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Redefining Charge-Transfer Interfaces for Next-Generation Electrochemical Power Sources

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REDEFINING CHARGE-TRANSFER INTERFACES FOR NEXT-GENERATION ELECTROCHEMICAL POWER SOURCES

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ABSTRACT

The ability to realize next-generation electrochemical power sources with unprecedented energy and power capability requires fundamental insights into the physicochemical processes at nanoscale electrode interfaces. The electrodes in practical power sources comprise complex 3D multifunctional structures that are challenging to characterize and model. The key objective of this research program was to create and analyze well-defined two-dimensional (2D) planar electrodes that effectively mimic the functionality of their 3D counterparts, but in forms that are amenable to a range of surface-sensitive spectroscopy, microscopy, and electroanalytical tools, coupled to new computational understanding of these simplified interfaces. Pyrolytic carbon (pyC) films prepared by chemical vapor deposition served as a planar stand-in for technologically relevant disordered carbons (from powder blacks to advanced 3D carbon architectures). Heteroatom doping of these pyC substrates with elements such as sulfur provided a means to tune their electronic and electrochemical properties, as well as enhancing their adsorptive characteristics for electrocatalytic functionalities such as precious-metal nanoparticles. Nanoscale manganese oxides at pyC substrates were investigated for mechanistic insights into key energy-relevant electrochemical reactions including pseudocapacitive charge-storage, zinc-ion charge storage, and electrocatalytic oxygen reduction. Ruthenium oxide nanoparticulate coatings were used to enhance electron-transfer kinetics at pyC, and also demonstrated effective oxygen-evolution activity and stability when applied to pyrolytic carbon surfaces. We have developed a perturbation theory to model electron transfer in a degenerate system. Using this perturbation theory, we showed that the application of a small electric field to a degenerate system causes the Fermi-level electron occupation numbers to change, shielding the effects of the external potential and preserving the degeneracy. We also used a phenomenological Heisenberg Hamiltonian in conjunction with density functional theory to model high-spin transition metal-containing systems. Lessons learned from fundamental experimental studies and computational modeling can ultimately be transitioned to a redesign/reformulation of 3D electrode architectures for increased energy and power delivery.

BACKGROUND

The increasing demand for safe, high-energy density power sources to support a wide range of DoD applications, including portable power for the warfighter and on-board power for unmanned vehicles, highlights a critical need for advanced battery technologies. Energy storage and conversion systems rely on active materials that are incorporated into multiphase, multifunctional, and multidimensional electrode structures. In this complex, heterogeneous heart of a battery or electrochemical capacitor or fuel cell, boundaries and interfaces at the nanoscale govern electrochemical performance at the device level.

An abiding challenge in energy-storage devices is accessing >0.5 electrons per redox center over hundreds of charge/discharge cycles and doing so at rates necessary to sustain on-demand power. Even scaling active materials to the nanometric regime and integrating reactions and current collection in three dimensions (3D), an area pioneered by Code 6171,^{1,2,3,4,5,6,7} has not solved this inability to extract the electron energy inherent in the active materials. A fundamental bottleneck exists — it has become clear that the nature of the interfacial contact between the electron bank (the supporting or contacting current collection surface, usually carbon) and the redox active material (oxide, polymer, sulfide) thwarts the magnitude and rate of charge transfer and thus, device performance.

With current state-of-the-art energy-storage devices leaving power (rate of electron delivery) and energy (capacity) on the table, we posit that the electronic structure, surface functionality, and crystalline orientation of disordered carbon — the electron-conducting substrate — impact electron-transfer rates and charge-storage capacities in the redox-active materials it contacts. To evaluate this hypothesis, we stepped back from 3D architectures to focus on model 2D interfaces in which the substrate properties can be tuned and then analyzed using characterization techniques difficult to apply to nonperiodic ultraporous architected electrodes.

TECHNICAL OBJECTIVE

The principal objectives of this program are to develop, analyze, and electrochemically evaluate model 2D electrodes, primarily based on disordered carbon, whose interfaces mimic those of the complex 3D electrodes used in electrochemical power sources. Pyrolytic-type disordered carbon films (“pyC”) prepared by a chemical vapor-deposition (CVD) protocol initially developed for 3D electrode structures,^{8,9} serve as the 2D platform for most of these investigations.^{10,11} The properties of these pyC substrates are tuned by heteroatom doping (with sulfur for example) in their bulk and by modifying their surfaces with functionalities such as metal nanoparticles, metal oxides, and electroactive polymers. The simplified geometry of these interfaces enable their interrogation by a variety of surface-sensitive spectroscopy and microscopy techniques, while their well-defined electrochemical surface area and lack of porous-electrode complexities enable the quantification of important kinetic parameters for energy-relevant reactions. The findings generated at planar electrodes are compared with those from targeted studies on comparable 3D electrode structures, providing important insights for the optimization of the latter for incorporation into practical electrochemical power sources.

In parallel with these experimental efforts, computational approaches are developed to predict relevant electronic properties at carbon. These theoretical explorations include the application of density-functional theory (DFT) to extend the functionality of conventional Marcus Theory and computing the impact of heteroatom doping on the electronic properties of a model graphene lattice.

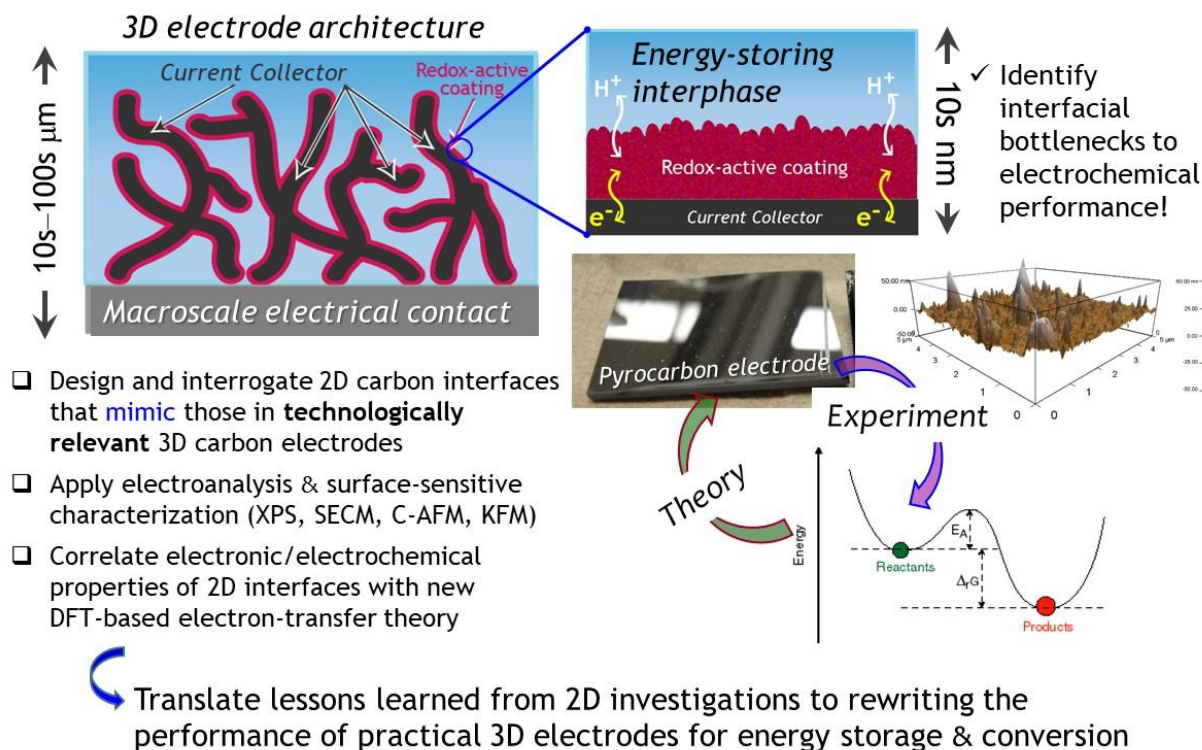


Figure 1 | A schematic depiction of our FY16–FY20 program using experimental and computational approaches to redefine charge-transfer interfaces for next-generation electrochemical power sources.

TECHNICAL APPROACH

At the onset of this FY16–FY20 6.1 program, we proposed to investigate a number of electrochemical and interfacial phenomena at energy-storing surfaces, developing the necessary materials and analytical strategies to ask and answer critical questions of ultimate relevance for electrochemical power sources. As the program evolved through its five-year duration, new opportunities in both the experimental and theory/computation areas were also identified and addressed.

Experimental

Synthesis and fundamental characterization of model 2D carbon substrates with tunable physicochemical properties. Chemical vapor deposition strategies were used to generate planar pyrolytic carbon films at fused-silica substrates. We intentionally chose to investigate disordered

forms of planar carbon because many technologically relevant forms of carbons, such as carbon blacks, are themselves disordered, as opposed to the graphene and related graphitic nanocarbon materials that are often reported in the recent scientific literature, but rarely incorporated into practical batteries and electrochemical capacitors. These pyC substrates served as the base platform for a wide range of electroanalytical investigations, as noted in tasks described below. The native and nanoparticle-modified 2D pyC films were extensively characterized with such surface-sensitive techniques as X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM; including in situ electrochemical AFM), Kelvin-force microscopy (KFM), scanning electrochemical microscopy (SECM), and scanning electron microscopy (SEM).

Electron-transfer kinetics at carbon electrodes. Carbon electrodes are well-known for exhibiting slow electron transfer to solution-based or adsorbed redox entities,¹² a property that may retard the power capabilities of numerous electrochemical systems that include carbon as the primary conductive component. We investigated multiple strategies for tuning the fundamental electron-transfer kinetics at pyC electrodes, including heteroatom doping of the carbon (e.g., with heterocyclic sulfur) and decorating the surface with nanoscale RuO₂ coatings. Activity was assessed using electroanalytical techniques and associated modeling to determine heterogeneous rate constants for solution-based redox probes. Charge-transfer to overlying manganese oxide (MnOx) coatings was also investigated.

Specific adsorption of electrocatalytic metal nanoparticles at carbon surfaces. Adventitious or deliberate functionalities at carbon surfaces affect ~~will impact~~ the adsorption and activity of nanoparticulate metals of interest for electrocatalytic reactions, such as those encountered in fuel cells, electrolyzers, and metal–air batteries. We used sulfur-doped pyC substrates to investigate such effects based on the known affinity of electrocatalytic metals of interest (platinum, gold, and palladium) to form chemical bonds with thiols and thiophene-like moieties. These “pyC~S” electrodes also serve as effective mimics of commercial Vulcan XC-72 carbon black, which contains adventitious sulfur that may impact electrochemical performance. Electrocatalytic metal nanoparticles were applied to pyC substrates using either spontaneous adsorption from pre-made sols or via controlled electrodeposition from ionic precursors.

Electronic and surface-orientation effects as potential bottlenecks for electron transfer at carbon substrates. Advanced electrode architectures commonly comprise a conductive carbon phase integrated with a poorly conducting charge-storage or electrocatalytic functionality, where charge-transfer between said phases may be limited by a mismatch in electronic structure or a lack of specific chemical bonding or affinity. We addressed this question in 3D by assessing nonaqueous charge storage at nanoscale MnOx as the oxide was crystal engineered from a lamellar (ca. six layer) to an upright structure;^{7,13} we addressed this question in 2D using planar pyC substrates that were then coated/modified with such moieties as nanoscale MnOx. The kinetics of electrochemical charge storage at the MnOx coating were assessed as a function of the physicochemical nature of the pyC substrate (and variants thereof). New electroanalytical protocols based on 3D interpretations of impedance data were developed to understand charge-storage kinetics at such interfaces.^{14,15,16}

Spatial distribution and coverage effects at MnOx + carbon electrodes for electrocatalytic reduction of molecular oxygen. Alkaline metal–air batteries commonly use an air-breathing cathode comprising carbon and MnOx powders in an ad hoc powder–composite construction. Carbon is a modest catalyst for the oxygen-reduction reaction (ORR) in alkaline media, so an open question is whether carbon serves as more than a current-collecting electron bank.¹⁷ In order to deconvolve the respective roles of carbon and MnOx constituents for the oxygen-reduction reaction (ORR), we used electrodeposition to controllably apply different loadings of nanoscale MnOx to pyC substrates, as verified by microscopy and spectroscopy methods. The ORR activity of the resulting electrodes was characterized by cyclic voltammetry, in conjunction with electroanalytical modeling to extract pertinent kinetic parameters.

Spatial constraints on the reversibility of “zinc–ion” charge storage reactions. Rechargeable zinc-ion batteries (ZIBs) have emerged in the past few years as a promising new power source with respect to safe operation, low cost, and competitive energy/power performance.¹⁸ Manganese oxides are effective positive-electrode active materials for ZIBs, but the associated charge-storage reactions involve complex precipitation/dissolution processes that determine reversibility and total capacity. We investigated this phenomena by comparing 2D versus 3D “MnOx@carbon” electrode designs as electrochemically characterized in aqueous zinc-ion electrolytes, resulting in important lessons on the role of porosity (or lack thereof).

Computation and Simulation. Early computation efforts focused on using density-functional theory (DFT) approaches to extend classical Marcus Theory description of charge-transfer phenomena. In the latter stages of this project, the effects of sulfur and nitrogen co-dopants in a model graphene lattice on the geometry, band structure, and density of states were computed, while active space SCF calculations are being developed to describe electronic transitions in manganese and other transition metals of relevance for electrochemical reactions.

TECHNICAL ACCOMPLISHMENTS

Pyrolytic carbon films: Synthesis and fundamental properties. Planar carbon films were prepared by adapting a previous NRL-developed protocol that is based on pyrolysis of an aromatic precursor vapor^{8,9} using an inert flat substrate (e.g., commercially sourced fused-silica plates) that can withstand the necessary deposition temperatures. In a typical deposition, pre-cut silica pieces are placed in a tube furnace and heated to 1000 °C, at which point a controlled flow of benzene vapor generated from a saturation flask with argon carrier gas is introduced to the furnace for a set period of time, usually tens of minutes (see Figure 2, left). At such temperatures, benzene rapidly pyrolyzes to form carbon coatings on available surfaces within the hot zone of the furnace.

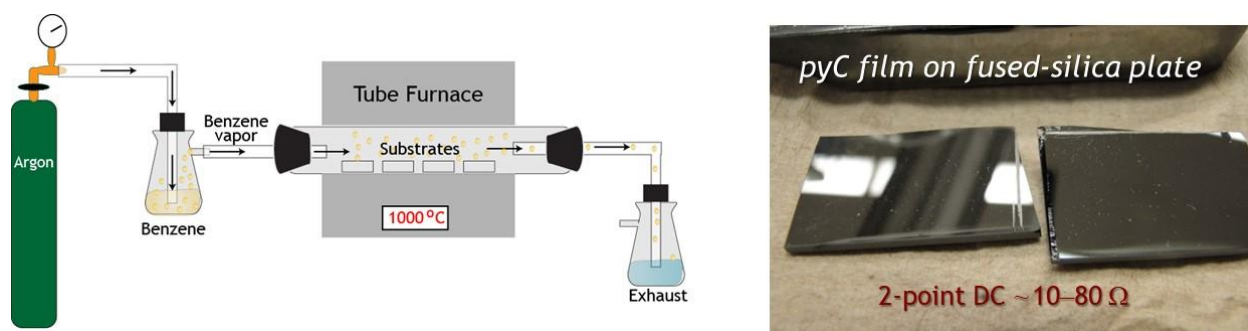


Figure 2 | (Left) Schematic of the set-up for chemical vapor deposition of pyrolytic carbon films; (Right) Mirror finish on ~100 nm-thick pyrolytic carbon films on fused silica substrates (inset: two-terminal resistance of the film).

Post-deposition, the silica substrates are coated by a reflective pyrolytic carbon film (Figure 2, right) that exhibits two-probe resistance on the order of 10–80 Ω , sufficient for their use as working electrodes. The thickness of pyrolytic films prepared by this method (with ~20 min total benzene exposure) is typically 100–200 nm, as measured by profilometry. We use AFM to assess

the nanoscale morphology of the top surfaces of the pyC films, showing that although not atomically flat, these substrates have relatively small/low features at the nanoscale, with root-mean-square (RMS) roughness values of < 3 nm (Figure 3).

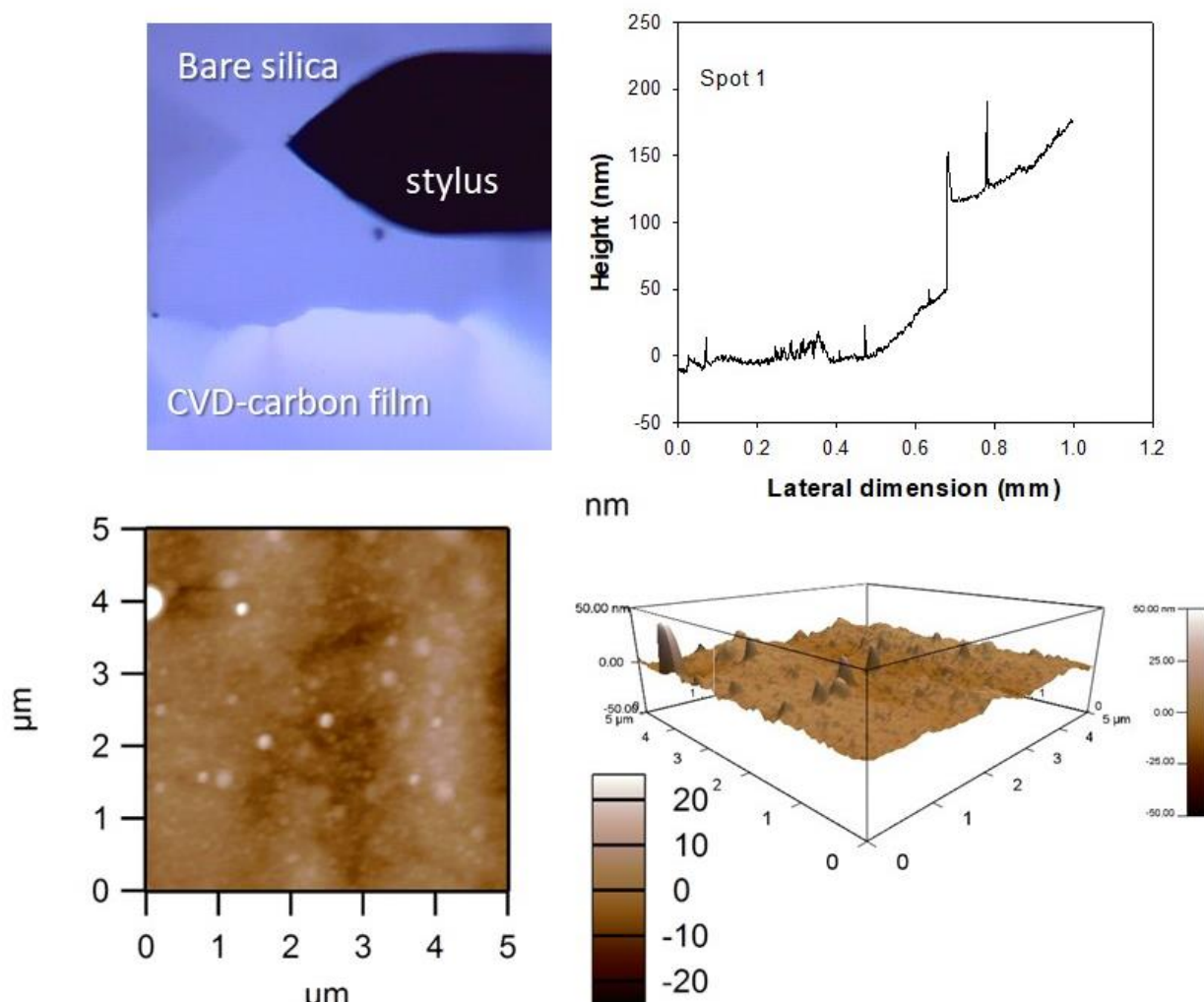


Figure 3 | (Top) Image and line-scan from profilometry measurement of typical pyC film with sections removed via razor blade to expose underlying fused-silica substrate to create a step edge; (Bottom) Atomic-force microscopy images showing the nanoscale texture of pyC films.

Raman scattering spectroscopy reveals that the pyC films exhibit a disordered-carbon solid structure reminiscent of that observed with commercial carbon blacks, where the “G-band” and “D-band” features common to disordered carbons are present in the spectra for both planar pyC and Vulcan XC-72 powder (Figure 4, right). Pyrolytic carbon films prepared from benzene also exhibit relatively low oxygen content (< 3 at.%), as verified by XPS (Figure 4, left). Thus, this form of pyC serves as a “blank slate” on which to build additional functionality. For example,

surface carbon–oxygen functionality can be controllably generated by simple RF-plasma treatment under air or O₂ partial pressures.

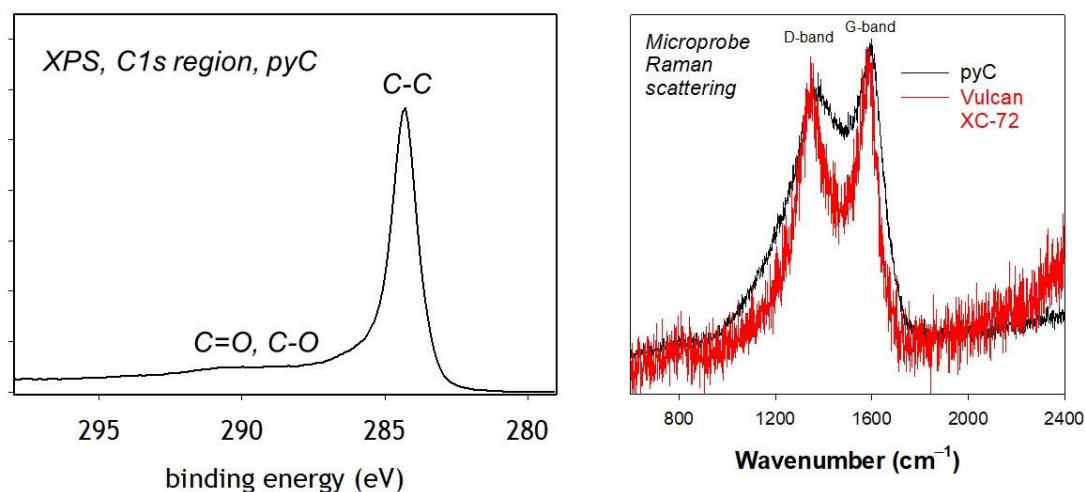


Figure 4 | (Left) High-resolution X-ray photoelectron spectrum of the C 1s region for a pyrolytic carbon film deposited on fused silica plate; (Right) Raman spectrum in the ordered (G) and disordered (D) region measured for a pyrolytic carbon film deposited on fused silica plate (**black**) and Vulcan carbon XC-72 powder (**red**).

Pyrolytic carbon films and variants thereof were routinely incorporated into specially designed electrochemical three-electrode half-cells (Figure 5, left) for assessment by such techniques as cyclic voltammetry and impedance spectroscopy. Early electrochemical tests on planar pyC electrodes used solution-based redox probes such as ferro/ferricyanide (Figure 5, right) to measure active surface area and electron-transfer kinetics parameters.¹⁰ These simple measurements showed that electrochemically measured surface area is consistent with geometric area, confirming that the pyC electrodes act as essentially planar surfaces for reactions of interest. Peak-splitting values from cyclic voltammetry show some electron-transfer kinetic limitations, as expected for carbon electrodes, although the electron-transfer rate constants measured for pristine pyC surfaces are some of the highest reported in the literature for carbon.

Another interesting feature of these pyC substrates is that they are reasonably hydrophilic (contact angle for H₂O at ~60°), unlike many graphene-type carbon substrates, which tend to be hydrophobic unless specially stored or treated. Further, the pyC films retain that H₂O-friendly character even after being stored for prolonged periods under uncontrolled conditions, or even when intentionally exposed to volatile hydrocarbons. As a model electroanalytical carbon

electrode, pyC films are readily fabricated in any laboratory without the handling and pre-treatment issues affecting glassy carbon, HOPG, and graphene.

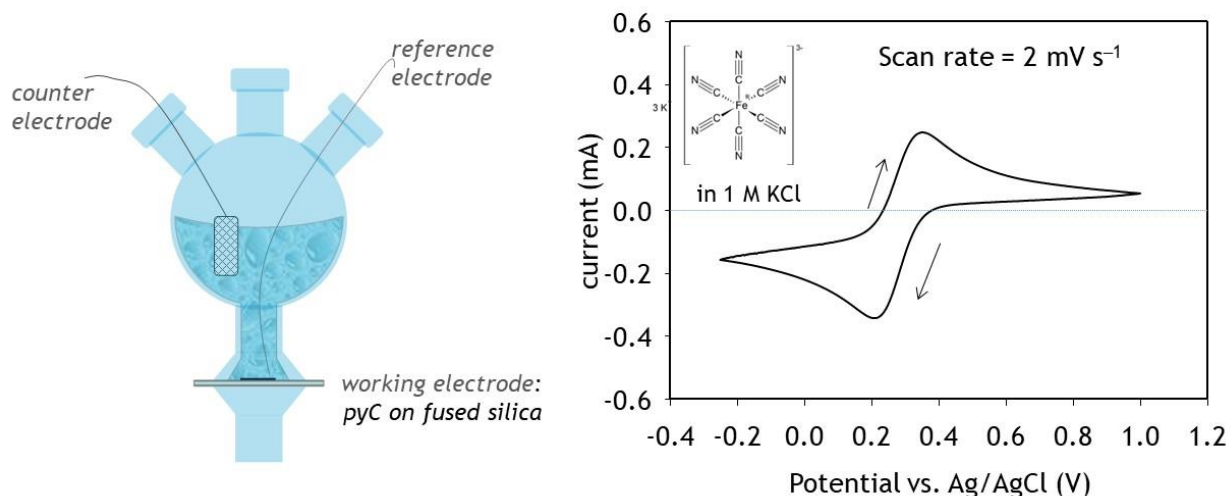


Figure 5 | (Left) Schematic of three-electrode cell used for electrochemical measurements; (Right) typical cyclic voltammogram for pyC in an aqueous ferricyanide-containing electrolyte.

Heteroatom doping of pyrolytic carbon films: Impact on physicochemical properties.

Adventitious and deliberate doping of carbon with such heteroatoms as nitrogen, sulfur, and phosphorous is known to significantly impact such properties as electron-transfer and electrocatalysis kinetics, affinity for binding with other moieties, and long-term stability. By expressing such heteroatom functionalities in a well-defined 2D carbon electrode, we were able to systematically investigate such effects. Our principal efforts focused on sulfur doping, achieved by replacing the benzene feed of our CVD process with mixtures of benzene and its sulfur-containing aromatic relative, thiophene, in volume:volume ratios of either 90:10 or 50:50 (Figure 6, left). Here, we designate the resulting samples derived from these modified feeds as either “pyC~S_{low}” or pyC~S_{high}” for the benzene-rich and 50:50 mixtures, respectively. The CVD process is otherwise identical, yielding similar carbon-coated fused-silica slides, although the reflective quality of sulfur-doped pyC substrates is generally lower than native pyC. The nanoscale surface morphology of pyC~S exhibits a low RMS roughness similar to that of pyC, as verified by AFM.¹¹

X-ray photoelectron spectroscopy analysis reveals that sulfur is successfully incorporated into the pyrolytic carbon films at sulfur loadings of ~ 0.9 and 1.5 at. % for $\text{pyC}\sim\text{S}_{\text{low}}$ and $\text{pyC}\sim\text{S}_{\text{high}}$, respectively, showing some degree of control based on the benzene:thiophene feed composition. Binding energy values for the doublet observed in the S $2p$ region are consistent with heterocyclic-type sulfur (Figure 6, right), confirming sulfur is incorporated into the aromatic-type structure of the pyrolytic carbon. The heterocyclic nature and range of sulfur content of $\text{pyC}\sim\text{S}_{\text{low}}$ are reminiscent of that observed with commercial XC-72 Vulcan carbon,¹⁹ making $\text{pyC}\sim\text{S}_{\text{low}}$ an effective 2D mimic of this technologically important carbon black.

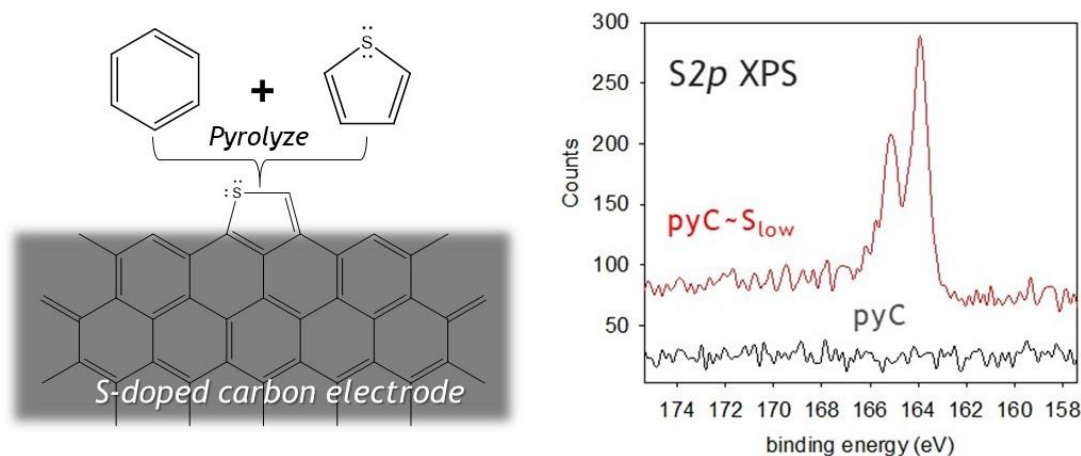


Figure 6 | (Left) Schematic of sulfur-doping into graphene-like structure based on the pyrolytic decomposition of benzene/thiophene vapor mixtures; (Right) X-ray photoelectron spectra in the S $2p$ region showing the incorporation of thiophene-like sulfur into a pyrolytic carbon film ($\text{pyC}\sim\text{S}_{\text{low}}$) and the absence of S $2p$ photoelectron intensity from a native pyC film.

Sulfur doping impacts other properties of the pyrolytic films. For example, Scanning Kelvin-probe (SKP) measurements showed that surface work function increases with sulfur doping, from 5.36 eV for pyC to 5.48 eV for both $\text{pyC}\sim\text{S}_{\text{low}}$ and $\text{pyC}\sim\text{S}_{\text{high}}$, attributed to greater electron density contribution from incorporated sulfur. In contrast, air-plasma treatment of pyC substrates to introduce carbon–oxygen surface functionality decreased work function to 5.18 eV. For all of these cases, measured work functions for these pyrolytic films fall within the range of those measured for many common carbon blacks, which is not the case for many graphene-like carbons that are typically used in fundamental studies of electronic and electrochemical properties. Sulfur doping also impacts electron-transfer properties at these pyrolytic films. Heterogeneous rate constants (k_s) measured for the ferro/ferricyanide couple in 1 M KNO_3 electrolyte are comparable for pyC and $\text{pyC}\sim\text{S}_{\text{low}}$ at $\sim 3.3 \times 10^{-3} \text{ cm s}^{-1}$, but decrease two-fold to $\sim 1.7 \times 10^{-3} \text{ cm s}^{-1}$ for $\text{pyC}\sim\text{S}_{\text{high}}$.¹¹

Binding electrocatalytic nanoparticles to carbon surfaces: The role of heteroatom functionality.

Noble metal nanoparticles are effective electrocatalysts for a number of energy-relevant reactions in electrochemical power sources. In order to minimize the quantity of expensive metal required while maximizing active interfaces, these metal nanoparticles are typically dispersed at low loadings (<10 at.%) on high surface-area carbons. The surface chemistry of these carbons may impact such factors as specific chemical binding, resistance to thermal sintering, accessibility to desired reactant, and electronic coupling. As noted above, sulfur moieties have particular affinity for binding electrocatalytic metal nanoparticles, whether present as adventitious impurities in Vulcan XC-72²⁰ or when deliberately incorporated in an engineered carbon, as we previously demonstrated with sulfur-modified carbon nanofoams (CNFs).^{21,22}

The 2D version of sulfur-doped pyrolytic carbon provides a convenient platform with which to further investigate such interactions. In an initial approach for introducing metal nanoparticles to these carbon substrates, we investigated spontaneous specific adsorption of preformed nanoparticles, in this case 5-nm Au, sourced from a commercial Au sol. Substrates of pyC, pyC~S_{low}, and pyC~S_{high} were soaked in Au sol at moderately elevated temperature (~50°C) for several hours, then copiously rinsed with deionized H₂O. Subsequent characterization by SEM showed that pyC~S_{high} retained the most Au nanoparticles, dispersed across the surface, whereas Au adsorption at pyC and pyC~S_{low} was minimal (Figure 7).

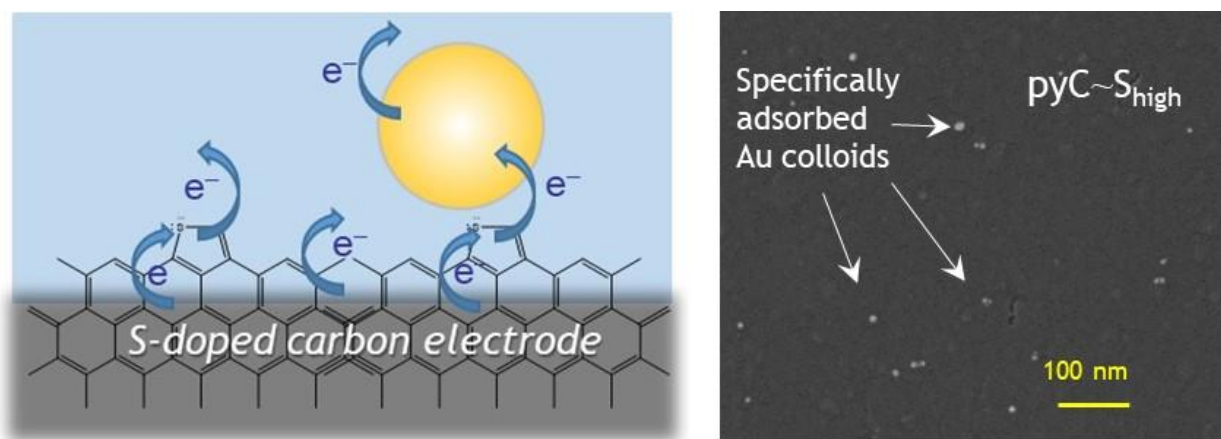


Figure 7 | (Left) Schematic of metal nanoparticle adsorption and electrochemical activity at sulfur-doped pyC; (Right) Scanning electron micrographs showing specific adsorption of pre-formed 5-nm Au colloids at pyC~S_{high}.

Analysis using X-ray photoelectron spectroscopy confirmed the presence of Au on pyC~S_{high} at ~1 at.% relative to carbon. Related 3D carbon nanofoams with thiophene-like surface functionalization previously showed up to 10 at.% Au uptake.²³ Our results with planar pyC~S_{high} demonstrate that while sulfur-functionalization of planar pyrolytic carbon does provide anchor sites for the specific adsorption of preformed metal colloids, the nanoscale roughness and porosity of 3D carbon substrates is required to achieve significantly higher metal nanoparticle loadings.

In the final year of this program, we also investigated the impact of surface sulfur moieties on the morphology and electrochemical activity of palladium nanoparticles applied to pyC and pyC~S substrates by controlled electrodeposition. Experiments are being finalized at the time of the writing of this report, but preliminary results show that the presence of the thiophene-like sulfur in pyC~S_{high} substrates has an impact on palladium nanoparticle size and distribution on the pyrolytic carbon surface, with positive implications for electrocatalytic reduction of molecular oxygen (see Figure 8).

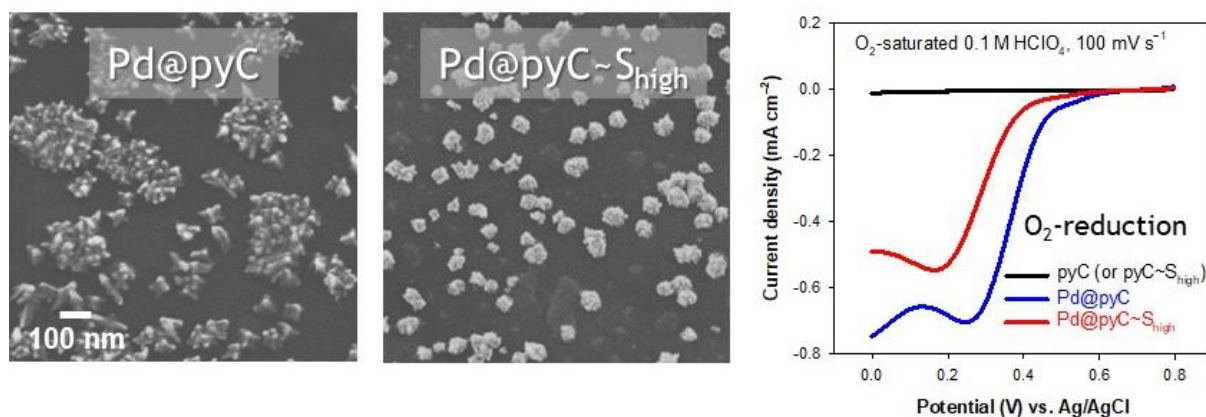


Figure 8 | (Left & Center) Scanning electron micrographs of pyC and pyC~S_{high} after potentiostatic electrodeposition of Pd nanoparticles from aqueous PdCl₂; (Right) Linear-sweep voltammograms for native and Pd-modified pyrolytic carbon films in O₂-saturated aqueous acid, showing differences in ORR activity.

Rewriting electron-transfer kinetics at carbon surfaces with “nanoskin” RuO₂ coatings. As noted above, carbon electrodes are known for sluggish electron-transfer kinetics compared to commonly used electrode metals (e.g., platinum). As one strategy to address this shortcoming, we used NRL-developed, liquid-phase protocols^{24,25} to electrolessly deposit disordered RuO₂ nanoparticles on pyC.¹⁰ Calcining RuO₂@pyC up to temperatures of 250°C was used to further

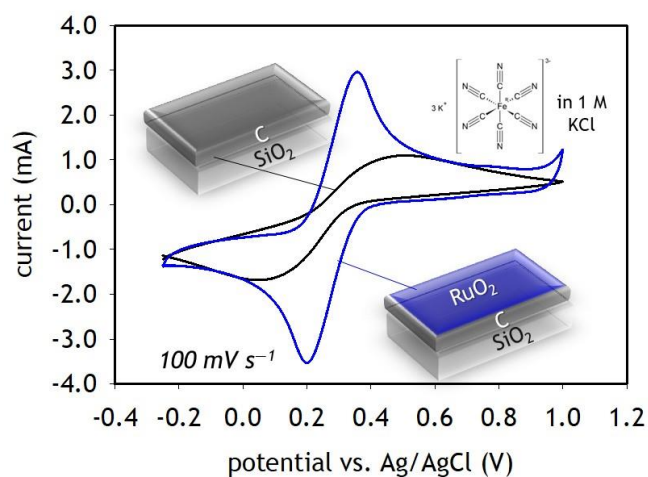


Figure 9 | Typical cyclic voltammograms for pyC and RuO₂@pyC electrodes in aqueous ferricyanide-containing electrolyte.

for Fe(H₂O)₆^{3+/2+} 30-fold — at which point RuO₂@pyC rewrites the pyC electron-transfer character to a surface that mimics the fast electron-transfer characteristic of Pt in aqueous¹⁰ and nonaqueous electrolytes.²⁶

Table 1 | Heterogeneous electron-transfer rate constants (k_s) for a series of pyC and RuO₂@pyC electrodes in the presence of the indicated redox probe.

Electrode	k_s for Fe(CN) ₆ ^{4-/3-} ($\times 10^{-3} \text{ cm s}^{-1}$)	k_s for Fe(H ₂ O) ₆ ^{2+/2+} ($\times 10^{-3} \text{ cm s}^{-1}$)
pyC	15	0.034
as-dep-RuO ₂ @pyC	16	0.14
150°C-RuO ₂ @pyC	110	0.48
200°C-RuO ₂ @pyC	110	1.9
250°C-RuO ₂ @pyC	510	1.9

Prior work demonstrated that this electroless route to nanoscale rutile-like ruthenia creates a nanomaterial in which its electrical conductivity can be tuned over three orders of magnitude by calcining without ripening the particles comprising the film.²⁴ Although some crystalline order appears, strong localization effects remain for electrons in the RuO₂ nanoparticles in the film;

tune the structural characteristics and electronic character of the RuO₂ layer. We then assessed the electron-transfer character of the resulting electrodes by performing cyclic voltammetry in half-cells with either Fe(CN)₆^{4-/3-} or Fe(H₂O)₆^{3+/2+} as the redox probe (Figure 9). DigiElch™ software was used to fit voltammetric data with established electroanalytical models in order to calculate k_s values (Table 1). Crystallizing the disordered RuOx nanoparticles by calcining RuO₂@pyC at 250°C increases the heterogeneous electron-transfer rate constant

calcination temperatures approaching 700°C are required before the still-nanoscopic oxide behaves as a Drude metal in terms of its AC conductivity.²⁷ The RuO₂ nanoparticles treated at 250°C that overwrite the modest electron-transfer rates at pyrolytic carbon thus do so as a nanomaterial that blends structural order and disorder.

The trends in the electrochemical and electronic properties of the disordered nanoscale RuO₂ may be understood by further examination of the solid-state structure of this material. We performed differential (thin film) pair distribution function (DPDF) analysis of X-ray diffraction data collected at the Advanced Photon Source at Argonne National Laboratory. For this analysis, the 2–3 nm thick RuO₂ nanoskins were deposited onto a 3D substrate (fused silica–fiber paper) in order to amplify the amount of material in the X-ray path length. With the medium-range structural information derived from the DPDF analysis and elemental verification of scattering features using X-ray near-edge structure (XANES) analysis, we were able to identify a previously unassigned Ru-centered scattering at ~ 2.4 Å as a corundum (Ru₂O₃) Ru–Ru face-sharing correlation present in the as-deposited oxide.²⁸ This feature diminishes with increasing calcination temperature (Figure 10), commensurate with the 1000-fold increase in electronic conductivity. Corundum ruthenium oxide is metastable and not found as a bulk material; the low-temperature nonaqueous route to nanoscale rutile-like ruthenium oxide permits the structural stabilization of a Ru₂O₃ shell over an ~ 1 -nm core of rutile RuO₂ and generates a nanomaterial with broadband transparency (ultraviolet to microwave wavelengths)²⁹ and a metal-to-insulator transition,³⁰ fundamental materials properties neither of which occur for RuO₂.

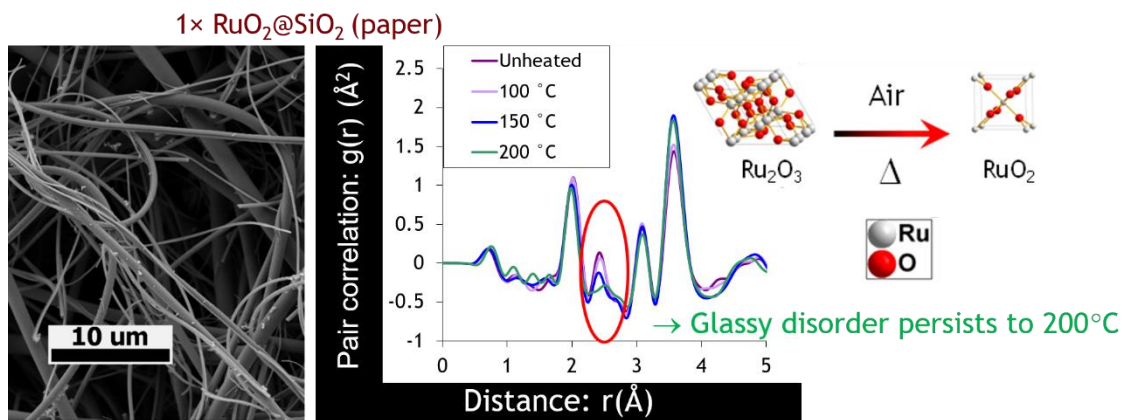


Figure 10 | (Left) scanning electron micrograph of a 2–3 nm shell of RuO₂ electrolessly deposited on the fibers of fused silica paper; (Right) differential pair-distribution analysis highlighting the loss of the 2.4 Å corundum correlation upon calcination (inset: structure of corundum Ru₂O₃ and rutile RuO₂).

This blending of order with disorder also has electrocatalytic implications. Modifying pyrolytic carbon shells deposited onto fused silica fiber paper with electrolessly deposited RuO₂ nanoparticles generates a stable, high activity, practical electrocatalytic electrode architecture for oxygen evolution (the difficult half of water electrolysis).³¹ The RuO₂@pyC@SiO₂ fiber–paper electrode retains high specific activity (40–60 mA mg^{−1} at a competitive overpotential of 330 mV) and preserves the desirable macroscale properties of SiO₂ fiber paper: porous, lightweight, flexible, and inexpensive. This dusting of still-disordered nanoscale RuO₂ over the pyC-coated fibers minimizes the amount of RuO₂ used (300–580× lower catalyst density than bulk RuO₂) and innately restricts the oxidizing potentials needed to meet a given rate of water oxidation, which diminishes dissolution of the catalyst and corrosion of its underlying current collector (the carbon), thereby extending anode lifetime.

Rethinking impedance analysis in three dimensions: Application to both 2D and 3D electrode systems. As charge-storage materials have been scaled to ever-smaller nanoscale dimensions, the distinctions between nominally “battery-like” and “capacitor-like” redox behavior have become increasingly blurred. The NRL has been a leader in developing such materials for the past two decades, particularly as directed toward their use in electrochemical capacitors and high-rate batteries. In order to understand the complexities of charge-storage dynamics in these materials, we have applied and adapted a range of electroanalytical protocols, including cyclic voltammetry, pulse voltammetry, and galvanostatic charge–discharge. Impedance spectroscopy is another technique that provides a wealth of frequency-dependent information on redox reactions at an electrode (in a half-cell) or in an assembled two-terminal device. Data derived from impedance are most often studied in Nyquist plots of real versus imaginary impedance contributions and then fitting the corresponding trends to circuit models that approximate the various types of processes involved.

Inspired by an under-utilized analysis previously reported by Bai and Conway to explore pseudoinduction,^{32,33} we adapted their methodology on generating Bode-plot representations comprising either real (C′) or imaginary (C′′) capacitance response versus frequency. The C′ response derives from the reversible charge storage available at a given frequency, while the C′′ values are a reflection of response time (essentially mapping out an equivalent time constant). When such plots are collected in small increments of DC bias across the operational potential or

voltage range of an electrode or device, the resulting data can be assembled into 3D graphs (potential/voltage versus frequency versus capacitance) that reveal additional complexities in the dynamics of charge storage when multiple mechanisms may be accessible at different potential/voltage or timescales.

We initially applied this “3D Bode” treatment to our carbon nanofoam-based electrode architectures surface-modified with either birnessite MnOx ¹⁴ or spinel- LiMn_2O_4 ,¹⁵ the former case yielding important insights on zinc-ion storage mechanisms (see the following section for more details on that phenomenon). The 3D Bode analysis was also used to probe double-layer and pseudocapacitance phenomena at 2D pyC electrodes, where porous-electrode contributions are eliminated to reveal the innate rate character of the active interface. Maps of real capacitance across a 0.0–0.7 V (vs Ag/AgCl) range at an unmodified pyC electrode in neutral-pH aqueous electrolyte show behavior more complex than expected for simple double-layer charge storage (Figure 11), possibly due to surface redox reactions centered around 0.45 V. Electrodeposition of a nanoscale-thick layer of MnOx amplifies the measured capacitance across this range by an order of magnitude due to pseudocapacitive reactions at the MnOx , but with the peak capacitance at 0.45 V, seemingly preserved from the underlying pyC substrate. In another variation, we first used electroless deposition to form a RuO_2 nanoskin coating at the pyC electrode (as described above), and then electrodeposited the same amount of MnOx at that RuO_2 @pyC electrode. With the resulting MnOx @ RuO_2 @pyC, the pseudocapacitive response of the overlying MnOx film qualitatively matches that of the RuO_2 (rather than the pyC). These preliminary results hint at the likely impact of substrate electronic state and surface functionality in electrically addressing nanoscale redox coatings on fast time scales, although additional work is needed to further validate such effects.

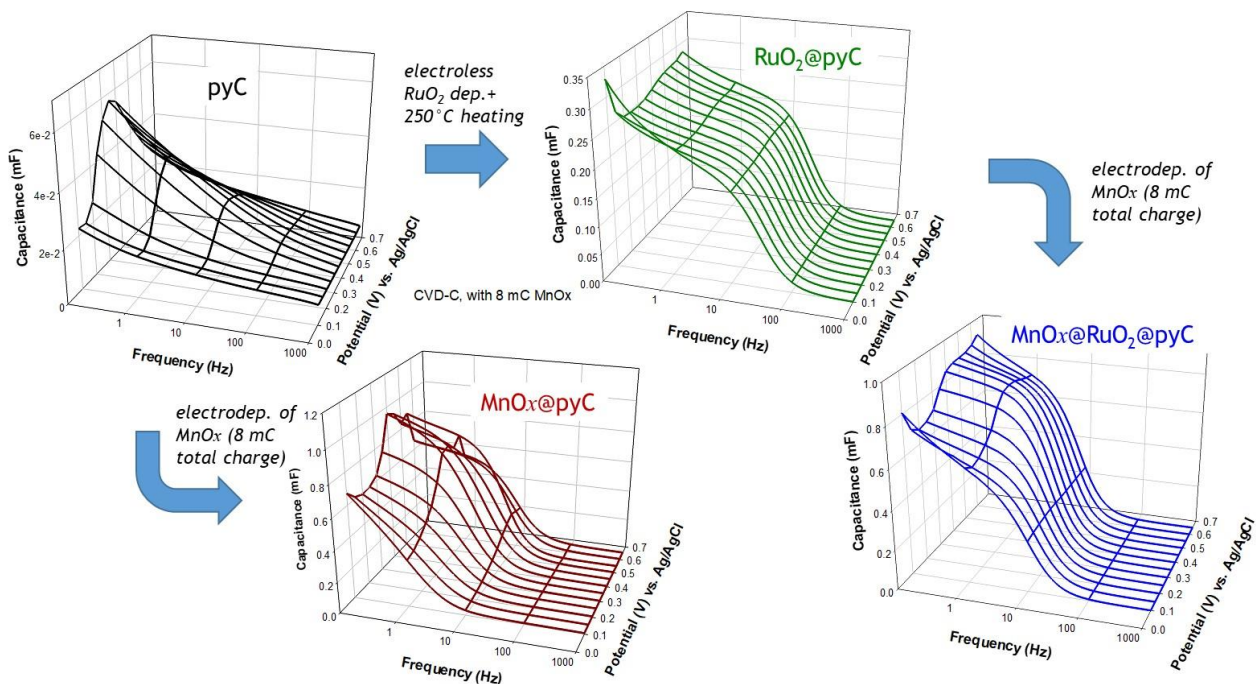


Figure 11 | 3D-Bode representations of potential- and frequency-dependent capacitance for native pyC, MnO_x@pyC, RuO₂@pyC, and MnO_x@RuO₂@pyC, as measured by half-cell impedance in aqueous 0.5 Na₂SO₄ electrolyte.

Deconvolving complex charge-storage mechanisms in Zn-ion batteries: The importance of open-medium surfaces versus confined porosity. Within the past few years, a prospective new rechargeable battery technology has emerged that is based on reversible charge-storage reactions involving Zn²⁺ in mild-pH aqueous electrolytes. These “Zn-ion” cells commonly use a Zn metal anode, a simple electrolyte such as 1 M ZnSO₄, and a cathode based on particular nanostructured transition metal oxides, with manganese oxides among the most promising candidates based on cost and performance considerations. We were able to quickly adapt and optimize NRL-developed MnO_x materials and electrode architectures for Zn-ion applications, beginning with 3D structures based on birnessite MnO_x-modified carbon nanofoams.^{14,34} Our investigations with such materials demonstrated previously unidentified pseudocapacitance functionality in Zn-ion electrolytes that also include alkali metal salts (e.g., Na₂SO₄),¹⁴ and also revealed complex charge-storage reactions that involve the formation/dissolution of Zn₄(OH)₆SO₄ species, driven by changes in local pH as the MnO_x undergoes proton-insertion and release during electrochemical cycling (Figure 12, left).³⁴ These findings with 3D electrodes also hinted at the importance of controlling ZnSO₄

transport to MnOx domains within the mesoporous architectures in order to achieve a high degree of charge–discharge reversibility.

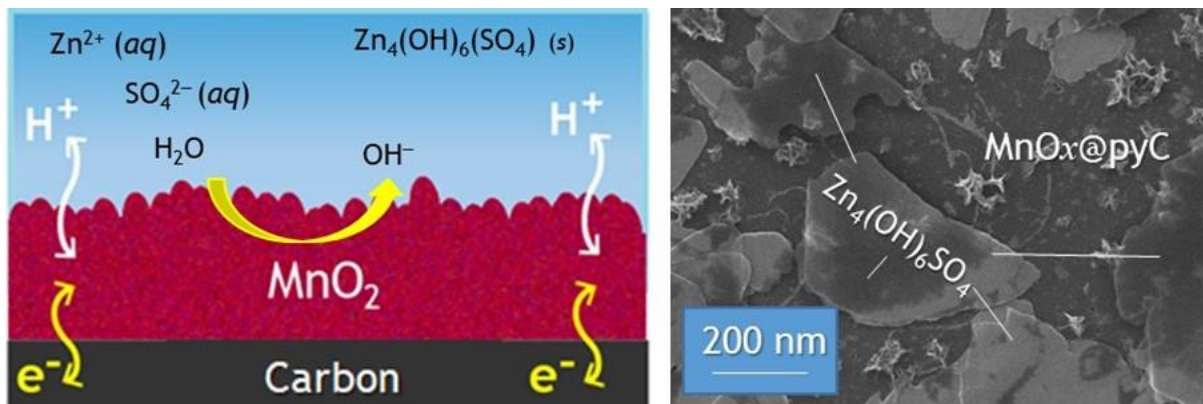


Figure 12 | (L) Schematic of proposed charge-storage reactions at MnOx in aqueous zinc-ion electrolytes; (R) Scanning electron micrograph of MnOx@pyC surface after reduction (i.e., discharge) in aqueous 10 mM ZnSO₄.

In order to test this hypothesis, we used anodic electrodeposition to apply ultrathin birnessite-MnOx coatings at pyC electrodes to serve as 2D mimics of the corresponding 3D CNF-based architectures. Electroanalysis of the resulting MnOx@pyC electrodes in typical Zn-ion electrolytes (0.1–1 M ZnSO₄) immediately showed detrimental irreversibility within the first few charge–discharge cycles, unlike their 3D counterparts. Modest reversibility was attained only when reducing the ZnSO₄ concentration to <10 mM, and even then charge-storage capacity fell below acceptable levels after 10 cycles. Representative MnOx@pyC electrodes conditioned to varying states-of-charge were examined *ex situ* by XPS, XRD, SEM, and AFM. Scanning electron microscopy reveals extensive surface coverage of platelet-like Zn₄(OH)₆SO₄ deposits in deeply discharged (reduced) MnOx@pyC (Figure 12, right), with many of these remaining after recharging (also confirmed by *ex situ* AFM). Zinc-ion reactions were also examined by *in situ* AFM with the MnOx@pyC electrodes under electrochemical control as the surface is intermittently scanned by the AFM probe (Figure 13). Similar plate-like deposits are observed upon reduction of the MnOx film, and are only partially removed on reoxidation.

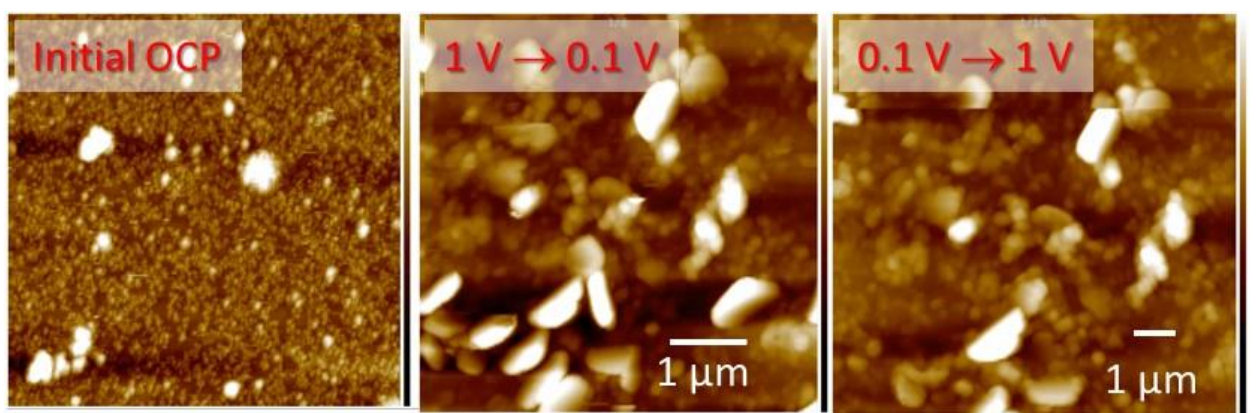


Figure 13 | *In situ* electrochemical AFM at MnOx@pyC substrate in 10 mM ZnSO₄ (aq), conditioned at: (L) initial open-circuit potential; (M) after sweeping from 1 V to 0.1 V vs. Ag/AgCl; (R) after subsequent sweep from 0.1 V back to 1 V vs. Ag/AgCl.

The persistence of these electrically insulating Zn₄(OH)₆SO₄ deposits at the surface of the planar electrode is consistent with the poor cycling behavior observed electrochemically. We posit that the open 2D MnOx@pyC surface experiences a high flux of ZnSO₄ from the bulk electrolyte, providing an opportunity for larger Zn₄(OH)₆SO₄ crystallites that are less readily redissolved upon electrochemical recharging. These findings at 2D electrodes serve as an important contrast to their 3D counterparts, confirming the importance of incorporating a well-designed pore structure in the electrode to contain and control the reactants and products involved in this complex charge-storage manuscript, as summarized in a manuscript-in-progress at the time of this report.

Investigating electrocatalytic oxygen reduction at MnOx@carbon interfaces. In addition to charge-storage functionality in electrochemical capacitors, zinc-ion cells and other battery systems, nanostructured MnOx is also a well-established electrocatalyst for oxygen reduction in aqueous alkaline electrolytes and is commonly used in commercial zinc–air cells. Because of the poor inherent conductivity of MnOx, conductive carbon must always be included when constructing electrodes, as in the case of the air-breathing cathode in zinc–air cells. We recently reported on the importance of uniform spatial distribution of MnOx and carbon phases when constructing air cathodes using conventional powder-composite methods.³⁵ Aside from enhancing electronic conductivity, the carbon component may also act as an electrocatalyst for oxygen reduction in alkaline electrolytes, although following a two-electron pathway rather than the

preferred four-electron reaction. Cooperative oxygen-reduction mechanisms between carbon and MnOx have also been proposed when the two components are in intimate contact.¹⁷

We proposed to address the question of synergistic ORR activity by preparing 2D pyC electrodes with controlled surface coverage of ultrathin MnOx, to include ad hoc and patterned deposits, with interrogation of the resulting substrates by electroanalytical methods and scanning electrochemical microscopy (SECM). Focused-ion beam (FIB) methods were used for preliminary patterning of substrates comprising electrodeposited MnOx films (nominally complete coverage) on pyC, with a reasonable degree of success creating controlled MnOx@pyC interfaces (Figure 14). These FIB-prepared substrates were designed and fabricated

for SECM analysis to map ORR activity across the patterned surface, contrasting bare pyC and MnOx areas with those at the MnOx@pyC interface. Unfortunately the Keysight™ SECM purchased from NRL CPP funds for use by the Chemistry Division experienced significant problems and was not sufficiently functional in time to perform the planned SECM experiments.

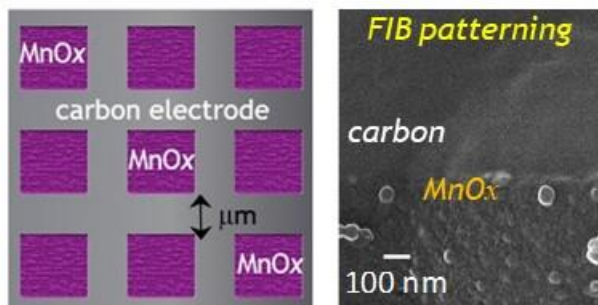


Figure 14 | (L) Schematic of proposed patterned MnOx@pyC substrate; (R) Scanning electron micrograph after FIB patterning of electrodeposited MnOx film on pyC.

As an alternative approach we used the electrodeposition protocol itself to apply nanoscale “patches” of MnOx on the pyC substrate, controlling coverage and feature size based on the deposition time under galvanostatic conditions. Oxygen-reduction activity for a range of such MnOx@pyC substrates was examined using cyclic voltammetry and modeling of the resulting voltammetric data. This study is ongoing at the time of writing, but preliminary results show that the presence of MnOx shifts the onset potential for oxygen reduction by ~ 250 mV more positive and increases current density by two-fold, indicating a probable four-electron ORR process (Figure 15). Additional findings will be the subject of a future publication.

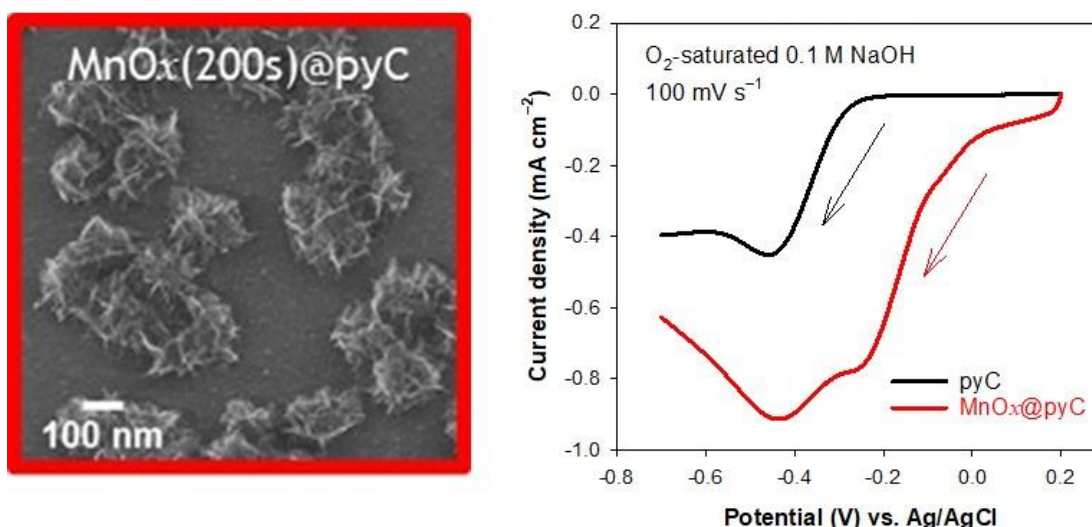


Figure 15 | (L) scanning electron micrograph of MnOx electrodeposited at a pyC substrate; (R) Oxygen reduction in alkaline electrolyte at a native pyC electrode vs. a MnOx@pyC electrode showing the electrocatalytic activity of MnOx over that of carbon alone.

Theory/Computation

Kohn–Sham density functional theory (KS DFT) uses a set of independent single-particle orbitals to reproduce the electron-density of a molecular system. The motion of each electron in this picture is uncorrelated with the others, because the exact electron–electron interaction energy is replaced by an approximate, nonlinear functional of the electron density. The wave function described by these independent orbitals is a Slater determinant, an antisymmetrized product of single-particle states. Although in most circumstances, the approximations of KS DFT are sufficient, and even highly accurate, there are a few situations relevant to electrochemistry where the independent particle description fails.

Transition metals and multi-Slater-determinant states. The first situation where KS DFT frequently fails is in transition metal-containing systems. Because transition metals have several unpaired *d*-orbital electrons, they can form complex spin states that can only be described by a multi-Slater-determinant wave function. Common molecular quantum chemistry codes allow for the Z component of spin to be specified in a calculation, but the true ground state of a system containing multiple transition metal atoms typically depends on both the Z component of spin and the total spin.

A common phenomenological way of modeling the relationship between the spin state and energy of systems containing multiple transition metal atoms is through a Heisenberg Hamiltonian. In the Heisenberg Hamiltonian, the exchange interaction between transition metal atoms is approximated as a dot product between individual atomic spins times some empirical coefficient and is given by

$$\hat{H}_{Heisenberg} = \sum_{i>j} C_{ij} \hat{S}_i \cdot \hat{S}_j,$$

where $\hat{S}_i$ and $\hat{S}_j$ are quantum mechanical spin operators for transition metal atoms *i* and *j*. We can then approximate the Hamiltonian for the entire molecule as

$$\hat{H}_{total} = \hat{H}_{Heisenberg} + C_0,$$

where C_0 is a constant energy independent of the spin state of the transition metal atoms.

To make use of this model in, we fit the coefficients C_{ij} and C_0 using the spin states that are accessible through broken-symmetry DFT. While we cannot constrain the Z component of spin associated with each atom, we can specify an initial guess for the wave function where the total spin points either up or down along the Z axis. We then optimize the wave function and check the Mulliken spins to ensure that in the final converged wave function, the spins still point in the desired directions.

Given that the energy only depends on the relative orientation of spins, for *N* transition metal atoms, we can generate 2^{N-1} unique states with DFT by holding the spin of the first transition metal atom in the up direction and allowing the remaining atomic spins to point either up or down. From these energies, we can then find the C_{ij} and C_0 coefficients of the Heisenberg Hamiltonian.

However, the number of unknown coefficients in the Heisenberg Hamiltonian is $N(N-1)/2+1$, which is less than 2^{N-1} if $N>3$. Therefore, our system of equations is usually overdetermined. We can find the C_{ij} and C_0 coefficients through least squares minimization by solving

$$\frac{\partial}{\partial C_{ij}} \left(\sum_{i>j} C_{ij} \langle \chi_k | \hat{S}_i \cdot \hat{S}_j | \chi_k \rangle + C_0 - E_k \right)^2 = 0,$$

where E_k is an energy computed with DFT and $|\chi_k\rangle$ is the corresponding spinor that describes the spin state of the entire molecule.

Once the coefficients have been fit, the Heisenberg Hamiltonian can describe spin states that are inaccessible to KS DFT calculations. Diagonalization of the Heisenberg Hamiltonian yields a new ground state with a lower energy than any of the individual DFT energies used to create it.

Using this methodology, we studied the oxygen-evolving complex (OEC) in Photosystem II, which contains four Mn ions that can be in various oxidation states with differing spins. The OEC undergoes a catalytic cycle to produce O_2 from water, known as the Kok cycle. The Kok cycle has five stages (referred to as S_0 – S_4), whereby an electron is transferred to a tyrosine residue at each stage.

Typically, O–O bond formation is thought to occur in the S_4 state after the fourth electron transfer from a Mn_4Ca cluster, but based on time-resolved X-ray emission spectroscopy, we proposed a model where O–O bond formation occurs before the final electron transfer. Our model of the S_3 state has all four Mn ions in the $4+$ state, with three unpaired d -orbital electrons each.

Because each Mn ion has a spin of $3/2$, the total spin can add up to any integer value between 0 and 6, inclusive. For any spin S , there are $2S+1$ S_Z states that the system can be in, for a total of 49 total possible spin states. Using the $2^3 = 8$ energies computed with DFT to fit the Heisenberg

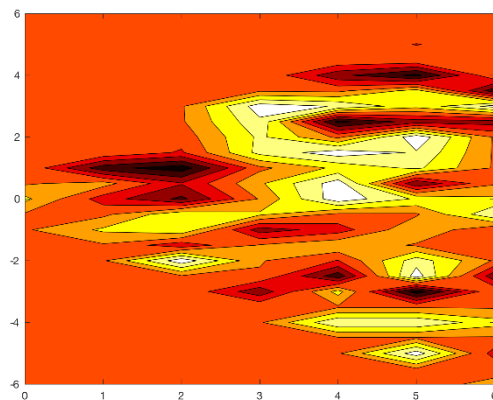


Figure 16 | Energy vs. total spin (horizontal axis) and Z component of spin (vertical axis) for the S_3 state of Photosystem II as fit to a Heisenberg Hamiltonian. Brighter colors represent higher energies.

Hamiltonian, we can compute the energies of all 49 states, which are plotted in Figure 15. In the lowest energy state found with broken-symmetry DFT, the spins of the four Mn ions, labeled Mn1–Mn4 (Figure 16) had the orientation up, down, down, up.

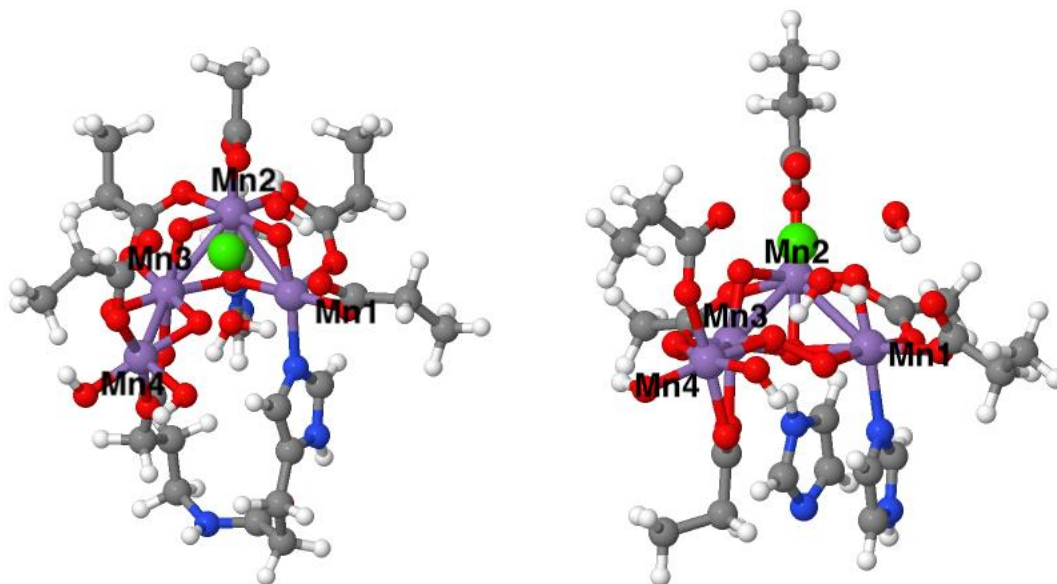


Figure 17 | (Left) a high spin S2 state of photosystem II; (Right) NRL-calculated S3 state. The four Mn atoms (purple) are labeled Mn1–Mn4. We also used this same Heisenberg Hamiltonian model to investigate the S2 state, which displays a high-spin EPR signal. The source of this high-spin is a subject of debate. We proposed various models of the S2 state where, under certain environmental conditions, the five-coordinated Mn center is susceptible to ligand binding. Two of our models displayed a high-spin ground state (spin 5/2 or 7/2) in when fit to a Heisenberg Hamiltonian. In the first, the oxidation states of Mn1–Mn4 were +4, +3, +4, +4, and in the second, they were +4, +4, +3, +4.

Degeneracy. Another electrochemically relevant situation in which standard KS DFT fails is in systems with degeneracy. Such systems are relevant to electrochemistry, because according to Marcus theory, electron transfer occurs between degenerate states.

The problem with KS DFT and degeneracy stems from a fundamental issue with reproducing the ground state electron-density of an interacting system with the ground state of a non-interacting system of particles in a local potential. Empirically, it has been shown that this is impossible for certain degenerate systems, such as the kind that occur when a bond is being broken. In such cases, the ground state electron-density can only be reproduced by a mixed state involving fractionally occupied KS orbitals.

The reason for this is that the KS eigenvalue equation is a nonlinear equation that depends on the electron density. Unlike in standard quantum mechanics, changing the occupation of KS

states changes the eigenvalue spectrum of the system. As electrons are moved out of a particular orbital, its eigenvalue tends to go down (although this depends on the exchange-correlation potential), and as electrons are moved into an orbital, its eigenvalue tends to go up. Therefore, situations can arise where it is impossible be in the ground state if every orbital is occupied by a whole number of electrons.

We have developed a perturbation theory for dealing with such situations where degeneracy arises. We found that because of this nonlinear behavior, small changes to the external potential do not break the degeneracy of the system. Instead, they cause the occupation numbers of the orbitals to change, shielding the system from the effects of the external potential, and preventing degenerate eigenvalues from splitting. This outcome is possible so long as the perturbation is small. If the perturbation becomes large enough, the degeneracy must break because it cannot be shielded by rearranging the degenerate electrons (Figure 17).

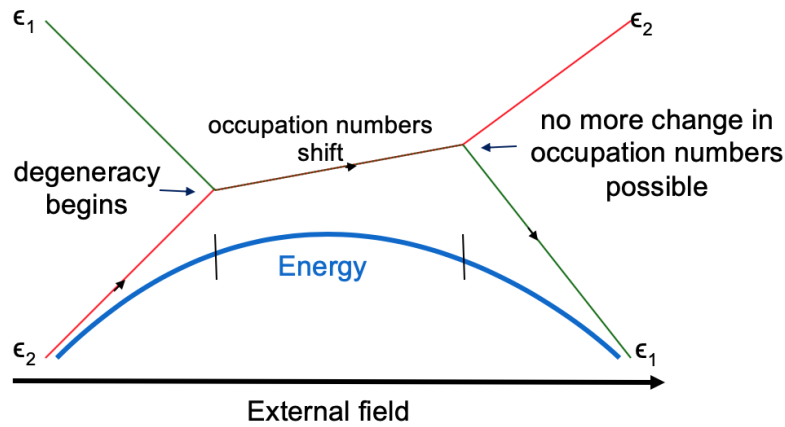


Figure 18 | Eigenvalues and energy versus external field strength.

One method of deriving the equations of our degenerate perturbation theory is by minimizing the energy of the system with respect to the Fermi-level occupation numbers. Consider a degenerate system perturbed by an external potential $\lambda V^{(1)}$. The energy of the perturbed system can be written as a Taylor series in powers of lambda as

$$E[\lambda] = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

Likewise, the Fermi-level occupation numbers can be written as

$$n_i[\lambda] = n_i^{(0)} + \lambda n_i^{(1)} + \lambda^2 n_i^{(2)} + \dots,$$

and the electron-density can be written as

$$\begin{aligned}\rho(\mathbf{r}, \lambda) &= \rho(\mathbf{r})_i^{(0)} + \lambda \rho(\mathbf{r})_i^{(1)} + \lambda^2 \rho(\mathbf{r})_i^{(2)} + \dots \\ &= \sum_i n_i^{(0)} \phi_i^{(0)} \phi_i^{(0)} + \lambda \left(n_i^{(1)} \phi_i^{(0)} \phi_i^{(0)} + 2n_i^{(0)} \phi_i^{(0)} \phi_i^{(1)} \right) + \dots\end{aligned}$$

We can minimize $\lambda^K E^{(K)}$ with respect to $\lambda^M n^{(M)}$ with the constraint that the total number of electrons is conserved by using a Lagrange multiplier with the constraint equation

$$\sum_i n_i = N = \sum_i n_i^{(0)} + \lambda n_i^{(1)} + \lambda^2 n_i^{(2)} + \dots$$

We then have,

$$\frac{\partial E^{(K)}}{\partial n_i^{(M)}} = \epsilon^{(K-M)},$$

where $\epsilon^{(K-M)}$ is a Lagrange multiplier. Given that $E^{(K)}$ is a K^{th} -order term and $n_i^{(M)}$ is an M^{th} -order term, the overall equation is of order $K-M$.

If K is equal to $M+1$, we can generate the first-order equation for perturbation theory. This equation is independent of the specific values of K and M , unless $M=0$, for reasons relating to self-consistency of the unperturbed solution. We find, then, that for degenerate orbitals ϕ_i and ϕ_k ,

$$\langle \phi_k | \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \rho^{(1)}(\mathbf{r}') d\mathbf{r}' + V^{(1)} | \phi_i \rangle = \epsilon^{(1)} \delta_{ik},$$

where $v_{ks}(\mathbf{r})$ is the Coulomb plus exchange-correlation potential, and we have made use of the fact from standard perturbation theory that for $i \neq k$,

$$\langle \phi_k^{(0)} | V_{total}^{(1)} | \phi_i \rangle = (\epsilon_i^{(0)} - \epsilon_k^{(0)}) \langle \phi_k^{(0)} | \phi_i^{(1)} \rangle = 0.$$

If we have N_D degenerate orbitals, the fact that the off-diagonal matrix elements between them must vanish imposes $N_D \times (N_D - 1)/2$ constraints on the first-order electron density. The requirement that the diagonal elements are equal imposes another $N_D - 1$ constraints. Therefore, we must have an equal number of adjustable parameters in the electron-density.

Three different sources of adjustable parameters sum together to the required number. First, there are N_D first-order occupation numbers, but the constraint that they sum to N reduces the number of free parameters to $N_D - 1$. Second, we can rotate equally occupied zeroth-order

degenerate orbitals into one another without changing the electron-density or the energy of the unperturbed system. Finally, we can perform a first-order orbital rotation between degenerate orbitals with different occupation numbers. These last two sets of parameters together total $N_D \times (N_D - 1)/2$.

The final equations for our degenerate perturbation theory then become

$$\langle \phi'_k | \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \sum_j \left(n_i^{(1)} \phi_j'^{(0)} \phi_j'^{(0)} + 2n_i^{(0)} \sum_l \mathbf{U}_{jl}^{(1)} \phi_j'^{(0)} \phi_l'^{(0)} \right) d\mathbf{r}' + V^{(1)} | \phi'_i \rangle = \epsilon^{(1)} \delta_{ik},$$

where the primed orbitals (e.g., ϕ'_i) have been rotated into other equally occupied degenerate orbitals, and $\mathbf{U}_{jl}^{(1)}$ is a first-order orbital rotation matrix that mixes orbitals with different occupation numbers.

FUTURE WORK

The advances described above provide a foundation for future innovations from fundamental measurements and computation/modeling to implementation in practical batteries, electrochemical capacitors, and fuel cells. The reflective pyC substrates developed in this program should be further exploited for *in situ* spectroelectrochemical analysis, as demonstrated in preliminary experiments performed with electrochromic films of MnOx electrodeposited at pyC and cycled in mild aqueous electrolyte.³⁶ Disordered, hard carbons have recently emerged as a promising negative electrode material for Na-ion batteries,³⁷ and pyC electrodes provide a planar stand-in to similarly investigate Na-ion charge-storage mechanisms. The chemical vapor deposition protocols used herein are also readily adapted to coat complex 3D substrates,⁸ for example as a means to modify other carbon-based architectures in order to tune their electronic character, electron-transfer kinetics, or specific adsorption properties according to the lessons derived from these 2D electrode studies. Future computational efforts should focus on ways to incorporate density functional theory into mean-field theory for describing electron-transfer in large-scale systems. Theoretical development should also be extended to describe realistic electrode-electrolyte interactions.

The key question of our program reduces to this: What would one do tomorrow to make the carbon current collectors used in energy storage better able to shuttle the inherent electrons banked by active materials? The answer may be designing in electron-transfer relays with fast heterogeneous rate constants — not unlike the way Adam Heller wired redox enzymes to create a \$1B USD glucose monitor.³⁸ The final stages of our program hint that the next steps to take involve wiring redox hot spots into the junctions where current-collecting carbon meets the charge-storing active material.

Program Productivity (as of August 2020)

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17. Y. Pushkar, K. M. Davis, M. C. Palenik, Model of the oxygen evolving complex which is highly predisposed to O–O bond formation. *J. Phys. Chem. Lett.* **2018**, 9, 3525–3531. **[17-1231-4298]**
18. K. M. Davis, B. T. Sullivan, M. C. Palenik, L. Yan, V. Purohit, G. Robison, I. Kosheleva, R. W. Henning, G. T. Seidler, Y. Pushkar, Rapid evolution of the Photosystem II electronic structure during water splitting. *Physical Review X* **2018**, 8, 041014. **[18-1231-3584]**
19. M. D. Donakowski, A. N. Mansour, I. R. Pala, C. N. Chervin, P. A. DeSario, J. W. Long, D. R. Rolison, Trapping a Ru₂O₃ corundum-like structure at ultrathin, disordered RuO₂ nanoskins expressed in 3D. *J. Phys. Chem. C* **2018**, 122, 28895–28900. **[18-1231-3685]**
20. J. S. Ko, M. D. Donakowski, M. B. Sassin, J. F. Parker, D. R. Rolison, J. W. Long, Deciphering charge-storage mechanisms in 3D MnOx@carbon electrode nanoarchitectures for rechargeable zinc-ion cells. *MRS Commun.* **2019**, 9, 99–106. **[18-1231-4379]**
21. J. H. Pikul, J. W. Long, Architected materials for advanced electrochemical systems. *MRS Bull.* **2019**, 44, 789–795. **(INVITED) [19-1231-3128]**
22. J. F. Parker, C. R. So, J. S. Ko, S. Jeon, M. B. Sassin, C. N. Chervin, J. C. Lytle, M. E. Helms, D. R. Rolison, J. W. Long, Pyrolytic carbon films with tunable electronic structure and surface functionality: A planar stand-in for electroanalysis of energy-relevant reactions. *ChemElectroChem* **2020**, 7, 672–683. **(INVITED) [19-1231-3588]**
23. J. S. Ko, C.-H. Lai, J. W. Long, D. R. Rolison, B. Dunn, J. N. Weker, Differentiating double-layer, pseudocapacitance, and battery-like mechanisms by analyzing impedance measurements in three dimensions. *ACS Appl. Mater. Interfaces* **2020**, 12, 14071–14078. **[19-1231-2970]**
24. J. W. Long, B. Dunn, D. R. Rolison, H. S. White, Three-dimensional architectures for batteries and electrodes. *Advanced Energy Materials* **2020**, 10, in the press. **(INVITED) [20-1231-2097]**
25. M. B. Sassin, M. E. Helms, J. F. Parker, C. N. Chervin, J. S. Ko, D. R. Rolison, J. W. Long, Nanocrystalline ZnMn₂O₄ affixed to 3D carbon electrode architectures: A platform for elucidating zinc-ion charge-storage reactions. *J. Mater. Chem. A* **2020**, in review.

Books and Chapters in Books

1. T. Brousse, O. Crosnier, D. Bélanger, and J. W. Long. Capacitive and pseudocapacitive electrodes for electrochemical capacitors and hybrid devices. In *Metal Oxides in Supercapacitors*, G. Korotcenkov, D. P. Dupak, P. Gomez-Romero (Eds.); Elsevier, Lausanne, Switzerland, **2017**, Ch. 1, pp. 1–24. **(INVITED) [17-1231-1523]**
2. D. R. Rolison, M. B. Sassin, J. W. Long, Aerogels: An architectural guide to advances in electrochemical energy storage. In *Handbook of Aerogels*, 2nd ed., M. Aegerter, S. A. Steiner (Eds.), Springer, Clifton, NJ, **2020**, Chapter 47, in the press. **(INVITED) [20-1231-2129]**

Recognition

1. D. R. Rolison: Editorial Advisory Board for *Chemical Reviews*, 2016–present
2. J. F. Parker: Presidential Early Career Award for Scientists and Engineers (PECASE), 9 January 2017
3. D. R. Rolison: Chair: Selection Committee for Fellows of the Materials Research Society, 2017–2021.

4. D. R. Rolison: Symposium Co-Organizer (with K. J. Stevenson and J. Rodríguez-López) of “Synthesis & Characterization of Materials for Energy Applications,” 253rd Meeting of the American Chemical Society, 2–6 April 2017, San Francisco, CA.
5. D. R. Rolison: 2018 William H. Nichols Medal (2018)
6. D. R. Rolison: Editorial Advisory Board for *ACS Applied Energy Materials* (2018–present)
7. M. B. Sassin: Elected, Member of the Board for the Society for Electroanalytical Chemistry
8. J. F. Parker: Kavli Fellowship (2018)
9. D. R. Rolison: Elected, Council Delegate, American Association for the Advancement of Science (2019–2021)
10. D. R. Rolison: External Advisory Board for the UCLA–led DOE–funded Energy Frontiers Research Center on Synthetic Control Across Length-scales for Advancing Rechargeables (SCALAR), Los Angeles, CA (2018–present)
11. M. B. Sassin: Member of the Board for the Society for Electroanalytical Chemistry (SEAC)
12. D. R. Rolison: External Advisory Board for the University of Utah–led NSF Center for Synthetic Organic Chemistry (2019–present)

Additional Information

Presentations

1. D. R. Rolison, Controlling the Rates of Electrochemical Environments through Architectural Design on the Nanoscale. Department of Chemistry, Oregon State University, Corvallis, OR, 3 November 2015. **(INVITED)**
2. D. R. Rolison, J. W. Long, C. N. Chervin, J. F. Parker, M. B. Sassin. Chemically Modified 3D Energy-Storage Architectures (Symposium on Nano-Electroanalysis for a Sustainable World), *Pittcon 2016*, Atlanta, GA, 6–10 March 2016. **(INVITED)**
3. J. W. Long, M. B. Sassin, C. N. Chervin, J. M. Wallace, D. R. Rolison, Understanding Pseudocapacitive Charge Storage in Transition Metal Oxides from Fundamental Interfacial Processes to 3D Electrode Design (ENFL Symposium on Batteries & Supercapacitors), 251st Meeting of the American Chemical Society, San Diego, CA, 13–17 March 2016. **(INVITED)**
4. P. E. Pehrsson, C. R. Field, K. Sullivan, M. Hammond, D. Ratchford, C. N. Chervin, D. Sofge, D. R. Rolison, S. Rose-Pehrsson, Carbon Monoxide Plume Detection with Nanowire-Based Sensors Mounted on an Unmanned Ground Vehicle (Symposium on Applications of Chemical Sensors), 16th International Meeting on Chemical Sensors (*IMCS 2016*), Jeju Island, Korea, 10–13 July 2016.
5. D. R. Rolison, Enhancing Electrochemical Energy Storage on the Macroscale via Architectural Design on the Nanoscale. National Institute of Standards & Technology, Gaithersburg, MD, 16 September 2016. **(INVITED)**
6. J. W. Long, M. B. Sassin, J. M. Wallace, D. R. Rolison, Understanding Pseudocapacitive Charge Storage in Transition Metal Oxides from Fundamental Interfacial Processes to 3D Electrode Design (Symposium on Electrochemical Capacitors and Related Devices: Fundamentals to Applications), 230th Meeting of the Electrochemical Society & Pacific Rim Meeting (*PRIME*), Honolulu, HI, 2–7 October 2016. **(INVITED)**
7. D. R. Rolison, Enhancing Electrochemical Energy Storage on the Macroscale via Architectural Design on the Nanoscale. Dept of Chemical & BioEngineering and the Energy Research Center, University of Maryland, College Park, MD, 21 October 2016. **(INVITED)**

8. D. R. Rolison, Designing Catalytic and Energy-Relevant Multifunctional Architectures. 2016 SNO (Sustainable Nanotechnology Organization) Conference, 10–12 November 2016, Orlando, FL. **(INVITED PLENARY)**
9. D. R. Rolison, M. D. Donakowski, J. M. Wallace, M. B. Sassin, K. W. Chapman, J. F. Parker, J. W. Long, Crystal Engineering Energy-Storage Materials in 3D: Converting Nanoscale Pseudocapacitive Lamellar Manganese Oxide to Battery-Relevant Cubic Spinel while Affixed to a Carbon Architecture (EC2: Facilitating Charge Transport in Electrochemical Energy Storage Materials), *Fall Meeting of the Materials Research Society*, Boston, MA, 27 November–2 December 2016.
10. M. C. Palenik, B. I. Dunlap, General Degeneracy in Density Functional Perturbation Theory *March Meeting of the American Physical Society*, New Orleans, LA, 13–17 March 2017.
11. D. R. Rolison, Solution-Deposition of Disordered RuO₂ Nanoskins: An Example from the Fourth Quadrant of Electronic Materials (Symposium in honor of Douglas A. Keszler, ACS Award in the Chemistry of Materials), 253rd Meeting of the American Chemical Society, San Francisco, CA, 2–6 April 2017. **(INVITED)**
12. D. R. Rolison, J. W. Long, C. N. Chervin, J. S. Ko, Something from Nothing: Enhancing Cathode Electrochemical Charge Storage with Cation Vacancies (Symposium in Honor of Michael Thackeray E. V. Murphree Award), 253rd Meeting of the American Chemical Society, San Francisco, CA, 2–6 April 2017. **(INVITED)**
13. J. W. Long, J. F. Parker, M. D. Donakowski, M. B. Sassin, J. M. Wallace, D. R. Rolison, Understanding Pseudocapacitive Charge Storage from Fundamental Interfacial Processes to 3D Electrode Design (ANYL/CATL Symposium on Synthesis & Characterization of Materials for Energy Applications), 253rd Meeting of the American Chemical Society, San Francisco, CA, 2–6 April 2017. **(INVITED)**
14. D. R. Rolison, M. D. Donakowski, J. M. Wallace, M. B. Sassin, K. W. Chapman, J. F. Parker, J. W. Long, C. N. Chervin, I. R. Pala, A. N. Mansour Thin-Film Pair Distribution Analyses of Energy-Storage Materials in Device-Ready 3D Electrode (ANYL/CATL symposium on Synthesis & Characterization of Materials for Energy Applications), 253rd Meeting of the American Chemical Society, San Francisco, CA, 2–6 April 2017. **(INVITED)**
15. J. C. Lytle, G. E. Kamm, A. D. McGovern, J. F. Parker, M. D. Donakowski, D. R. Rolison, J. W. Long, Studying the Kinetics of Electrochemical Reactions on Ruthenia-Coated Carbon Electrodes (ANYL/CATL symposium on Synthesis & Characterization of Materials for Energy Applications), 253rd Meeting of the American Chemical Society, San Francisco, CA, 2–6 April 2017. **(INVITED)**
16. G. E. Kamm, A. D. McGovern, J. C. Lytle, J. F. Parker, M. D. Donakowski, D. R. Rolison, J. W. Long, Modifying Carbon Electrodes to Behave Like Precious Metals (ANYL/CATL symposium on Synthesis & Characterization of Materials for Energy Applications), 253rd Meeting of the American Chemical Society, San Francisco, CA, 2–6 April 2017.
17. D. R. Rolison, Aerogels: An Architectural Guide to Advances in Energy (NM3: Aerogels and Aerogel-Inspired Materials), *Spring Meeting of the Materials Research Society*, Phoenix, AZ, 17–21 April 2017. **(INVITED)**
18. D. R. Rolison, Why Are We Leaving So Much Power & Energy on the Table? 10th Potters Lodge Meeting (PLM10), Blue Mountain Lake, NY, 6–10 September 2017.
19. J. W. Long, J. S. Ko, M. B. Sassin, J. F. Parker, D. R. Rolison, Interfacial Phenomena at the Junction of Conductive Carbon with Pseudocapacitive Metal Oxides and Polymers: Implications for Electrochemical Capacitors (A07: Fast Electrochemical Processes & Devices), 232nd Meeting of the Electrochemical Society, National Harbor, MD, 1–5 October 2017.
20. J. S. Ko, J. W. Long, M. B. Sassin, J. F. Parker, D. R. Rolison, Combining Battery-Like and Pseudocapacitive Charge Storage in 3D MnO_x–Carbon Electrode Architectures for Zinc-Ion

- Cells (A07: Fast Electrochemical Processes & Devices), 232nd Meeting of the Electrochemical Society, National Harbor, MD, 1–5 October 2017.
21. P. A. DeSario, C. N. Chervin, E. S. Nelson, M. B. Sassin, D. R. Rolison, Demonstrating the Activity and Stability of Conformal RuO₂ “Nanoskins” on Technologically Relevant, 3D Electrode Supports for Water Oxidation in Acid Electrolyte (L02: Photocatalysts, Photoelectrochemical Cells, and Solar Fuels), 232nd Meeting of the Electrochemical Society, National Harbor, MD, 1–5 October 2017.
 22. J. S. Ko, M. B. Sassin, J. F. Parker, D. R. Rolison, J. W. Long, Designing and Understanding Fast Redox Processes of Manganese Oxide at Time Scales Relevant to Battery-Like and Pseudocapacitive Charge Storage. Gordon Research Seminar on Batteries, Ventura, CA, 24–25 February 2018.
 23. J. S. Ko, M. B. Sassin, J. F. Parker, D. R. Rolison, J. W. Long, Designing and Understanding Fast Redox Processes of Manganese Oxide at Time Scales Relevant to Battery-Like and Pseudocapacitive Charge Storage. Gordon Research Conference on Batteries, Ventura, CA, 25 February–2 March 2018.
 24. J. C. Lytle, G. E. Kamm, T. Le, E. M. Ness, J. F. Parker, D. R. Rolison, J. W. Long, Studying the Rate of Electron Transfer at Pyrolytic Carbon Electrodes (ENFL symposium on Innovative Chemistry and Materials for Electrochemical Energy Storage), 255th Meeting of the American Chemical Society, New Orleans, LA, 18–22 March 2018.
 25. G. E. Kamm, T. Le, E. M. Ness, J. C. Lytle, J. F. Parker, D. R. Rolison, J. W. Long, Electrochemical Analysis of Gold-Modified Carbon Electrodes for Energy Storage Applications (ENFL symposium on Innovative Chemistry and Materials for Electrochemical Energy Storage), 255th Meeting of the American Chemical Society, New Orleans, LA, 18–22 March 2018.
 26. G. E. Kamm, T. Le, E. M. Ness, J. C. Lytle, J. F. Parker, D. R. Rolison, J. W. Long, Decorating Carbon Electrodes with Gold Nanoparticles to Study the Kinetics of Redox Reactions (ENFL symposium on Innovative Chemistry and Materials for Electrochemical Energy Storage), 255th Meeting of the American Chemical Society, New Orleans, LA, 18–22 March 2018 (poster).
 27. D. R. Rolison, M. D. Donakowski, M. B. Sassin, J. M. Wallace, K. W. Chapman, C. N. Chervin, A. N. Mansour, J. W. Long, Crystal Engineering Pseudocapacitive Materials in 3D Architectures (EN13: Capacitive Energy Storage: Fundamentals, Materials & Devices), *Spring Meeting of the Materials Research Society*, Phoenix, AZ, 2–6 April 2018. **(INVITED)**
 28. J. W. Long, J. S. Ko, J. F. Parker, M. B. Sassin, D. R. Rolison, Expressing Battery-Like and Pseudocapacitive Charge Storage in 3D MnOx@Carbon Electrode Architectures via Control of Nanocrystalline Oxide Structure and Electrolyte Composition (EN13: Capacitive Energy Storage: Fundamentals, Materials & Devices), *Spring Meeting of the Materials Research Society*, Phoenix, AZ, 2–6 April 2018. **(INVITED)**
 29. J. W. Long, J. S. Ko, M. B. Sassin, J. F. Parker, D. R. Rolison, Rechargeable, Aqueous Zinc-Ion Batteries with Pulse-Power Capability Enabled by Nanostructured Manganese Oxides and Mixed-Salt Electrolytes. 48th Power Sources Conference, Denver, CO, 11–14 June 2018.
 30. J. W. Long, J. S. Ko, M. B. Sassin, J. F. Parker, D. R. Rolison, Differentiating Double-Layer, Pseudocapacitance, and ‘Fast Battery’ Mechanisms in Charge-Storing Nanomaterials—From Model 2D Interfaces to Multifunctional Electrode Architectures. 256th Meeting of the American Chemical Society, Boston, MA, 19–23 August 2018. **(INVITED)**
 31. D. R. Rolison, M. D. Donakowski, M. B. Sassin, J. M. Wallace, K. W. Chapman, C. N. Chervin, A. N. Mansour, J. W. Long, Crystal Engineering Energy Storage into 3D Architectures (Symposium on Innovative Chemistry, Materials & Characterizations for Electrochemical

- Energy Storage), 256th Meeting of the American Chemical Society, Boston, MA, 19–23 August 2018. **(INVITED)**
32. J. W. Long, J. S. Ko, M. B. Sassin, J. F. Parker, D. R. Rolison, Deconvolution of Double-Layer, Pseudocapacitance, and Battery-Like Contributions to Charge-Storage in MnOx@Carbon Electrode Architectures and Interfaces (A03: Fast Electrochemical Processes and Devices (Electrochemical Capacitors and Batteries) 2), 234th Meeting of the Electrochemical Society and SMEQ Joint International Meeting, 30 September–4 October 2018, Cancún, Mexico. **(INVITED)**
 33. M. B. Sassin, Enhancing Energy on the Macroscale via Architectural Design on the Nanoscale. Colloquium to the Department of Chemical Engineering, University of Virginia, Charlottesville, VA, 6 December 2018. **(INVITED)**
 34. M. B. Sassin, Energy-Storage Research in the Advanced Electrochemical Materials Section and Student Internship Opportunities at the US NRL. Student Seminar Series, Department of Chemistry, Xavier University, New Orleans, LA, 17 January 2019. **(INVITED)**
 35. M. B. Sassin, Enhancing Energy Storage on the Macroscale via Architectural Design on the Nanoscale and Student Internship Opportunities at the US NRL. Department of Mechanical Engineering, University of Maryland-Baltimore County, Baltimore, MD, 1 March 2019.
 36. E. N. Ness, J. E. Kelm, J. C. Lytle, J. F. Parker, D. R. Rolison, J. W. Long, Studying the Rate of Redox Reactions on Gold-Modified Pyrolytic Carbon Electrodes (ENFL: Innovative Chemistry and Materials for Electrochemical Energy Storage), 257th Meeting of the American Chemical Society, Orlando, FL, 31 March – 4 April 2019.
 37. J. E. Kelm, E. N. Ness, J. C. Lytle, J. F. Parker, D. R. Rolison, J. W. Long, Modifying Carbon Electrodes with Sulfur and Gold Nanoparticles to Study the Kinetics of Redox Reaction (ENFL: Innovative Chemistry and Materials for Electrochemical Energy Storage), 257th Meeting of the American Chemical Society, Orlando, FL, 31 March – 4 April 2019.
 38. J. W. Long, J. S. Ko, M. B. Sassin, J. F. Parker, C. N. Chervin, D. R. Rolison, Pyrolytic Carbon Films with Tunable Electronic Structure and Surface Functionality: A Planar Stand-In for Electroanalysis of Energy Relevant Reactions (CP04: Interfacial Science and Engineering—Mechanics, Thermodynamics, Kinetics and Chemistry), Spring Meeting of the Materials Research Society, Phoenix, AZ, 22–26 April 2019.
 39. J. W. Long, J. S. Ko, M. B. Sassin, C. N. Chervin, J. F. Parker, S. Jeon, C. R. So, D. R. Rolison, Battery-Like versus Pseudocapacitive Behavior at Nanostructured Manganese Oxides: Mechanistic Insights from 2D Interfaces to Advanced 3D Electrode Architectures. *International Symposium on Enhanced Electrochemical Capacitors (ISEECap 2019)*, Nantes, France, 6–10 May 2019. **(INVITED)**
 40. D. R. Rolison, J. F. Parker, J. S. Ko, B. J. Hopkins, C. N. Chervin, P. A. DeSario, M. B. Sassin, J. W. Long, Effect of Architecturally Expressed Electrodes and Catalysts on Energy Storage/Conversion in Aqueous Electrolytes (I05: Heterogeneous Functional Materials for Energy Conversion and Storage 2), 235th Meeting of the Electrochemical Society, Dallas, TX, 26–31 May 2019. **(INVITED KEYNOTE)**
 41. D. R. Rolison, Aerogels: An Architectural Guide to Advances in Energy. *NERM 2019 (Northeast Regional Meeting of the American Chemical Society)*, Saratoga Springs, NY, 23–26 June 2019. **(INVITED KEYNOTE)**
 42. M. Helms, M. B. Sassin, A. N. Hoffmaster, C. N. Chervin, J. F. Parker, J. S. Ko, M. D. Donakowski, D. R. Rolison, J. W. Long, Elucidating the Charge-Storage Mechanisms of Zn-Ion Batteries Comprising 3D MnOx-Based Electrode Architectures and Aqueous Electrolytes. *NERM 2019 (Northeast Regional Meeting of the American Chemical Society)*, Saratoga Springs, NY, 23–26 June 2019.

43. J. W. Long, J. S. Ko, M. B. Sassin, C. N. Chervin, J. F. Parker, S. Jeon, C. R. So, D. R. Rolison, Straddling the Battery–Capacitor Boundary with Nanostructured Manganese Oxides: Mechanistic Insights from 2D Interfaces to Advanced 3D Electrode Architectures (A05: Alternative Battery Chemistries and High-Power Devices), *Electrochemical Conference on Energy and the Environment (ECEE 2019): Bioelectrochemistry and Energy Storage*, Glasgow, Scotland, 21–26 July 2019. **(INVITED)**
44. M. B. Sassin, J. W. Long, J. S. Ko, C. N. Chervin, J. F. Parker, M. E. Helms, S. Jeon, C. R. So, D. R. Rolison, Bifunctional Charge Storage via Nanostructured Electrolytes and Electrolyte Composition. *6th International Conference on Advanced Capacitors*, Ueda, Japan, 8–12 September 2019. **(INVITED KEYNOTE)**
45. J. W. Long, J. S. Ko, M. B. Sassin, C. N. Chervin, J. F. Parker, S. Jeon, C. R. So, D. R. Rolison, The Intersection of Battery and Capacitor Function in Nanostructured Manganese Oxides for Zinc-Ion Cells: Insights from 2D Interfaces to 3D Electrodes. *236th Meeting of the Electrochemical Society*, Atlanta, GA, 13–17 October 2019. **(INVITED)**
46. C. N. Chervin, J. W. Long, M. B. Sassin, J. F. Parker, C. R. So, S. Jeon, D. R. Rolison, Pyrolytic Carbon Films with Tunable Electronic Structure and Surface Functionality: A Planar Stand-In for Electroanalysis of Energy-Relevant Reactions (B01: Carbon Nanostructures: From Fundamental Studies to Applications and Devices), *236th Meeting of the Electrochemical Society*, Atlanta, GA, 13–17 October 2019.
47. D. R. Rolison, M. B. Sassin, J. F. Parker, C. N. Chervin, J. W. Long, The Importance of Modifying the Nothing within 3D Electrode Architectures for Solid-State Energy Storage (MS2: Science and Technology for Manufacturing: Solid State Batteries), *66th AVS International Symposium*, Columbus, OH, 20–25 October 2019. **(INVITED KEYNOTE)**
48. D. R. Rolison, Scalable Multifunctional Nanoarchitectures for Energy Storage. Department of Chemistry, Ohio State University, Columbus, OH, 22 October 2019. **(INVITED)**
49. D. R. Rolison, Scalable Multifunctional Nanoarchitectures for Energy Storage. Department of Materials Science & Engineering, University of Pennsylvania, Philadelphia, PA, 24 October 2019. **(INVITED)**
50. M. E. Helms, M. B. Sassin, J. F. Parker, C. N. Chervin, J. S. Ko, D. R. Rolison, J. W. Long, Next-Generation Zn-Ion Batteries with Enhanced Rechargeability and High-Rate Operation via 3D Nanostructured Electrodes and Mixed Salt Electrolytes (Hot Topics: Materials for High-Energy and Safe Electrochemical Energy Storage), *Fall Meeting of the Materials Research Society*, Boston, MA, 1–6 December 2019.
51. M. B. Sassin, J. F. Parker, C. R. So, S. Jeon, M. E. Helms, C. N. Chervin, J. W. Long, D. R. Rolison, Pyrolytic Carbon Films with Tunable Electronic Structure and Surface Functionality: A Planar Stand-In for Electroanalysis of Energy-Relevant Reactions. *Pittcon 2020*, Chicago, IL, 1–5 March 2020.
52. D. R. Rolison, Architectural Design, 1D Walls, 3D Plumbing, and Painting Blind en Route to Scalable Multifunctional Nanoarchitectures for Energy Storage. Graduate Student Seminar Series, Department of Chemistry, Georgia Institute of Technology, Atlanta, GA, 10 March 2020. **(INVITED)**
53. M. B. Sassin, M. E. Helms, J. F. Parker, C. N. Chervin, J. S. Ko, D. R. Rolison, J. W. Long, Rechargeable Zn-Ion Batteries via Multifunctional 3D Electrodes and Mixed-Salt Electrolytes. (Batteries and Energy Storage), *PRiME 2020 (ECS, ECSJ, & KECS Joint Meeting)*, Honolulu, HI, 4–9 October, 2020. **(VIRTUAL)**

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- ² J. W. Long, B. M. Dening, T. M. McEvoy, D. R. Rolison, Carbon aerogels with ultrathin electroactive poly(*o*-methoxyaniline) coatings as high-performance electrochemical capacitors. *J. Non-Cryst. Solids* **2004**, *350*, 97–106.
- ³ A. E. Fischer, K. A. Pettigrew, D. R. Rolison, R. M. Stroud, J. W. Long, Incorporation of homogeneous, nanoscale MnO₂ within ultraporous carbon structures via self-limiting electrodeposition: Implications for electrochemical capacitors. *Nano Lett.* **2007**, *7*, 281–286.
- ⁴ D. R. Rolison, J. W. Long, J. C. Lytle, A. E. Fischer, C. P. Rhodes, T. M. McEvoy, M. E. Bourg, A. M. Lubers, Multifunctional 3D architectures for energy storage and conversion. *Chem. Soc. Rev.* **2009**, *38*, 226–252.
- ⁵ J. W. Long, M. B. Sassin, A. E. Fischer, D. R. Rolison, A. N. Mansour, V. S. Johnson, P. E. Stallworth, S. G. Greenbaum, Multifunctional MnO₂–carbon nanoarchitectures exhibit battery and capacitor characteristics in alkaline electrolytes. *J. Phys. Chem. C* **2009**, *113*, 17595–17598.
- ⁶ M. B. Sassin, J. W. Long, C. N. Chervin, and D. R. Rolison, Redox deposition of nanoscale metal oxides on carbon for next-generation electrochemical capacitors. *Acc. Chem. Res.* **2013**, *46*, 1062–1074.
- ⁷ M. D. Donakowski, J. M. Wallace, M. B. Sassin, K. Chapman, J. W. Long, J. F. Parker, D. R. Rolison, Crystal engineering in 3D: Converting nanoscale lamellar manganese oxide to cubic spinel while affixed to a carbon architecture. *Cryst. Eng. Commun.* **2016**, *18*, 6035–6048.
- ⁸ J. C. Lytle, T. H. Zimmerman, K. A. Pettigrew, and D. R. Rolison, *ECS J. Solid-State Sci. Technol.* **2013**, *2*, M3078–M3083.
- ⁹ J. C. Lytle, T. H. Zimmerman, and D. R. Rolison, US Patents nr. **8,475,698** (July 2, 2013) and **9,017,780** (April 28, 2015).
- ¹⁰ J. F. Parker, G. E. Kamm, A. D. McGovern, P. A. DeSario, D. R. Rolison, J. C. Lytle, J. W. Long, Rewriting electron-transfer kinetics at pyrolytic carbon electrodes decorated with nanometric RuO₂. *Langmuir* **2017**, *33*, 8416–942.
- ¹¹ J. F. Parker, C. R. So, J. S. Ko, S. Jeon, M. B. Sassin, C. N. Chervin, J. C. Lytle, M. E. Helms, D. R. Rolison, J. W. Long, Pyrolytic carbon films with tunable electronic structure and surface functionality: A planar stand-in for electroanalysis of energy-relevant reactions. *ChemElectroChem* **2020**, *7*, 672–683.
- ¹² P. H. Chen, M. A. Fryling, R. L. McCreery, Electron-transfer kinetics at modified carbon electrode surfaces—the role of specific surface sites. *Anal. Chem.* **1995**, *67*, 3115–3122.
- ¹³ M. B. Sassin, S. G. Greenbaum, P. E. Stallworth, A. N. Mansour, B. P. Hahn, K. A. Pettigrew, D. R. Rolison, J. W. Long, Achieving electrochemical capacitor functionality from 3D nanoscale LiMn₂O₄. *J. Mater. Chem. A* **2013**, *23*, 2431–2440.
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