

REPORT DOCUMENTATION PAGE

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14. ABSTRACT Based on the Phase I research results, we identified that carbon supported Pd-based catalysts, such as Pd/C and PdRu/C, had better electrocatalytic activity toward the ethanol oxidation reaction (EOR) than Pt-based catalysts. However, the selective C-C bond cleavage in the EOR on the Pd-based catalysts, leading to carbon dioxide, was not a major reaction pathway. During this research period, we aim to study the EOR activity and selectivity on Pt based catalysts with and without Pb(IV) additives, including solution phase Pb <sup>2+</sup> presented in the electrolytes and solid phase Pb in Pt/C or Pd/C or Pt/C catalysts.					
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## Report Title

Development of a Direct Ethanol Fuel Cell System with Anion Exchange Membranes

### ABSTRACT

Based on the Phase I research results, we identified that carbon supported Pd-based catalysts, such as Pd/C and PdRu/C, had better electrocatalytic activity toward the ethanol oxidation reaction (EOR) than Pt-based catalysts. However, the selective C-C bond cleavage in the EOR on the Pd-based catalysts, leading to carbon dioxide, was not a major reaction pathway. During this research period, we aim to study the EOR activity and selectivity on Pt based catalysts with and without Pb(IV) additives, including solution phase Pb<sup>2+</sup> presented in the electrolytes and solid phase Pb in Pt/C or Pd/C or Rh/C catalysts.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
01/15/2015 1.00	Hui He, Liang Ma, Andrew Hsu, Rongrong Chen. PdRu/C catalysts for ethanol oxidation in anion-exchange membrane direct ethanol fuel cells, Journal of Power Sources, (11 2013): 696. doi: 10.1016/j.jpowsour.2013.04.051
<b>TOTAL:</b>	<b>1</b>

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
<b>TOTAL:</b>	

**Number of Papers published in non peer-reviewed journals:**

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### (c) Presentations

1. Invited talk "Polymeric Electrolytes and Catalysts for Anion-Exchange-Membrane Fuel Cells", PRICM, WAIKOLOA, Hawaii, Aug. 4-8, 2013.
2. "Carbon-supported AgCo Catalysts for Oxygen Reduction Reactions in Anion Exchange Membrane Fuel Cells", presented in the Fall ECS meeting, Oct., 2013.

Number of Presentations: 2.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**(d) Manuscripts**

Received      Paper

**TOTAL:**

Number of Manuscripts:

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**Books**

Received      Book

**TOTAL:**

Received      Book Chapter

**TOTAL:**

**Patents Submitted**

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**Patents Awarded**

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**Awards**

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Liang Ma	0.50
<b>FTE Equivalent:</b>	<b>0.50</b>
<b>Total Number:</b>	<b>1</b>

**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Rongrong Chen	0.55	
<b>FTE Equivalent:</b>	<b>0.55</b>	
<b>Total Number:</b>	<b>1</b>	

**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

**Names of Personnel receiving masters degrees**

<u>NAME</u>
<b>Total Number:</b>

**Names of personnel receiving PHDs**

<u>NAME</u>
<b>Total Number:</b>

**Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Sub Contractors (DD882)**

## **Inventions (DD882)**

### **Scientific Progress**

The key accomplishments during these four months include:

1. The EOR kinetics on various Pt/C, Pd/C, Rh/C and their binary and ternary catalysts with and without Pb additives have been studied by using potentiodynamic and potentiostatic measurements in NaOH solutions containing ethanol. Among the tested catalysts, the Rh-Pb(upd) catalysts showed the best EOR activity, which will be further tested in DEFCs. Experimental methods for monitoring EOR products, including acetaldehyde, acetate and carbonate (CO<sub>2</sub> in NaOH solutions), were also investigated. A quantitative method to detect acetaldehyde has been successfully established, while analyzing acetate and carbonate needs further developments.
2. The solution Pb species enhanced EOR kinetics on Pt/C, which confirms the results reported by Mukerjee, et al. However, it is debatable if the Pb addition changes the functionality of the Pt catalyst surface for efficient promotion of CO oxidation or prevents aldol reaction and polymerization reaction of the EOR reaction intermediates (acetaldehyde) in alkaline media.
3. The deposited Pb species on Pt/C catalysts showed limited promotion effect of EORs in concentrated NaOH solutions (> 1M), but had some promotion effects in diluted NaOH solutions (e.g. 0.1M).
4. It was demonstrated that the polymerization or/and aldol reaction by-product of acetaldehyde has poisoning effect for the Pt electrode in alkaline solutions, but not in acid solutions. By adding Pb(Ac)<sub>2</sub> species in 1M NaOH solutions, acetaldehyde poisoning effects on Pt/C electrodes for the EOR kinetics were hindered. However, adding Pb(Ac)<sub>2</sub> species in 1M NaOH solutions did not promote the EOR on Pd/C catalysts. In contrast, the EOR kinetics were reduced significantly on Pd/C electrodes in Pb (Ac)<sub>2</sub> containing 1M ethanol and 1M NaOH solutions.
5. The Pb species promoted the ethanol oxidation on alloy catalyst in general. Multifunctional catalyst design promotes the ethanol oxidation significantly. Gas chromatography (GC) is valid for acetaldehyde analysis, but unsuccessful for acetate analysis.

### **Technology Transfer**

***Tremont Technology, LLC.***

*9880 Douglas Floyd Parkway, Noblesville, IN 46060-7900, (317) 460-7934*

[tremonttechceo@gmail.com](mailto:tremonttechceo@gmail.com)

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**Development of a Direct Ethanol Fuel Cell System with  
Anion Exchange Membranes**

*Report I for SBIR Phase I Option Funding (CLIN 0002)*

Period of Performance: Oct. 22, 2012 – Jan. 21, 2013  
SBIR Topic Number: Topic Number: A11-022  
Contract number: W911NF-11-C-0207  
CIN: 00102153290001AA

Principle Investigator:

Rongrong Chen, Ph.D

317-460-7934, [tremonttechceo@gmail.com](mailto:tremonttechceo@gmail.com)

For:

U.S. Army Research Office

Attn: AMSRD-ARL-RO-SG-SI (Reports)

P.O. Box 12211

Research Triangle Park, NC, 27709-2211

**OVERVIEW.**

Based on the Phase I research results, we identified that carbon supported Pd-based catalysts, such as Pd/C and PdRu/C, had better electrocatalytic activity toward the EOR than Pt-based catalysts. However, the selective C–C bond cleavage in the EOR on the Pd-based catalysts, leading to carbon dioxide, was not a major reaction path. Recently, it was reported that improved selectivity and activity of the EOR on Pt/C catalysts in alkaline media could be achieved by using a solution-phase co-catalyst based on Pb(IV) acetate, which could affect the ethanol adsorption so as to facilitate direct activation of the C–C bond [1]. It was proposed that the simultaneously formed under-potentially deposited (UPD) Pb and surface lead hydroxide change the functionality of the catalyst surface for efficient promotion of CO oxidation. It is essential to achieve a good understanding if and how Pb(IV) acetate could lead the selective C–C bond cleavage of EOR on Pt-based catalysts, which will help us designing high activity and selectivity catalysts for EOR in alkaline media.

During the period, we aim to study the EOR activity and selectivity on Pt based catalysts with and without Pb(IV) additives, including solution phase  $\text{Pb}^{+2}$  presented in the electrolytes and solid phase Pb in Pt/C or Pd/C or Rh/C catalysts.

**REPORT CONTENT.****1. Experimental Methods:****a. Materials (purchase or preparation)**

The carbon-supported electrocatalysts Pt/Vulcan XC 72 and Pd/ Vulcan XC 72 (both are 20 wt % metals on carbon) were purchased from E-TEK. All aqueous solutions were prepared using Millipore ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ). To prepare the catalyst suspension, 4.0 mg of the catalyst was dispersed ultrasonically in 2 ml of diluted Nafion solution (2 mg/ml catalyst), which contains 950  $\mu\text{l}$  ethanol, 950  $\mu\text{l}$  ultrapure water, and 100  $\mu\text{l}$  Nafion solution (Aldrich, 5% Nafion). The thin film electrodes were then prepared by pipetting and drying the 20  $\mu\text{l}$  catalyst suspension on the surface of a mirror-polished glass carbon electrode with a 5 mm diameter (Pine Instruments). The resulting thin film electrodes had a metal loading of  $40.76 \mu\text{g cm}^{-2}$ .

**b. Electrochemical Characterizations**

All the electrochemical measurements were conducted using a Solartron 1287 potentiostat. The electrochemical experiments were carried out in an Ar-purged NaOH solution (or NaOH + ethanol solution) using a standard three-electrode electrochemical cell with a jacket. A gold foil electrode and an Hg/HgO electrode (the concentration of NaOH varied according to the solution tested) served as the counter electrode and the reference electrode, respectively. However, all the potentials in this study were reported with respect to the reversible hydrogen electrode (RHE). Prior to the potentiodynamic and potentiostatic measurements for ethanol electro-oxidation, the prepared thin film electrodes were firstly cycled between 0.06 and 1.2 V in the Ar-saturated blank NaOH solution. For the tests of Pb species effect, on each series of experiment, the Pt thin-film electrode was firstly cycled in NaOH + ethanol solution, and then desired amount of lead

acetate was added to the solution. After tested in NaOH + ethanol + lead acetate solution, the Pt thin-film electrode was further rinsed with pure water and re-immersed in NaOH + ethanol solution. The CV tested after re-immersed in NaOH + ethanol solution corresponding to the ethanol oxidation behavior on underpotential deposited (UPD) lead on Pt electrode ( $\text{Pb}_{\text{UPD}}$ -Pt electrode). For the tests of acetaldehyde effect, desired amount of acetaldehyde were introduced into the blank NaOH solution or the in NaOH + ethanol solution.

## 2. Results and Discussions

### 2.1. Effects of Solution Phase $\text{Pb}^{2+}$ on the EORs Using Pt/C or Pd/C Catalysts

Fig. 1 showed the cyclic voltammetry (CV) curves obtained with Pt/C (20 wt.%) electrodes in different concentrations of ethanol and 1 M NaOH solutions. Obviously, the addition of the lead acetate in solution greatly improved the ethanol oxidation activity on Pt electrode. The CVs of Pt electrode in (NaOH + ethanol + lead acetate) solutions not only showed the lowest onset potential, but also showed much higher oxidation peak current. Furthermore, it was noticed that the CVs of Pt electrode in (NaOH + ethanol + lead acetate) solution showed much smaller hysteresis loop, indicating that the poison of Pt electrode was less significant as comparison to that in (NaOH + ethanol) solution. In all the tested concentrations (0.1, 0.5 and 1 M), the highest ethanol oxidation activities were obtained when lead acetate presented in solutions. Fig. 2 showed the static potentiostatic test results of ethanol oxidation on Pt/C electrodes in (1 M NaOH + 1 M ethanol)

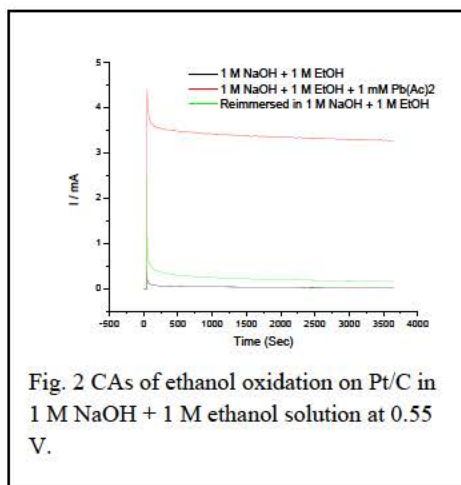


Fig. 2 CAs of ethanol oxidation on Pt/C in 1 M NaOH + 1 M ethanol solution at 0.55 V.

solution at 0.55 V. While the  $\text{Pb}_{\text{UPD}}$ -Pt electrode

showed some extent of promotion for ethanol oxidation, as shown in green lines in Fig.1 and 2, the promotion effect was much smaller than solution phase of  $\text{Pb}(\text{Ac})_2$ . If we can attributed the promotion effect of the  $\text{Pb}_{\text{UPD}}$ -Pt electrode to the bi-functional mechanism as suggested in numerous literature reported earlier, the different ethanol oxidation behavior between the solution Pb species and the deposited Pb species (the

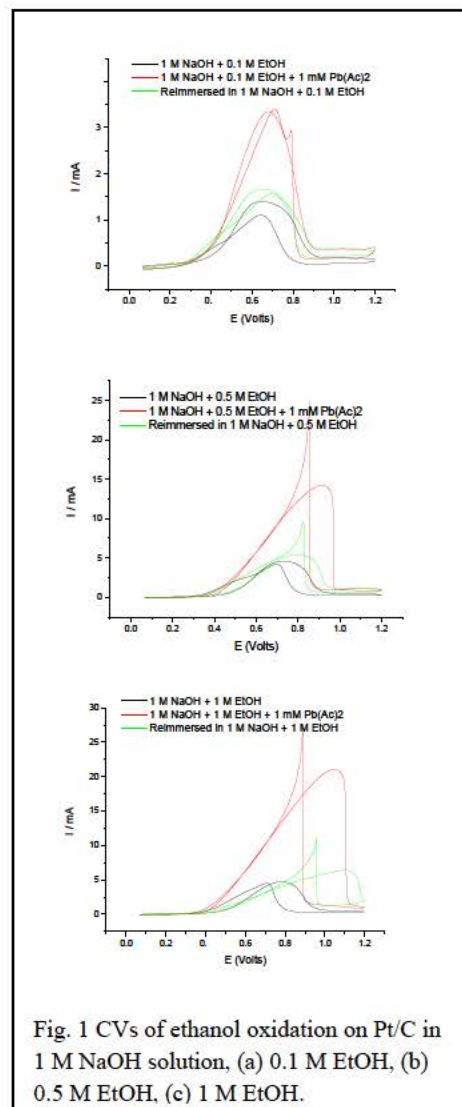
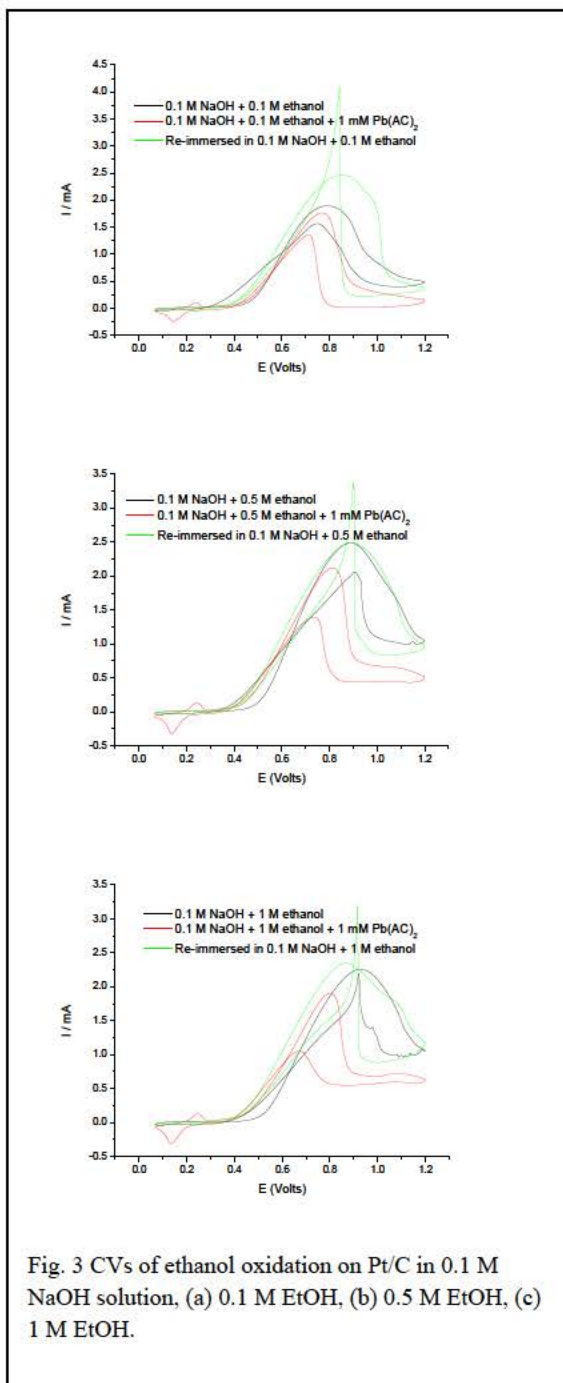


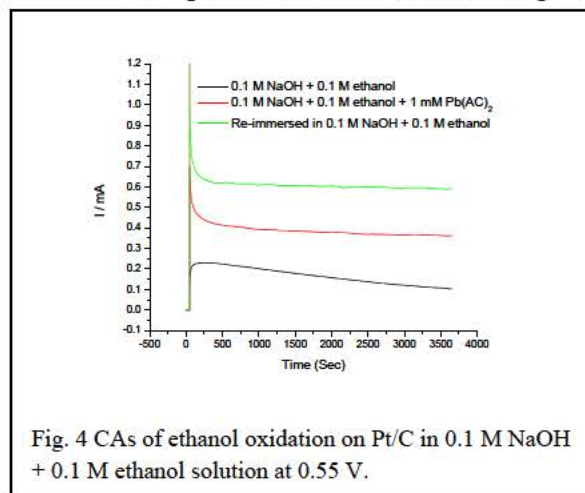
Fig. 1 CVs of ethanol oxidation on Pt/C in 1 M NaOH solution, (a) 0.1 M EtOH, (b) 0.5 M EtOH, (c) 1 M EtOH.

Pb<sub>UPD</sub>-Pt electrode) indicated that the promotion effect of the solution Pb species could not solely be attributed to the bi-functional mechanism. When lead acetate presented in solution, some of the Pb species was likely deposited on the Pt electrode functioned like the Pb<sub>UPD</sub>-Pt electrode, while the rest of Pb species in solution could play a role to promote the ethanol oxidation.



showed the static potentiostatic results of ethanol oxidation in (0.1 M NaOH + 0.1 M) ethanol solutions at 0.55 V. Clearly, the deposited Pb species (the Pb<sub>UPD</sub>-Pt electrode) showed the highest steady current, consistent with the CV results. When the NaOH concentration was lower,

To further understand the ethanol oxidation mechanism in alkaline media, the ethanol oxidation behaviors on Pt/C in 0.1 M NaOH solutions with and without Pb(Ac)<sub>2</sub> additives were further tested. Fig. 3 showed the CVs of ethanol oxidation in 0.1 M NaOH solutions. It can be seen that both the solution Pb species and the deposited Pb species promoted the ethanol oxidation on Pt electrode. However, different ethanol oxidation behaviors from those in 1 M NaOH solution, the deposited Pb species (the Pb<sub>UPD</sub>-Pt electrode) showed the highest ethanol oxidation activity (green lines). Furthermore, comparable peak current were observed in 0.1 M NaOH solutions no matter if there was Pb species present in solution or/and electrode or not, which is opposite from the observations that much higher peak currents were obtained in (1 M NaOH + 1 M ethanol + 1 mM Pb(Ac)<sub>2</sub>) solutions in comparison to those in (1 M NaOH + 1 M) ethanol solutions (Fig.1). This may indicate that when the NaOH solution was diluted, there was not promotion effect of solution Pb species on EOR kinetics. Fig. 4



both the solution Pb species and the deposited Pb species play similar roles, namely, the bi-functional mechanism. Unlike the optimized UPD Pb-Pt electrode, the excessive of the Pb species in solution may lower the Pt active surface, thus reduced the ethanol oxidation activity.

It is likely that the NaOH concentration influences the precursor for ethanol oxidation. In the diluted NaOH solutions, the precursor of ethanol oxidation may most likely to be ethanol molecule, while in the concentrated NaOH solutions the precursor of ethanol may be ethoxy anion. The adsorption of ethoxy anion would be much easier than the ethanol molecule since no C-H bond break is needed. In the diluted NaOH solutions, the dissociated ethanol adsorption may become a main limitation step, therefore, the difference between the promotion effect of solution Pb species and deposited Pb species was smaller. Another hypothesis is that the concentration of NaOH solutions influenced the reactive intermediates. It is known that acetaldehyde could go through the keto-enol tautomerism in alkaline media. When pH of solution is comparable to the  $pK_a$  of the  $\alpha$ -H, the amount of enolate anion is considerable, and the aldol reaction takes place.

To verify our hypothesis, we deliberately investigated the effect of acetaldehyde on ethanol oxidation kinetics on the Pt/C electrodes. It was reported that acetaldehyde is the reactive intermediates of ethanol oxidation in alkaline media. Fig. 5 showed the CVs of acetaldehyde oxidation on Pt/C in (1 M NaOH + 0.01 M)  $\text{CH}_3\text{CHO}$  solution. The first cycle of CV showed a significant oxidation peak located around 0.7 V. The peak current decreased significantly with successive cycles. After 30 cycles, the corresponding peak almost disappeared. At the same time, it was found that the solution gradually turned to yellow when acetaldehyde added to the NaOH solution, as shown in Fig. 6. It is well known that the acetaldehyde is prone to polymerization or/and go through the aldol reaction in strong alkaline media. It means that the reactive acetaldehyde may be consumed by homogeneous chemical reaction in alkaline media. Moreover, the by-product may also be induced extra poison species on the Pt electrode.

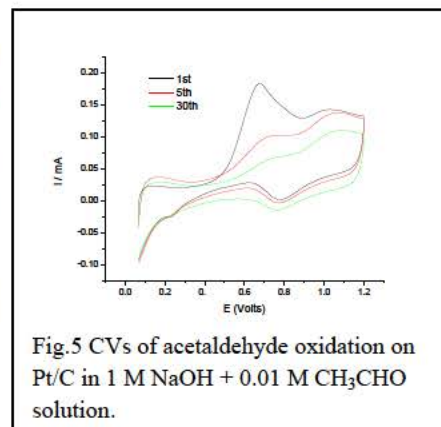


Fig. 7 showed the CVs of Pt thin-film electrode before and after acetaldehyde oxidation in 1 M NaOH solution. Before the acetaldehyde oxidation test, the Pt thin-film electrode showed a typical CV shape in NaOH solution, in which the hydrogen region, double layer region and the oxygen region was clearly separated. After the acetaldehyde oxidation test, the hydrogen region was greatly blocked. Moreover, significant oxidation current was found in higher potential region. Similar results also found on the Pt thin-film electrode which was immersed in aged 0.01 M  $\text{CH}_3\text{CHO}$  + 1M NaOH solution in advance. Clearly, the by-product of the acetaldehyde side reaction in alkaline media poisoned the Pt thin-film electrode, which supported our hypothesis. It was demonstrated that the polymerization or/and aldol reaction by-product of acetaldehyde has poisoning effect of the Pt electrode in alkaline solutions, but not in acid solutions.



Fig. 6. Images of 0.01 M acetaldehyde + 1 M NaOH solution (a) before acetaldehyde added; (b) 2 min, (c) 10 min, (d) 0.5 h, (e) 1 h, and (f) 2h after acetaldehyde added.

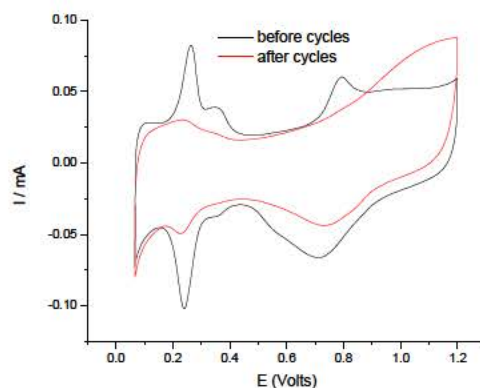


Fig. 7 CVs of Pt thin-film electrode before and after acetaldehyde oxidation in 1 M NaOH solution

In contrast, in acid solutions, the acetaldehyde showed no poison effect on Pt/C. Fig. 8 showed the CVs of acetaldehyde oxidation in (0.5 M  $\text{H}_2\text{SO}_4$  + 0.01 M  $\text{CH}_3\text{CHO}$ ) solution. The first cycle of CV showed a significant oxidation peak located around 0.83 V. After ca. 1.0 V, the oxidation current resurged. The peak current showed very limited decrease with successive cycles. After 30 cycles, the corresponding peak decreased in a much smaller degree, mostly due to the growing of Pt particles by dynamic potential cycles. At the same time, it was found that the solution keep colorless and clear. After the CV cycles in (0.5 M  $\text{H}_2\text{SO}_4$  + 0.01 M  $\text{CH}_3\text{CHO}$ ) solution, the Pt thin-film electrode was washed with deionized water and re-tested in 0.5 M  $\text{H}_2\text{SO}_4$  solution. As shown in Fig. 9, the electrode showed no change in CV shape but a slightly lower current after the CV cycles in (0.5 M  $\text{H}_2\text{SO}_4$  + 0.01 M  $\text{CH}_3\text{CHO}$ ) solution, indicating the growing of the Pt particles.

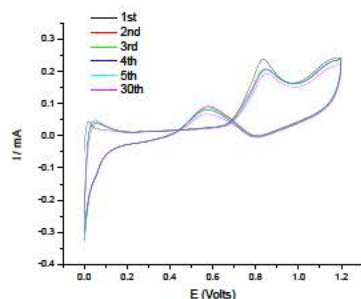


Fig. 8 CVs of acetaldehyde oxidation on Pt/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M CH<sub>3</sub>CHO solution.

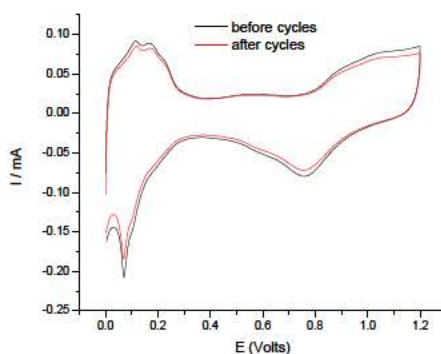


Fig. 9 CVs of Pt thin-film electrode before and after acetaldehyde oxidation in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

Fig. 10 showed the CVs of acetaldehyde oxidation on Pt/C electrodes in (1 M NaOH + 0.01 M CH<sub>3</sub>CHO + 1 mM Pb(Ac)<sub>2</sub>) solution. The first cycle of CV showed three peaks in the positive scan. The first peak located ca. 0.2 V was related to the redox of solution Pb species on the Pt/C in alkaline solution, which could also be found in the cases of ethanol oxidation as shown in Fig.1 and Fig. 3 above. The other two peaks located at ca. 0.45 V and 0.88 V were related to the oxidation of acetaldehyde in the presence of solution Pb species. The acetaldehyde oxidation current decreased with the successive cycles but the CV shapes did not changed. Moreover, compared with that showed in the Fig. 5, the presence of the solution Pb species slowed down the degree of current decay. Fig. 11 compared the first CV cycle of acetaldehyde oxidation in presence/absence of solution Pb species. Clearly, the presence of solution Pb species promoted the acetaldehyde oxidation significantly. The dramatically shift of oxidation peak indicated that some strong interaction between the acetaldehyde and the solution Pb species happened.

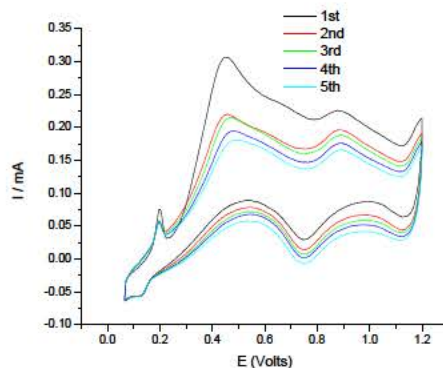


Fig. 10. CVs of acetaldehyde oxidation on Pt/C in 1 M NaOH + 0.01 M CH<sub>3</sub>CHO + 1 mM Pb(Ac)<sub>2</sub> solution

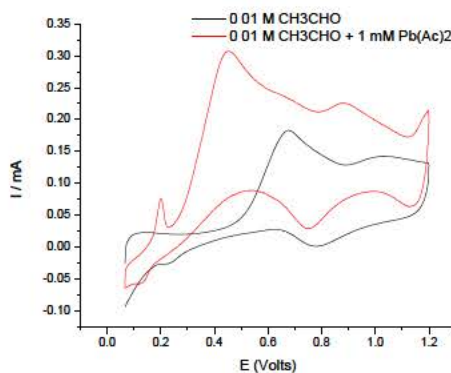


Fig. 11. CVs of acetaldehyde oxidation on Pt/C in the presence/absence of Pb(Ac)<sub>2</sub> species in 1 M NaOH solution

To further confirm the poison effect of acetaldehyde derives on Pt/C electrodes in alkaline media, Fig. 12 compared the CV of ethanol oxidation on Pt/C in 1 M NaOH solution in the presence/absence of acetaldehyde and solution Pb species. As shown in Fig. 12, after acetaldehyde added to the test solution, the ethanol oxidation depressed significantly; when further added lead acetate to the solution, the ethanol oxidation current increased significantly, even larger than the original ethanol oxidation current gotten in the (1 M NaOH + 1 M ethanol) solution. However, this current is still smaller than the ethanol oxidation current obtained in the (1 M NaOH + 1 M ethanol + 1 mM Pb(Ac)<sub>2</sub>) solution. It was also noticed that when Pb(Ac)<sub>2</sub> presented in the solution, the CV shapes almost the same although the current was different, indicating the solution Pb species functioned the same whether or not the acetaldehyde been added to the solution. The potentiostatic test results of ethanol oxidation in Fig.13 showed similar trend.

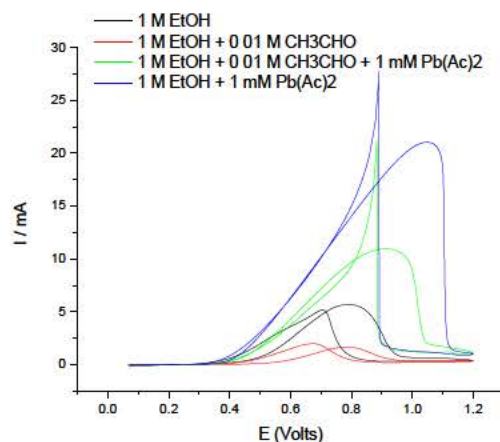


Fig. 12. CVs of ethanol oxidation on Pt/C in 1 M NaOH solution.

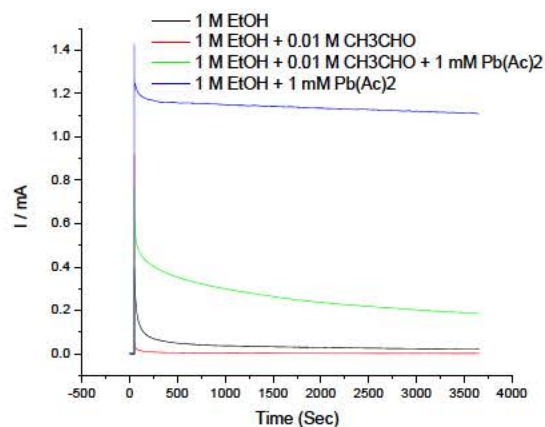


Fig. 13. CAs of ethanol oxidation on Pt/C in 1 M NaOH solution at 0.45 V.

Different concentrations of acetaldehyde were introduced into the (1M ethanol and 1M NaOH) test solution. As shown in Fig. 14, the ethanol oxidation current decreased with the increasing of acetaldehyde introduced. Moreover, it was noticed that the  $I_f/I_b$  ratio ( $I_f$ , forward peak current;  $I_b$ , backward peak current) decreased with the increasing of acetaldehyde, indicating that more severe poisoning happened on the Pt/C catalyst. Similar trends were also found in the CA tests, as shown in Fig. 15. Summarized the data showed above, it could be concluded that the by-products of the homogeneous reaction of the acetaldehyde in alkaline media is prone to poison the Pt electrode.

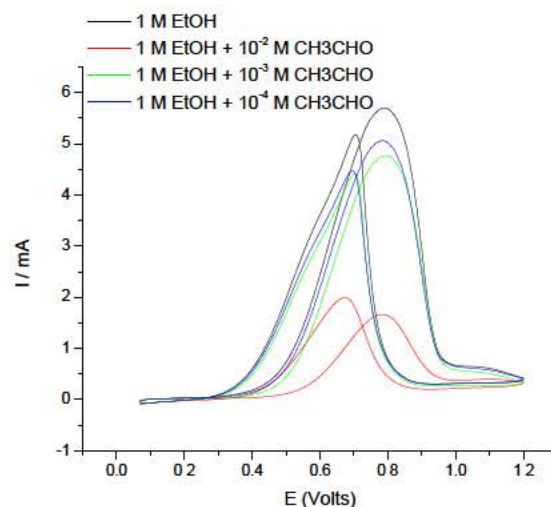


Fig. 14. CVs of ethanol oxidation on Pt/C in 1 M NaOH solution.

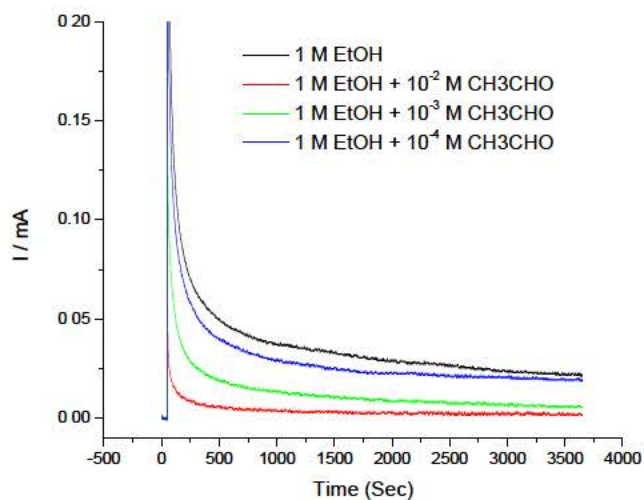


Fig. 15. CAS of ethanol oxidation on Pt/C in 1 M NaOH solution at 0.45 V.

We also tested the ethanol oxidation behaviors on Pd/C in the presence/absence of solution Pb species in 1 M NaOH solution. However, different from the ethanol oxidation behavior on Pt/C, the present of Pb species poisoned the Pd/C significantly. As shown in Fig. 16, the ethanol oxidation current was largely depressed, indicating that the Pd surface were largely covered by the Pb species. Since the active sites for ethanol adsorption were decreased, it is understandable that the ethanol oxidation activity was decreased significantly. Fig. 17 showed the CVs of acetaldehyde oxidation on Pd/C in 1 M NaOH + 0.01 M CH<sub>3</sub>CHO solution. The first cycle of CV showed two sharp peaks located around 0.68 V and 0.82 V. The peak current decreased significantly with successive cycles. At the 5<sup>th</sup> cycle, those two peaks almost disappeared. After the CV cycles in 1 M NaOH + 0.01 M CH<sub>3</sub>CHO solution, the Pd thin-film electrode was washed with deionized water and re-tested in 1 M NaOH solution. As shown in Fig. 18, the electrode showed almost no change in CV shape but a slightly higher current at higher potentials.

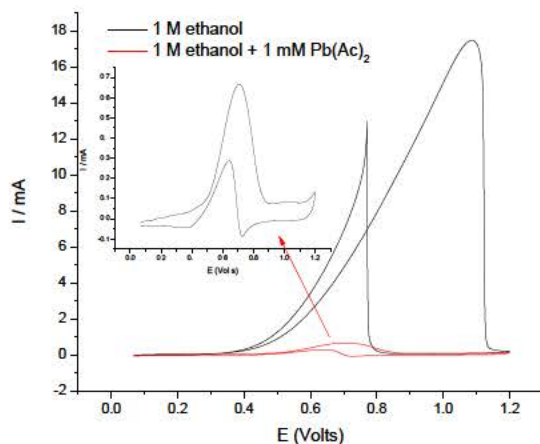


Fig. 16. CVs of ethanol oxidation on Pd/C in 1 M NaOH solution.

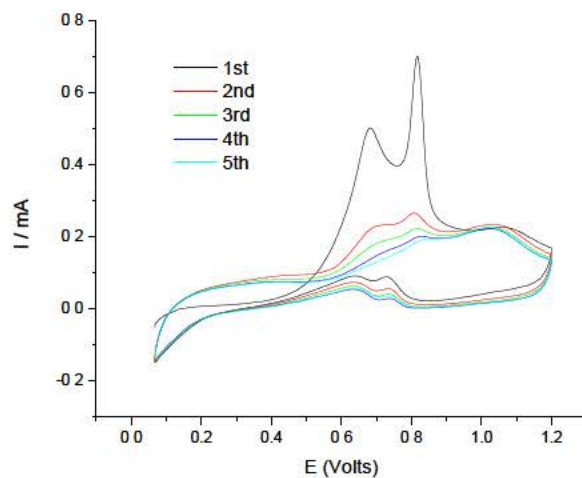


Fig. 17. CVs of acetaldehyde oxidation on Pd/C in 1 M NaOH + 0.01 M CH<sub>3</sub>CHO solution.

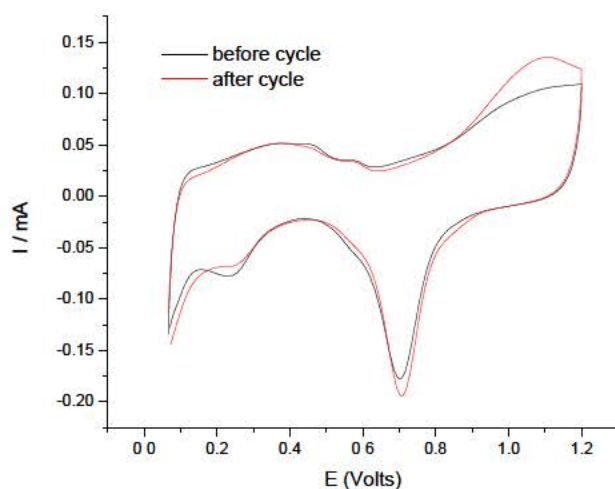


Fig. 18. CVs of Pd thin-film electrode before and after acetaldehyde oxidation in 1 M NaOH solution.

Fig. 19 showed the CVs of ethanol oxidation on Pd/C in 1 M NaOH + 1 M ethanol + 0.01 M acetaldehyde solution. As shown in Fig. 19, the Pd/C showed similar CV shapes for ethanol oxidation before and after acetaldehyde been introduced into the test solution. After introduced the acetaldehyde into the test solution, the first cycle CV showed much lower current for ethanol oxidation. However, in the successive cycles, the ethanol oxidation current first increased and then decreased. Compared to the Pt/C, the decreasing of the ethanol oxidation current was much smaller. This result coincides with above acetaldehyde oxidation result, indicating that smaller poisoning effect of acetaldehyde derives in alkaline media was obtained on the Pd/C electrode.

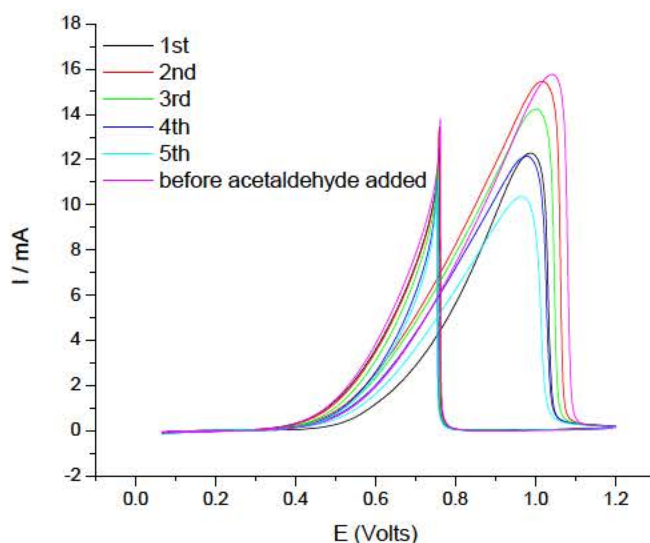


Fig. 19 CVs of ethanol oxidation on Pd/C in 1 M NaOH + 1 M ethanol + 0.01 M acetaldehyde solution.

## 2.2. Effects of Solid State Pb in Pt/C or Pd/C or Rh/C for the EORs

Fig. 20 showed the CVs of different composition PtPb/C catalysts in 1 M NaOH blank solution and 1 M NaOH + 1 M ethanol solution, respectively. Clearly, all the hydrogen regions of the PtPb/C catalysts were blocked due to the Pb co-deposition, as shown in Fig. 20a. Furthermore, a small shoulder peak located around 0.7 V was observed on all the PtPb/C catalysts. Compared with the Pt/C catalyst, all the PtPb/C catalysts showed a much more positive oxidation peak. At the potential higher than 1.1 V, the oxidation current resurged on the PtPb/C catalysts. Among various PtPb/C catalysts, the PtPb/C showed the biggest electrochemical surface area (ECSA) based on the calculation of integral coulomb of oxygen region, while the Pt<sub>3</sub>Pb/C showed the smallest ECSA. It is known that the PtPb can form different alloy phase such as PtPb<sub>4</sub>, PtPb and Pt<sub>3</sub>Pb at room temperature according to the phase diagram. This indicated that different PtPb alloy may possess different activity for ethanol oxidation, which was affirmed by the CV tests shown in Fig. 20b. The PtPb/C showed the highest ethanol oxidation activity in the CV tests. All the PtPb/C catalysts showed higher activity for ethanol oxidation than the Pt/C. Fig. 21 showed the static currents of ethanol oxidation on different composition PtPb/C

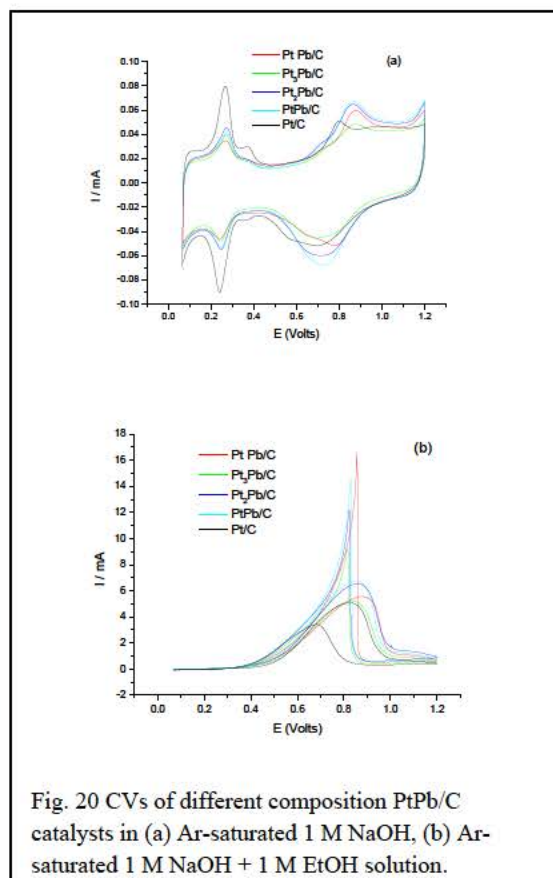


Fig. 20 CVs of different composition PtPb/C catalysts in (a) Ar-saturated 1 M NaOH, (b) Ar-saturated 1 M NaOH + 1 M EtOH solution.

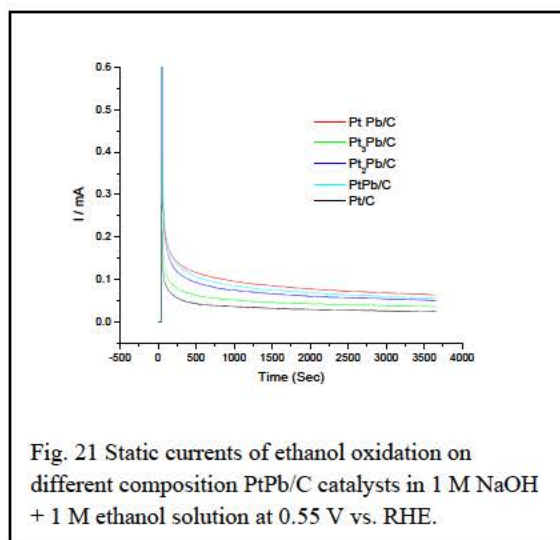


Fig. 21 Static currents of ethanol oxidation on different composition PtPb/C catalysts in 1 M NaOH + 1 M ethanol solution at 0.55 V vs. RHE.

Fig. 21 showed the static currents of ethanol oxidation on different composition PtPb/C catalysts in 1 M NaOH + 1 M ethanol solution at 0.55 V. However, unlike the CV results, the Pt<sub>4</sub>Pb/C catalyst showed the highest activity for the ethanol oxidation in the potentiostatic test. In both the CV and potentiostatic tests, the Pt<sub>3</sub>Pb/C showed the lowest activity among the PtPb catalysts. This indicated that the PtPb alloy structure influence the ethanol oxidation behavior significantly.

From the results above, clearly, the Pb species promotes the ethanol oxidation on Pt/C catalyst. Pb UPD catalysts were also prepared to compare the promotion effect for ethanol oxidation with the Pb co-deposition catalysts. Fig. 22 shows the CVs of Pt/C and Pt-Pb<sub>upd</sub>/C in 1 M NaOH blank solution and 1 M NaOH + 1 M ethanol solution, respectively. Clearly, the UPD Pb also promoted the ethanol oxidation on Pt/C catalyst. Fig. 23 shows the static currents of ethanol oxidation on Pt/C and Pt-Pb<sub>upd</sub>/C catalysts in 1 M

NaOH + 1 M ethanol solution at 0.55 V. The ethanol oxidation activity of the Pt-Pb/C catalyst was higher than that of PtPb/C co-deposition catalyst (Fig. 21), which is more significant than the CV tests.

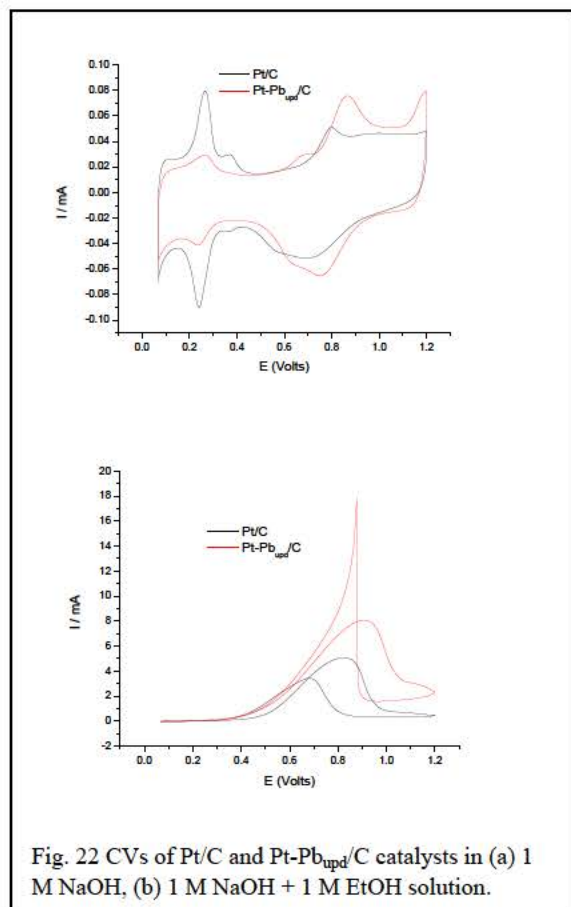


Fig. 22 CVs of Pt/C and Pt-Pb<sub>upd</sub>/C catalysts in (a) 1 M NaOH, (b) 1 M NaOH + 1 M EtOH solution.

The effect of the Pb UPD on ethanol oxidation on Pd/C and Rh/C catalysts were also investigated. Fig. 24 showed the CVs of Pd/C and Pd-Pb<sub>upd</sub>/C catalysts in 1 M NaOH blank solution and 1 M NaOH + 1 M ethanol solution, respectively. As shown in Fig. 24a, the UPD of Pb on Pd/C totally blocked the hydrogen absorption and adsorption. Also, the Pd-Pb<sub>upd</sub>/C catalyst showed a sharp reduction peak at the reverse scan, indicating that strongly interaction existed between the Pd and Pb species. The Pd-Pb<sub>upd</sub>/C catalyst showed higher activity in the lower potential range and lower activity in the higher potential range for ethanol oxidation in the CV tests. Fig. 25 shows the static currents of ethanol oxidation on Pd/C and Pd-Pb<sub>upd</sub>/C catalysts in 1 M NaOH + 1 M ethanol solution. At lower potentials, the Pd-Pb<sub>upd</sub>/C showed slightly higher activity for

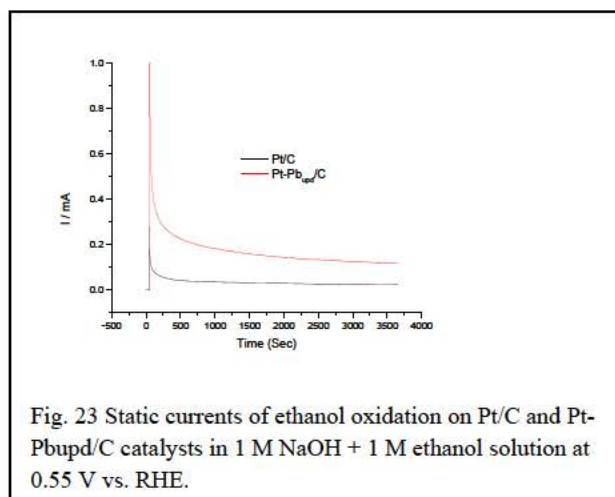


Fig. 23 Static currents of ethanol oxidation on Pt/C and Pt-Pb<sub>upd</sub>/C catalysts in 1 M NaOH + 1 M ethanol solution at 0.55 V vs. RHE.

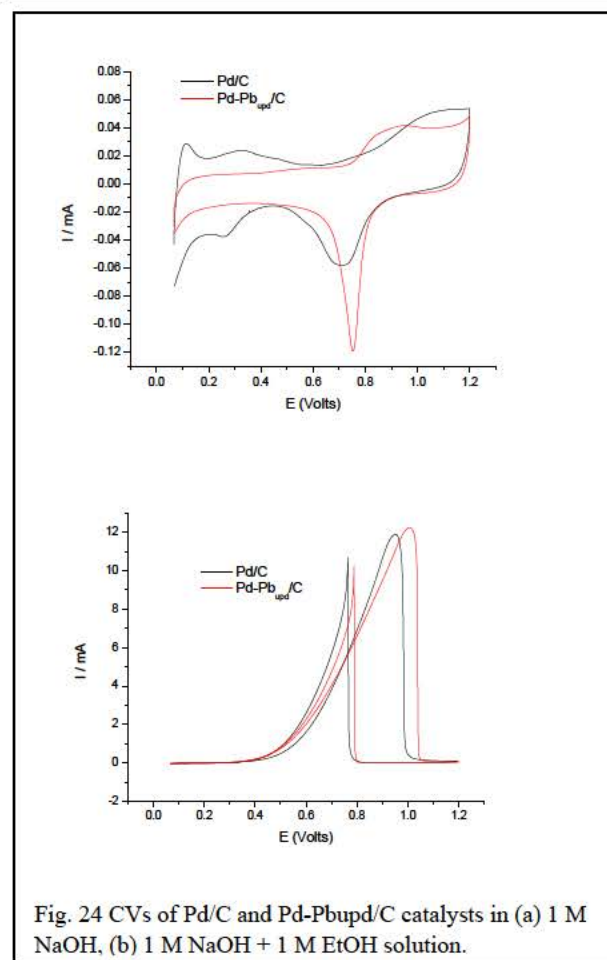
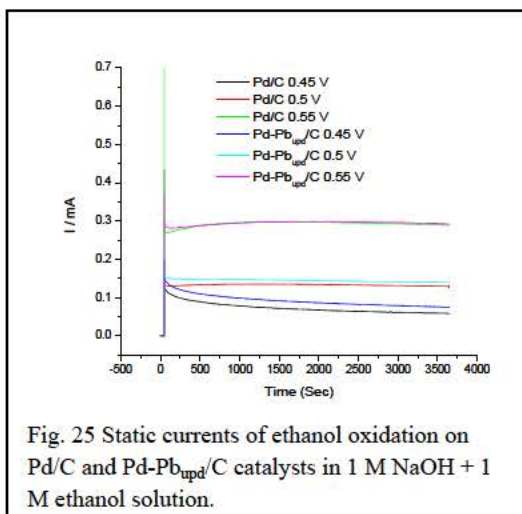
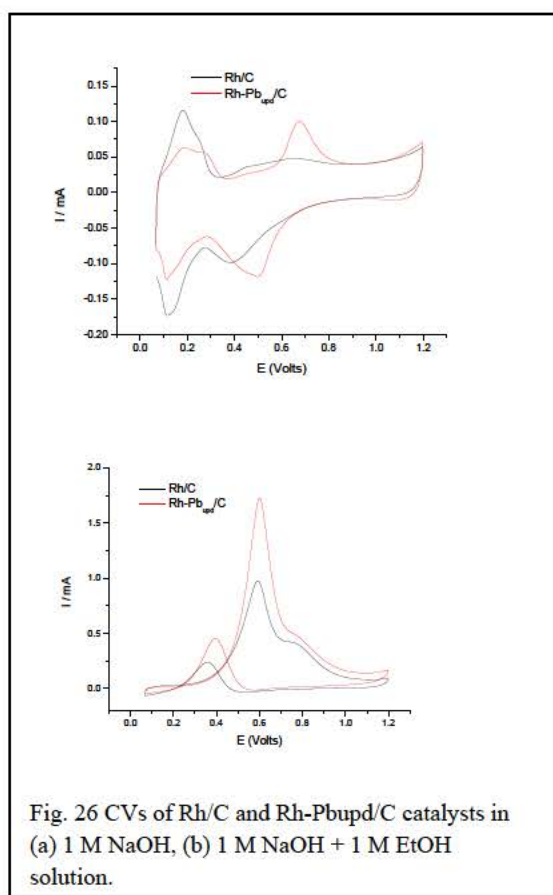


Fig. 24 CVs of Pd/C and Pd-Pb<sub>upd</sub>/C catalysts in (a) 1 M NaOH, (b) 1 M NaOH + 1 M EtOH solution.

1 M NaOH + 1 M ethanol solution. At lower potentials, the Pd-Pb<sub>upd</sub>/C showed slightly higher activity for

ethanol oxidation than the Pd/C. At 0.55 V, both catalysts showed similar activities. Clearly, the promotion effect of Pb UPD on ethanol oxidation on Pd/C was quite different from that on Pt/C.

Fig. 26 shows the CVs of Rh/C and Rh-Pb<sub>upd</sub>/C catalysts in 1 M NaOH blank solution and 1 M NaOH + 1 M ethanol solution, respectively. The CV of Rh/C in blank solution showed a pair of peaks located at potentials lower than 0.3 V, which is ascribed to the hydrogen adsorption/desorption. The Rh/C is oxidized immediately at potential positive than 0.3 V, indicating the Rh/C is much prone to oxidation than the Pt/C. After Pb UPD, the hydrogen region was blocked and a new peak located around 0.7 V appeared in the positive scan. This peak came from the oxidation of surface Pb species. After Pb UPD, the ethanol oxidation current enhanced. In addition, the Rh-Pb<sub>upd</sub>/C showed similar CV profile for ethanol oxidation. Fig. 27 showed the CAs of ethanol oxidation on Rh/C and Rh-Pb<sub>upd</sub>/C catalysts in 1 M NaOH + 1 M ethanol solution. Interestingly, the ethanol oxidation current did not increased proportionally with potential on Rh/C catalyst. At 0.55 V, the ethanol oxidation current was even lower than that at 0.5 V, indicating complicated ethanol oxidation behavior on the Rh/C catalyst. The Rh-Pb<sub>upd</sub>/C catalyst showed much higher ethanol oxidation current than Rh/C in the potentiostatic tests.



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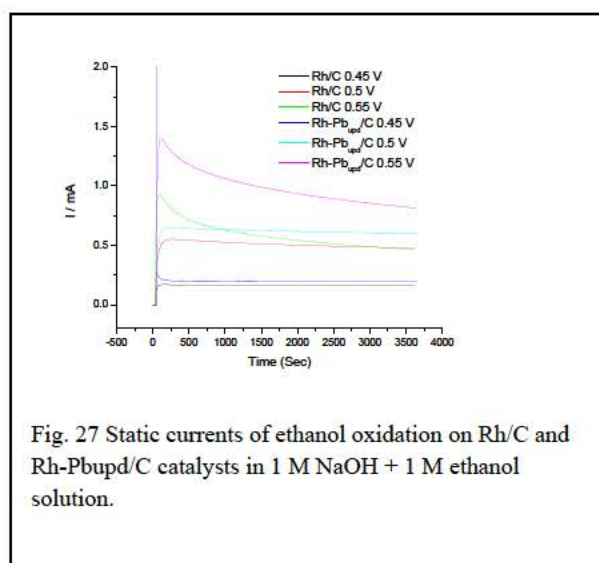
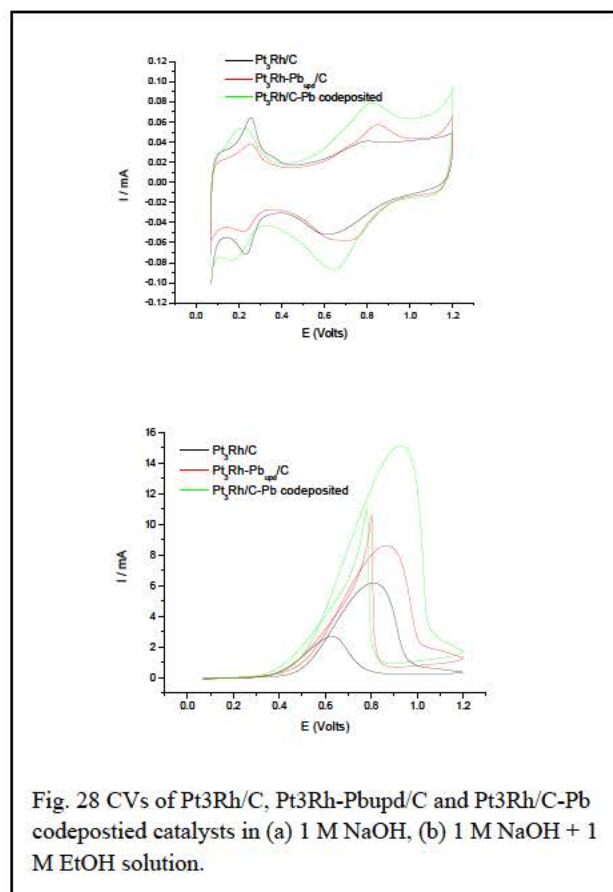
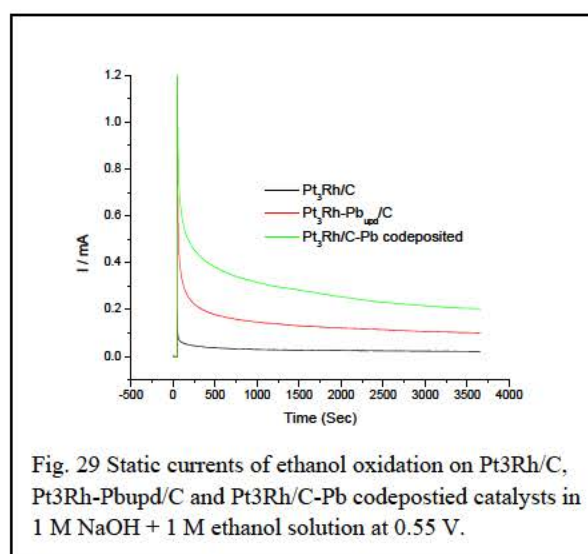


Fig. 28 shows the CVs of Pt<sub>3</sub>Rh/C, Pt<sub>3</sub>Rh-Pb<sub>upd</sub>/C and Pt<sub>3</sub>Rh/C-Pb codeposited catalysts in 1 M NaOH blank solution and 1 M NaOH + 1 M ethanol solution, respectively. Similar with the case of Pb UPD on the Pt/C catalyst, the Pt<sub>3</sub>Rh-Pb<sub>upd</sub>/C catalyst showed blocked hydrogen region and an additional shoulder peak in the CV after Pb UPD on the Pt<sub>3</sub>Rh/C catalyst. The Pt<sub>3</sub>Rh/C-Pb codeposited catalyst, however, showed much larger ECSA based on the calculation of oxygen region, indicating more Pb species present on the catalyst surface. The Pb UPD on the Pt<sub>3</sub>Rh/C catalyst enhanced ethanol oxidation significantly. Among the catalysts, the Pt<sub>3</sub>Rh/C-Pb codeposited catalyst showed the highest activity for ethanol oxidation. Fig. 29 shows the static currents of ethanol oxidation on Pt<sub>3</sub>Rh/C, Pt<sub>3</sub>Rh-Pb<sub>upd</sub>/C and Pt<sub>3</sub>Rh/C-Pb codeposited catalysts in 1 M NaOH + 1 M ethanol solution at 0.55 V.



Pt<sub>3</sub>Rh/C-Pb codeposited catalysts in 1 M NaOH + 1 M ethanol solution at 0.55 V. Consistent with the CV results, *the Pt<sub>3</sub>Rh/C-Pb codeposited catalyst shows the highest activity towards the ethanol oxidation reactions*. The performance of these catalysts in direct ethanol fuel cells needs to be validated in practical direct ethanol fuel cells (DEFCs).



### 3. Conclusions:

- a. The EOR kinetics on various Pt/C, Pd/C, Rh/C and their binary and ternary catalysts with and without Pb additives have been studied by using potentiodynamic and potentiostatic measurements in NaOH solutions containing ethanol. Among the tested catalysts, the Rh-Pb<sub>upd</sub> catalysts showed the best EOR activity, which will be further tested in DEFCs. Experimental methods for monitoring EOR products, including acetaldehyde, acetate and carbonate (CO<sub>2</sub> in NaOH solutions), were also investigated. A quantitative method to detect acetaldehyde has been successfully established, while analyzing acetate and carbonate needs further developments.

- b. The solution Pb species enhanced EOR kinetics on Pt/C, which confirms the results reported by Mukerjee, et al [1]. However, it is debatable if the Pb addition changes the functionality of the Pt catalyst surface for efficient promotion of CO oxidation or prevents aldol reaction and polymerization reaction of the EOR reaction intermediates (acetaldehyde) in alkaline media.
- c. The deposited Pb species on Pt/C catalysts showed limited promotion effect of EORs in concentrated NaOH solutions ( $> 1M$ ), but had some promotion effects in diluted NaOH solutions (e.g. 0.1M).
- d. It was demonstrated that the polymerization or/and aldol reaction by-product of acetaldehyde has poisoning effect for the Pt electrode in alkaline solutions, but not in acid solutions. By adding  $Pb(Ac)_2$  species in 1M NaOH solutions, acetaldehyde poisoning effects on Pt/C electrodes for the EOR kinetics were hindered. However, adding  $Pb(Ac)_2$  species in 1M NaOH solutions did not promote the EOR on Pd/C catalysts. In contrast, the EOR kinetics were reduced significantly on Pd/C electrodes in  $Pb(Ac)_2$  containing 1M ethanol and 1M NaOH solutions.
- e. The Pb species promoted the ethanol oxidation on alloy catalyst in general. *Multifunctional catalyst design promotes the ethanol oxidation significantly.* Gas chromatography (GC) is valid for acetaldehyde analysis, but unsuccessful for acetate analysis.

#### REFERENCES.

1. Q. He, B. Shyam, K. Macounová, P. Krtil, D. Ramaker and S. Mukerjee, ‘Dramatically Enhanced Cleavage of the C–C Bond Using an Electrocatalytically Coupled Reaction’, J. Am. Chem. Soc. 2012, 134, 8655–8661.