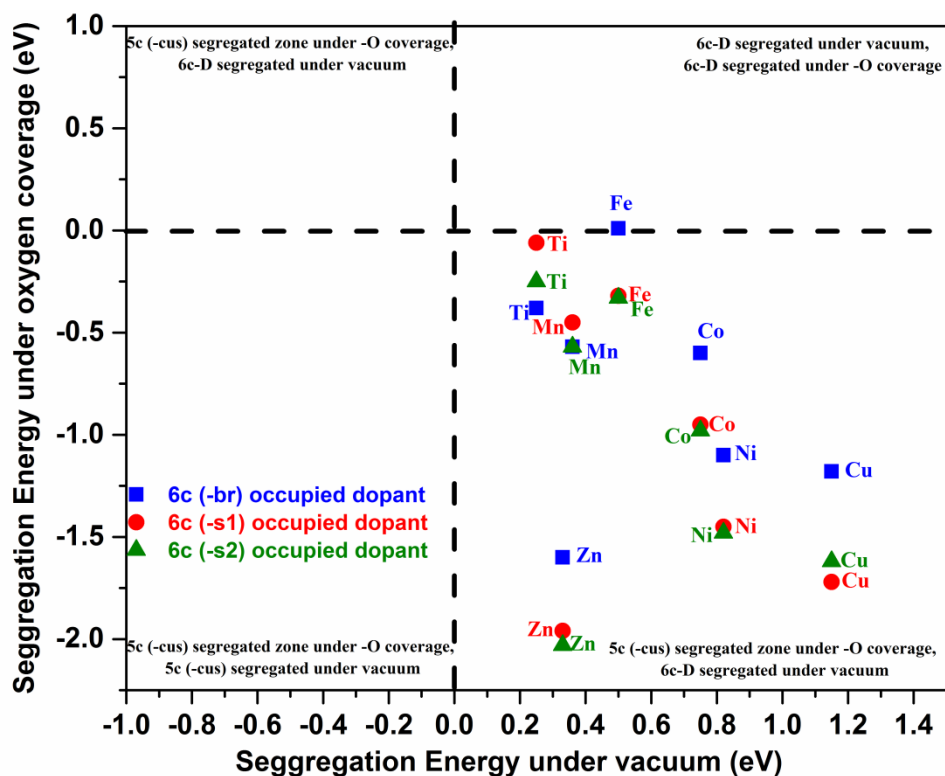


Figure 4: Segregation energy of different dopants towards under co-ordinated 5c (-cus) sites in RuO_2 (110) surface with respect to oxygen adsorption energy on 5c (-cus) sites of the respective systems.

The stability of dopant in different sites varies depending upon its relative valency as a stable oxide against the host oxide structure and their relative sizes (34, 35). Hence, we have considered particularly two sites for dopants during calculations for selectivity that are (1) dopants occupying the surface metal -cus sites or active sites and (2) the most stable site of the dopant in a RuO_2 (110) structure with a dopant concentration of 2.5% wherein both surface and subsurface dopant sites are considered (Figure 2). The stabilities of various dopants at different sites are computed by evaluating the segregation energies with respect to -cus occupancy by dopants for adsorbate-poor and O-rich conditions using the following equation,

$$\Delta E_s = E_{A-D-RuO_2} - E_{A-5c-D-RuO_2}$$

where $E_{A-5c-D-RuO_2}$ and $E_{A-D-RuO_2}$ correspond to adsorbate (A) covered -cus (5c)-occupied doped (D) RuO_2 and adsorbate (A) covered doped (D) RuO_2 respectively. To mimic the adsorbate poor conditions, no adsorption on surfaces are carried out computationally. These type of conditions mimic the synthesis conditions wherein vacuum or low oxygen

chemical potential are employed. A negative segregation energy indicates that dopants would segregate towards that particular dopant site (Figure 4).

The energy differences between the surface and subsurface arrangements of dopants are considered in presence of adsorbate coverage in the present study with respect to surface-5c (-cus) which gives an estimate of the thermodynamic driving force behind dopants ordering. The first-row-transition-metal dopants prefer five co-ordinated -cus site at the surface of RuO₂ (110) under adsorbate-poor conditions. This may be due to foreign dopant atoms exerting stress in the host lattice structure because of diverse D-O bond-distance in comparison to Ru-O bond-distance and hence preferring surface position as compared to subsurface position in the host lattice structure.

Though the bare surface structure allows doping to different degrees, the thermodynamic preference of dopants at surface and bulk positions differ under complete oxygen coverage which surface structure is an intermediate one in both OER and CER conditions (36). The considered dopants found to segregate towards surface -cus sites under oxygen coverage while they prefer six co-ordinated sites of RuO₂ under vacuum. While the bigger dopants (i.e. Ti, Mn) prefer to be at surface six co-ordinated sites as they offer least strain (i.e. bridge sites), the smaller dopants (Fe, Co, Ni, Cu and Zn) tend to segregate towards subsurface sites due to combination of surface adsorption energy and strain considerations. This is concomitant with the understanding that larger dopants tend to surface segregate while smaller dopants tend to bulk segregate under adsorbate covered conditions(34, 36). However, these segregation preferences reflect only enthalpy conditions and the kinetics associated with the segregation towards a specific dopant site would more be dictated by associated activation barrier of the transition pathway which is not in the purview of the present study.

Overpotentials of OER and CER under electrochemical conditions: The potential determination step (PDS) of OER following CET pathway and associated overpotentials for different doped RuO₂ are calculated. The PDS for undoped RuO₂ is the change of surface adsorbate structure O- → HOO- with an OER overpotential of 0.47 V which is in agreement with literature results (4, 37). A weakening of binding of O- adsorbate when surface -5c (cus) sites are occupied by dopants such as Co, Ni, Cu and Zn (i.e. having greater number of d-electrons), has been observed. This results in an increase of OER overpotential with change of the PDS to HO- → O- on electrocatalyst surface. Among all the dopants, Co is found to suppress OER the most while occupying the -cus sites among all considered dopants. This conclusion has been reached assuming that OER follows a CET pathway. However, Rossmeisl et al has reported that there is a probability of activation of alternative OER pathways during these conditions which results in overall higher OER rate while RuO₂ is doped with Co- and Ni-dopants (38). The reaction pathways in addition to CET pathway of OER generally involves creation of oxygen vacancy at surface O_{br} sites, which is followed by Ru_{br} also acting as an active sites (13, 22, 38). Under undoped conditions, RuO₂ (110) surface does not get activated through formation of oxygen vacancy which probably explains why RuO₂ is not a good oxidation catalysts for reactions involving Ru_{br} sites (27). The formation of oxygen vacancies at O_{br} leading to exposure of Ru_{br} sites require high energy (2.41 eV) in undoped RuO₂ leading to lower reaction kinetics of OER with HOO- → O₂ as PDS. The overpotential of OER involving -br sites is comparable to that of -cus sites when Zn and Cu occupies surface 6c-br sites with PDS as O- → HOO. This leads to considerable OER following this reaction mechanistic pathway for this type of low-valent cation dopant (13, 39).

A stronger binding of O-adsorbates with surface also leads to suppression of OER. The PDS in these cases are generally surface transition of $O^- \rightarrow HOO^-$. The above results confirm our understanding from Sabatier principle which states that *reaction adsorbates should not bind too strongly or weakly with catalyst surface for faster reaction kinetics*(40, 41).

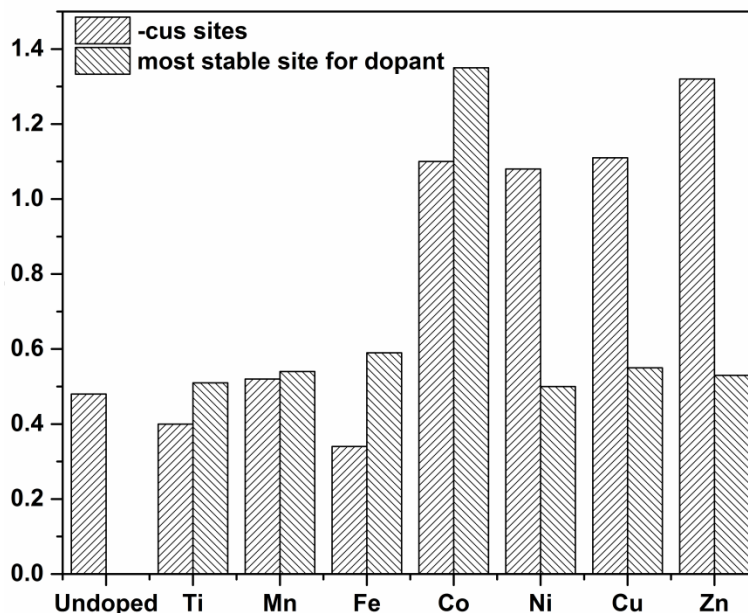


Figure 5: Theoretical overpotential (η^{OER}) of OER on undoped RuO_2 (110) and doped RuO_2 (110) surface with dopant at $-cus$ site and most preferred stable site for dopant considered.

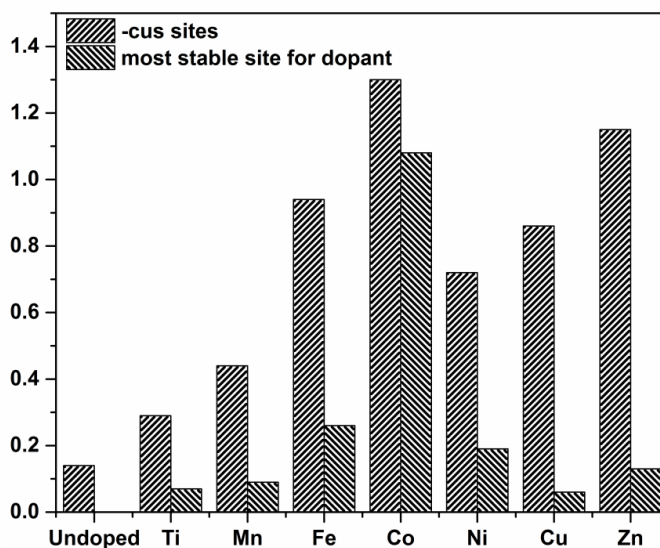


Figure 6: Theoretical overpotential (η^{CER}) of CER on undoped RuO_2 (110) and doped RuO_2 (110) surface with dopant at $-cus$ site and most preferred stable site for dopant considered.

In CET of CER, the surface $-cus$ sites behave like as an active sites as like OER. However, Cl^- adsorbate does not necessarily adsorb on it and they adsorb over O-adsorbates on undoped RuO_2 (110) surfaces which has been pointed out before (4).

Similar to OER, when dopants occupy surface –cus sites, it leads to suppression of CER with increase in CER overpotentials (Figure 6). Co, Ni, Cu, Zn in –surface positions and (Mn, Ni, Cu) in subsurface positions have found reduce the CER overpotentials in great degree as can be observed Figure 6.

To experimentally validate our theoretical propositions regarding CER selectivity, we prepared doped RuO₂ structures. The maximum CER selectivity achieved by the doped RuO₂ and the corresponding dopant concentration at their CER selectivity are summarized in Table 2. The maximum CER selectivity achieved by this doping is for Cu at a dopant concentration of 2% wherein 95% CER selectivity have been achieved. In Cu-doped RuO₂, Cucus sites do not promote neither OER nor CER as they bind weakly both OER and CER intermediates. However, at its preferred dopant site at subsurface, Cu increases the overpotential towards OER reducing its activity. This might be due to charge transfer effect in RuO₂ host lattice structure which reduces the oxidation state of active site of Ru-atom by 0.1 order. This is in agreement with previous observations that Ru active sites with lower oxidation states require higher OER overpotential (31). However, the binding energy of ClO⁻ or Cl⁻ gets only weakly affected due to Cu-doping as these are soft bases. On the contrary, CER intermediates binds energetically more favorably when Cu occupies subsurface site with a reduction of theoretical overpotential of CER (η_{CER}) by 0.04 eV has been observed. This is demonstrated experimentally in almost three times enhancement of specific activity of CER in doped RuO₂ in comparison to undoped RuO₂. However, the propensity to form oxygen vacancies at bridge position in Cu-doped RuO₂ increases with increase in doping concentration which promotes lattice-oxygen-vacancy promoted OER thereby decreasing the CER selectivity at higher dopant concentration (Table 3).

Table 2. Maximum CER selectivity (%) achieved by doping first row transition metals and corresponding dopant concentration at their maximum CER selectivity.

Dopant	Maximum CER Selectivity Achieved (%)	Dopant Concentration at Maximum Selectivity (%)
Ti	85%	10%
Cr	90%	6%
Mn	84%	6%
Fe	80%	4%
Co	48%	3%
Ni	77%	4%
Cu	95%	2%
Zn	79%	2%

Table 3: Comparison of the activity of electrodeposited RuO₂, Cu doped RuO₂ and mixed Ru_{1-z}Cu_zO_x on titanium support

Electrodes	Current density of CER (mA/cm ²) at 0.37 V Overpotential	Specific activity of CER (μA/cm ²) at 0.37 V Overpotential	Chlorine selectivity
RuO ₂	7.63	20.2	0.39
Ru _{0.98} Cu _{0.02} O _x	51.27	65.9	0.95
Ru _{0.97} Cu _{0.03} O _x	35.26	61.7	0.86
Ru _{0.94} Cu _{0.06} O _x	28.88	61.4	0.76
Ru _{0.78} Cu _{0.22} O _x	12.98	31.7	0.59

Similarly, lattice-oxygen-vacancy promoted OER dissociation path are reported to dominate in Zn-doped RuO_2 as the formation of $-\text{O}_{\text{br}}$ vacancy get lowered in RuO_2 (13, 39). Furthermore, Zn-doped RuO_2 structures have the propensity to transform to RuZnO_3 which is a good OER electrocatalyst (13). Theoretical results suggest ‘-cus’ occupied Zn dopant decreases CER selectivity, though when Zn-dopants occupy its preferred subsurface sites, the CER selectivity should increase in comparison to undoped RuO_2 . However, Zn prefer to segregate towards -cus sites as they mostly form 4 co-ordinated oxides (wurtzite ZnO) which can be responsible for lowering of CER selectivity at higher concentration. These factors contribute to the maximum CER selectivity of 77% achieved through Zn-doping at a concentration of 2%.

Ti-doped RuO_2 structure shows a maximum CER selectivity of 85% achieved at 10% dopant concentration. Ru-doped TiO_2 structure is CER selective while Ti-doped RuO_2 structure is more OER selective(42). Ti-dopant in RuO_2 interacts with host Ru- atom and enhances the oxidation state of Ru which is confirmed by our previous XPS studies too(43). This leads to reduction of OER overpotential without much change in CER overpotential. The otherwise benign surface Ti-dopant while occupying -cus sites are activated by RuO_2 towards OER.

Theoretical studies also predict Fe-doped RuO_2 to show minimum CER selectivity while occupying surface -cus position. However, bulk segregation of Fe-dopant might occur in presence of adsorbates relevant to OER and CER (Table 2). Though, surface occupation of Fe-dopants suppresses CER which has been previously observed experimentally too(12), sub-surface positions of Fe-dopant favour CER selectivity. Similar type of behaviour is also shown by Mn-dopant though the extent of suppression of CER is much less in comparison to Fe-dopant which is reflected in the experimental studies too as maximum CER selectivity achieved through Fe- and Mn-dopants are 80% and 84% respectively.

Both Co- and Ni-dopants were found to suppress CER selectivity as corroborated by previous studies too (10, 44, 45). Maximum CER selectivity is found in the lowest achievable dopant concentration as Co- and Ni-dopant found to favour OER with all dopant configurations (Figure 6). The lowering of CER selectivity is further aided by activation of O_{br} which forms HO_{br} on the surface thereby drastically reducing the OER overpotential and aiding OER kinetics to surpass its *volcano-limitation*(38). Experimentally, Co-doped RuO_2 has been found to show lowest CER selectivity among all dopants with a value of 71%.

The following study leads to better understanding of experimental conditions for electrochemical CER in presence of doped RuO_2 electrocatalyst. The binding energies of OER intermediates get altered more with respect to CER intermediates and in the process transforming CER selectivity. The binding energies of OER intermediates (particularly O- adsorbate) weakens more drastically in comparison to CER intermediates with increase in d-electrons of dopants. The above phenomenon is reflected in (1) change of potential determination step to $\text{HO}^* \rightarrow \text{O}^*$ as opposed to $\text{O}^* \rightarrow \text{HOO}^*$ in undoped RuO_2 when dopants are occupying the active -cus sites and (2) increase in CER selectivity. However, increasing dopant concentration reduces oxygen vacancy formation energy particularly at bridge site leading to vacancy mediated OER pathway and in the process reduction in CER selectivity as can be observed for Cu- and Zn-dopants. Other first-row-transition-metal dopants (Co, Ni and Fe) having higher or equal number of d-electrons tend to suppress CER selectivity while affecting OER and CER overpotentials in equal measure when they occupy surface positions. Dopants having lower number of d-

electrons (Mn, and Ti) tend to favour CER selectivity in subsurface positions which may be ascribed to charge transfer effect. However, Ti and Mn was found to favour increased OER selectivity while occupying surface positions. We believe that this may be due to variable splitting of d-bands which is responsible for change in adsorption energies of relevant reaction intermediates(46, 47). These dopants do not favour vacancy mediated OER pathway. The above correlations can provide better guiding principle for designing better electrocatalysts for CER.

Conclusion

In the present study, CER selectivity of first row transition metal doped RuO₂ has been investigated through DFT-based computational and experimental studies. Computational studies suggest that low-valent dopant (e.g. Cu, Zn) tend to surface segregate and weaken the binding of adsorbates relevant to OER (HO-, O-, HOO-) and CER (ClO-, Cl-) with the surface. However, these doping have less effect on the binding strength of CER intermediates resulting in lesser increase in CER overpotential and ultimately leading to higher CER selectivity. The effect of the dopants on binding energies of adsorbates are more pronounced when they occupy surface *-cus* sites in comparison to other configurations like surface bridge sites or subsurface positions. Computational studies suggest that Cu (d⁹)-doped RuO₂ would show maximum CER selectivity which has been corroborated by our experiments with Cu-doped RuO₂ through co-electrodeposition means. The electrodeposited Cu-doped RuO₂ (2% dopant concentration) has been found to show 95% CER selectivity at acidic pH medium. However, doping of d-enriched metals also lower the vacancy formation energy of oxygen at bridge sites which may activate *lattice-oxygen-vacancy aided water dissociation pathway* and in the process aid the selectivity of OER. This may result in an optimum doping concentration wherein CER selectivity is maximum which is observed for Cu- and Zn-doped RuO₂ electrocatalysts experimentally. The present work offers insight on catalyst design taking account of selectivity of CER and OER during electrochemical Cl₂ production.

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