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Electrode Reactions Probed by In Situ NMR: The Dawn of a New Understanding

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14. ABSTRACT

Electrochemical reactions play a critical role within the Navy and Marine Corps in areas ranging from fuel cells to corrosion. In this program our team has worked to develop new experimental tools for in situ electrochemical nuclear magnetic resonance (NMR) and X-ray absorption spectroscopy (XAS) and new theoretical tools involving density perturbation theory for practical quantum chemical calculations of chemical perturbations which together will yield fundamental new insights into these reactions.

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Objective

Electrochemical reactions play a critical role within the Navy and Marine Corps in areas ranging from fuel cells to corrosion. Our objective in this program is to obtain a fundamental understanding of electrochemistry at the atomic level. We will build an electrochemical cell compatible with nuclear magnetic resonance (NMR) and X-ray absorption spectroscopy (XAS) under reaction conditions and we will use the experimental results in theoretical modeling which incorporates electrostatics in a self-consistent way. The in-situ, atomic detail of support, electrocatalyst, and electrolyte double layer will provide a mechanistic framework to understand degradation processes such as oxide formation and chloride interactions and advanced monolayer synthesis techniques. The results of this work will aid in the design of improved materials, e.g., improved fuel cell catalysts and corrosion resistant surfaces, possible strategies to extend operational lifetime and first principle corrosion behavior for performance based maintenance programs, with broad impact to the Navy, other DoD and industry.

Manuscript approved January 14, 2020.

Technical Approach

The two major components to this project are the theoretical work by Dunlap and the experimental work by Natishan and Klug. In the initial stages our goals were to simultaneously develop the theoretical and experimental tools to study a model canonical system, pure Pt particles, and, most importantly, to demonstrate consistency between the two methods. As this is both new approach and experimental procedure, it is important to start with a simple system such as the Pt particles in order to ensure fidelity of the modeling and experiments.

Nuclear Magnetic Resonance

While there have been some reports of in-situ NMR characterization of supported fuel cell catalysts, we propose to build a unique *in-situ* electrochemical NMR cell which will allow us to perform room temperature NMR measurements under well controlled applied voltage conditions. It is crucial that we demonstrate relevant electrochemical behavior for this cell, i.e., cyclic voltammograms which show minimal IR loss, diffusion limitations, etc. The key issue in this design will be to maximize the amount of catalyst material in the NMR-sensitive region of the cell while at the same time maintaining optimal electrochemical performance. Once the cell has been tested, we will measure spectra for the metal catalysts and supports themselves, e.g., ^{195}Pt and ^{13}C NMR, as well as for bound surface species, e.g., ^{13}C and ^{1}H NMR, and ionic species present in the double-layer e.g., ^{23}Na and ^{35}Cl NMR. In this way we will directly probe changes in catalyst/support structure, bonding and reactions of surface species, and the changes in the double layer, all as a function of applied cell potential. This complete characterization of the catalyst system using *in-situ* NMR has not been done.

X-ray absorption spectroscopy

In a previous ONR D&I program, NRL Code 6134 developed a novel technique that provides more insight into x-ray absorption near edge structure (XANES) data. The technique entails constructing a molecular model that reflects the proposed chemistry and calculating the theoretical XANES spectra of the model. The XANES of the model is then compared to the experimental data. This modeling technique provided insights into oxide film breakdown on aluminum leading to pitting corrosion by comparing X-ray absorption spectra with theoretical models that investigated how the spectrum changes with chloride in different sites in the oxide. A similar approach could reveal how the platinum catalyst interacts with oxygen, hydrogen and other low Z elements and these results will complement the information obtained from the NMR data.

Theory

Electrochemistry is driven by local voltage differences which determine the rates of electrochemical events. The local voltage difference, however, is altered self-consistently by local imbalances between ionic and electronic charges. That charge imbalance affects the electric moments seen at the sites of NMR-active nuclei, which can be measured or computed through the solution of the Poisson's equation. Thus NMR is sensitive to electrochemistry. The atomic specificity of NMR provides unique and precise experimental characterization of the local electrochemical environment at each nucleus on the surface of a catalyst. Theoretical NMR chemical shifts and electric field gradients are available from electronic structure computer codes through quantum-mechanical perturbation theory. Electrochemical fields apply an additional

perturbation. Theory provides unique and precise, but model-dependent, characterization of the local electrochemical environment at each nucleus on the surface of a catalyst. External voltages and unbalanced charges create long-range forces that tilt the barriers to ionic chemical reactions over the entire double layer. The dynamics of the electrochemical double layer is a self-consistent-field (SCF) problem similar to the electronic structure of atoms and molecules. The self-consistency of the chemistry in the double layer will be treated via Arrhenius rates for ionic reactions that are tilted by the local electric field. Self-consistency will fundamentally alter our understanding of electrochemistry as it did for electronic structure calculations. This approach has successfully modeled an entire solid-oxide fuel cell, including both double layers.

Results and Discussion

Technical Progress—Year 1

In December 2014 the team visited Professor YuYe Jay Tong at Georgetown University to meet with Professor Tong and his research group. We learned more about their research in electrochemical NMR and agreed to future collaborative studies of some novel materials.

Although this program officially began in FY15, some preliminary data was obtained during the application process which demonstrated a proof of concept. Platinum-195 NMR spectra were obtained at low field for two very different materials, unsupported relatively monodisperse Pt nanoparticles and a commercial Pt on carbon catalyst, typical of those which will be studied in this program—Figure 1. The significant differences in the two spectra demonstrated our ability to obtain information about catalyst structure from ^{195}Pt NMR spectra.

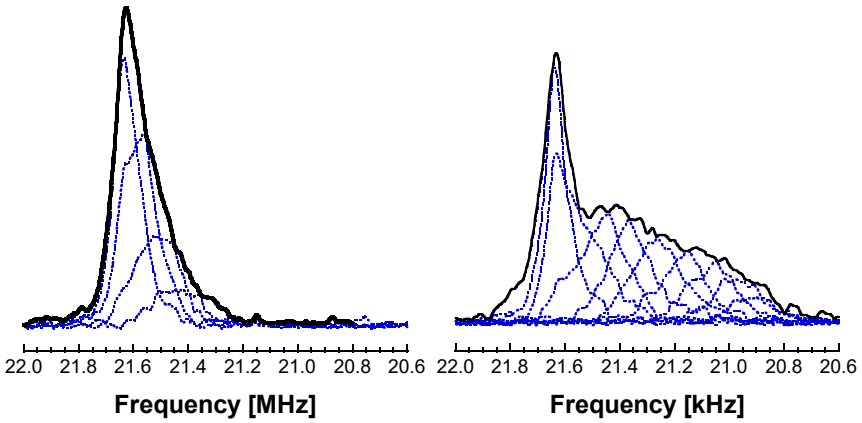

Figure 1: ^{195}Pt NMR spectra obtained for relatively monodisperse nanoparticles and a commercial 20wt% Pt/C catalyst. These spectra were obtained by combining a series of sub-spectra (shown in blue).

During the first year of this program Natishan's group in Code 6134 began working on designing a novel electrochemical cell suitable for NMR measurements. They initially planned to use CAD software and 3-D-printing technologies to produce a plastic cell. This would allow that once the first-generation cell is produced, future modifications would be made easily. An initial electrode-only cell was constructed to test the NMR sensitivity and assess whether multiple parallel electrodes were feasible.

During the first year of this program Klug performed NMR measurements of as-received catalytic materials with the goal of optimizing the signal-to-noise of the spectrometer in the frequency regime near 20 MHz, the resonance frequency for ^{195}Pt at 2.35 T. Two commercial Pt on carbon catalysts with Pt loadings of 20% and 30% were fully characterized at room temperature. Demonstration of improved sensitivity at low fields is a significant result counter to the prevailing NMR literature. In addition, Klug began pursuing another novel approach for studying broad NMR spectra which involves moving the NMR probe within the superconducting magnet so that the sample experiences different fields. Equipment for doing this via automation was assembled and the concept was tested during the summer of 2015.

During the first year of this program, Dunlap and an NRL Post-Doc, Mark Palenik, partially supported by this project, have defined density perturbation theory—Reference 2. The focus of density perturbation theory (DPT) is the change in electronic density due to a perturbation such as an applied voltage or electron transfer. It is based on density-functional theory (DFT) and is computationally faster than wavefunction perturbation theory in DFT because focusing the density eliminates the need to apply coupled-perturbed Kohn-Sham theory independently to each molecular orbital. DPT is most efficient when both the original and perturbed densities are variationally fitted—Reference 3.

Atom-precise metal clusters allow detailed comparison between NMR experiment and theory. Metalloid clusters are atom-precise metal clusters that are big enough to have interior atoms bound only to other metal atoms, but are protected with organic ligands. Like C_{60}, they are likely to be icosahedral for enhanced electronic and magnetic stability. That enhanced stability enables self-assembly. A particularly intriguing metalloid cluster is $Al_{50}Cp^*_{12}$, where Cp* is fully methylated cyclopentadiene. It self assembles (from special precursors). Precise atomic positions are known. All but the central eight aluminum atoms are in icosahedral positions ($Al_{50}C_{120}H_{180}$: A Pseudofullerene Shell of 60 Carbon Atoms and 60 Methyl Groups Protecting a Cluster Core of 50 Aluminum Atoms, J. Vollet, J. R. Hartig, and H. Schnöckel, Angew. Chem. Int. Ed. 43, 3186-3189 (2004)). NRL developed Solid-Harmonic-Gaussian Density-Functional Theory (SHGDFT) geometry optimizations of these and related compounds have been performed. The core has 50 Al atoms because icosahedral $Al_{55}Cp^*_{12}$ has an open electronic shell. The 55-metal atom core can be stabilized best with an Mn, but other valence-2 atom might also lead to self-assembly.

Technical Progress—Year 2

During FY16 Carlos Hangarter became the primary participant from Code 6134, taking over the role of Paul Natishan, although Natishan still provided guidance. In addition to design of the *in situ* electrochemical NMR cell, Hangarter focused on optimizing the electrodes which will be compatible with the *in situ* electrochemical NMR cell. Optimization involves ensuring adequate NMR sensitivity (see below), mechanical robustness, and proper electrochemical behavior. The current electrode consists of Pt at 3 mg/cm^2 loaded on a carbon fiber matrix on a gold current collector. This corresponds to roughly 4440 cm^{2}Pt/cm^2. A flow cell design was produced and manufactured. A closed cell design was tested electrochemically and prepared to interface with the NMR system during the interim.

Hangarter received beamtime at the National Synchrotron Light Source II (NSLS II) at Brookhaven National Lab in December 2016. A new cell was designed to observe complimentary Pt catalysts as those utilized in the NMR cell. The cell is shown schematically in the figure below. A flow cell design was incorporated to facilitate in-situ surface functionalization, however flow was utilized during Pt catalyst characterization as the cyclic pressure profile from the pump imposed dynamic behavior in Kapton windows that interfered with XAS measurements. The electrochemical configuration consisted half cells for the working and counter electrode separated by a 25 micron Nafion membrane. The work electrode was a mechanically robust Pt catalyst layer placed on a gold current collector containing a hole to minimize beam attenuation. The counter electrode consisted of the same carbon support as the

working electrode sans Pt and had a ring geometry to minimize beam attenuation. The assembled cell contained an electrolyte of 0.1 $HClO_4$ as perchlorate is electrochemically non-adsorbing and spectroscopically non-absorbing. Three different commercial Pt catalysts were examined, 10% Pt, 20%Pt and 30%Pt. While the loading indicates the mass loading of Pt the synthesis process for these different loadings results in vendor specified sizes of <2nm, 2-3nm and 2-5 nm, respectively.

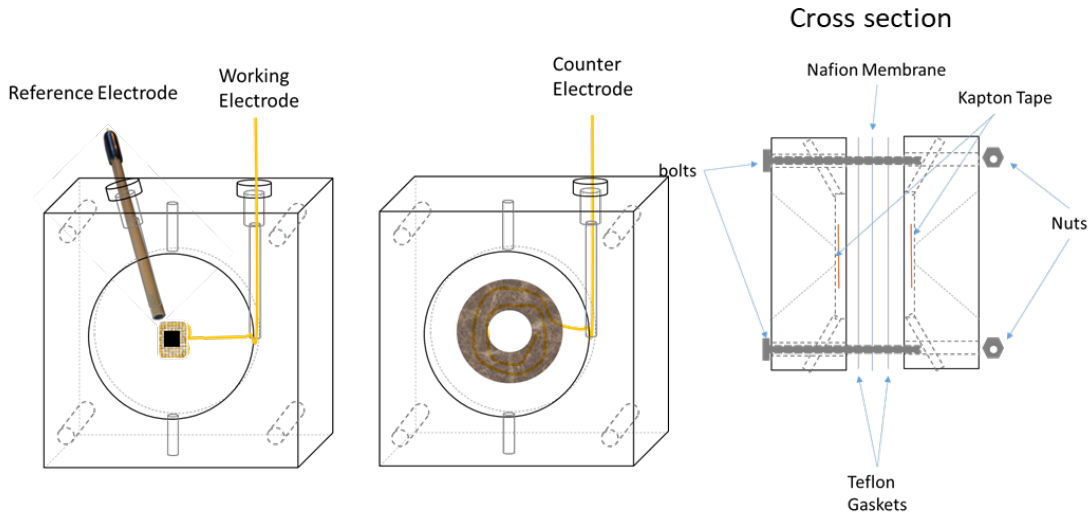

Figure 2: Schematic depiction of the XAS electrochemical cell.

The actual electrochemical cell was fashion from acrylic with a countersunk window to facilitate fluorescence measurements, however, the high Pt loading utilized for these electrodes, ~2.4-4.8 mg/cm^2 were better suited for transmission measurements. XAS measurements were performed on beamline 8-ID, a high flux, fast scanning damping wiggler spectroscopy beamline. Each sample was first cycled at a scan rate of 20 mV/s between 50 mV_{RHE} and 1100 mV_{RHE} to clean the Pt catalyst. After cycling the catalyst was held potentiostatically and XAS measurements was taken in triplicate, generally 30-90 sec per scan, after double layer current and adsorption charge relaxed (Figure 3).

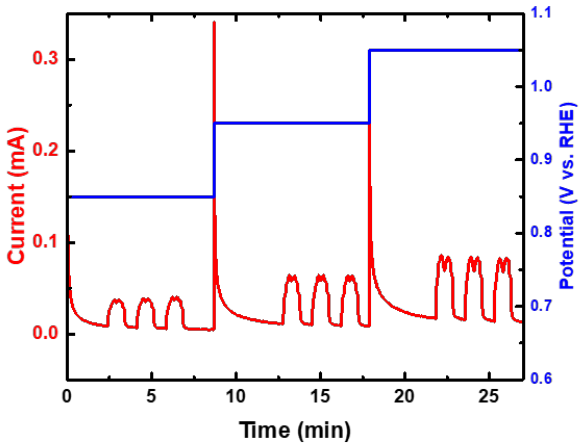

Figure 3: Current (left) and potential (right) profile of in-situ electrochemical XAS measurements.

The current displayed a unique photocurrent response not typically observed in electrochemical XAS measurements. The origins of this behavior appears to be an electrochemical form of total electron yields. The forward and reverse energy sweeps of the XAS monochromator result in a symmetric profile which is shown in triplicate for each potential. The photocurrent had a clear potential dependence with larger current responses observed at more positive potentials.

The XANES and EXAFS data for 20%Pt is shown in Figure 4 for 100mV steps from 50mV to 1150mV. The XANES shows a clear white line increase at more positive potentials. The Fourier transform (k-weight = 2) of the EXAFS also displays a potential dependent trend. The R-space profile is similar to an atomic radial distribution function and gives information of nearest neighbors in terms of atomic distance, coordination and disorder. The EXAFS plot below gives is qualitatively consistent with increased oxidation at higher potentials as indicated by a truncated Pt-Pt peak (2.72 Å) and increased Pt-O contribution (1.99 Å). These results were quantitatively fit to support NMR analysis with nearest neighbor coordination number and bond length values for both Pt-Pt and Pt-O interactions.

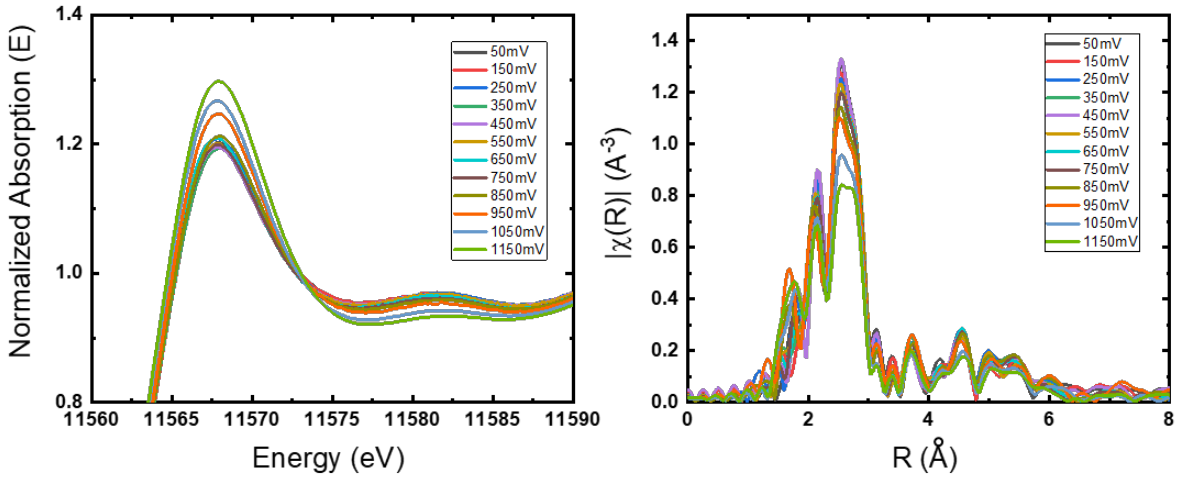

Figure 4: XANES (left) and EXAFS (right) of 20%Pt nanoparticles at indicated potentials relative to the reversible hydrogen potential.

Klug continued to optimize hardware related to the acquisition of ^{195}Pt NMR spectra. In particular he demonstrated an automated method for acquiring broad NMR spectra which involved moving the NMR probe within the superconducting solenoid magnet. This was first applied to acquire ^{195}Pt NMR spectra, but plans were made to apply this to other nuclei such as ^{19}F relevant to a DOE-funding project. Klug began measurements of ^{195}Pt NMR spectra for planar electrode materials prepared by Carlos Hangarter of Code 6130. Switching from powdered catalysts in small 3 mm diameter tubes to planar electrodes of dimensions roughly 1 cm X 5 cm X 2 mm required some modification of the NMR probe's RF coil, but the initial results and sensitivity tests were promising. Klug also began an NMR study of metalloid cluster compounds prepared at the University of Maryland—see below.

Dunlap and an NRL Post-Doc, Mark Palenik, partially supported by this project, continued to develop density perturbation theory, a tool with applicability to the modeling of large symmetric metal clusters relevant to electrocatalysis. A focus of the work was metalloid clusters, atom-precise metal clusters that are big enough to have interior atoms bound only to other metal atoms, but are protected with organic ligands. Thus they have both "surface" and "bulk" metal atoms. A collaboration with Professor Eichhorn at the University of Maryland began—he provided materials to NRL for analysis via solid state NMR by Klug. The experimental results will be compared to theoretical results using DFT methods. Data for the first sample, a presumably ionic crystal, with metalloid anion having a core of Al_5Li_4 surrounded by phenyl (Ph) ligands was synthesized for the first time at the U. of MD and shipped to NRL for analysis. An exhaustive set of NMR data on this molecule and the simpler ionic molecule $LiAlH_4$ was taken by Klug—Figures 5 and 6. This work again demonstrated the advantages of working at lower magnetic fields. The bigger molecule, called Al_5 for short, has 1012 atoms in its unit cell, which normally would make DFT calculations impossible, but all these metalloid material are highly symmetric. The Crystal14 computer code uses all crystal symmetries efficiently and self-consistent field calculations, with the help of the developers of the code, have been performed at the experimental X-ray structure using an excellent basis set, of 6-311G(d,p) quality. Mulliken population analysis shows that the crystal is clearly ionic. Two geometry optimization steps have been performed on the DOD supercomputers to show that optimization will be possible.

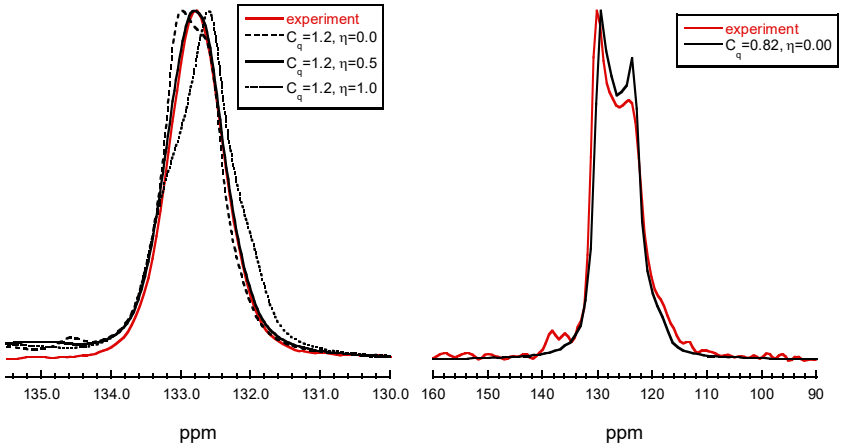

Figure 5: ^{27}Al NMR spectra for LiAlPh4 obtained at a) 11.7 T and b) 2.35 T

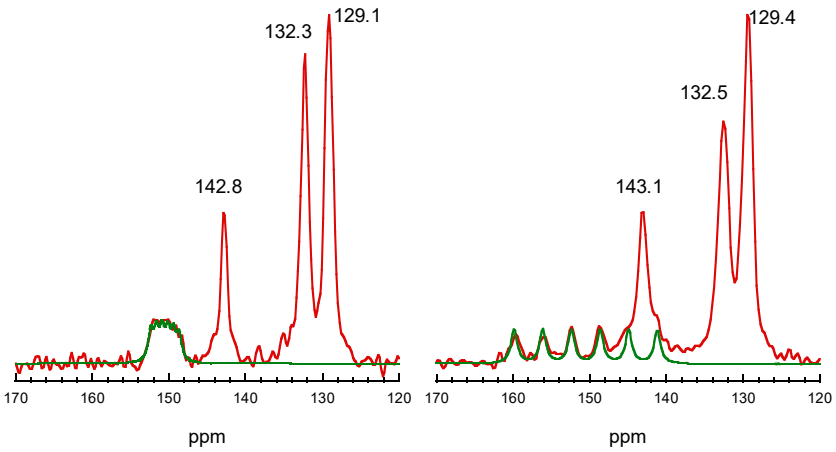

Figure 6: ^{13}C NMR spectra for $LiAlPh_4$ obtained at a) 11.7 T and b) 2.35 T

Technical Progress—Year 3

During FY17 Carlos Hangarter was again the primary participant from Code 6134. Hangarter produced three prototype electrochemical cells. Key improvements included optimization of the input connectors for the liquids to minimize leaks and optimization of the electrodes and their electrical connections. There were two electrodes, each consisting of Pt at 5 mg/cm^2 loaded on a carbon fiber matrix on a gold current collector. This represented nearly an order of magnitude increase in the total amount of Pt within the cell compared to earlier versions which will significantly improve the signal-to-noise of the NMR measurements.

Klug continued to optimize hardware related to the acquisition of ^{195}Pt NMR spectra and a manuscript was submitted which outlined the development of the technique for automated detection of broad NMR spectra at low field—Reference 9 and Figure 7. In particular he obtained ^{195}Pt NMR signals for planar electrodes prepared by Hangarter both as isolated electrodes within cylindrical quartz tubes and as electrodes within prototype electrochemical cells with and without liquid. These different electrode configurations required different RF coils and numerous designs were tested to optimize the signal-to-noise. An important factor is increasing the RF power delivered to the NMR probe's RF coil which can lead to significant improvements in signal-to-noise but also requires careful optimization of the RF coils to avoid arcing due to high voltages. Fortunately, Klug was able to use Code 6122's previous experience in RF coil designs for imaging and large scale NQR which minimize electric fields.

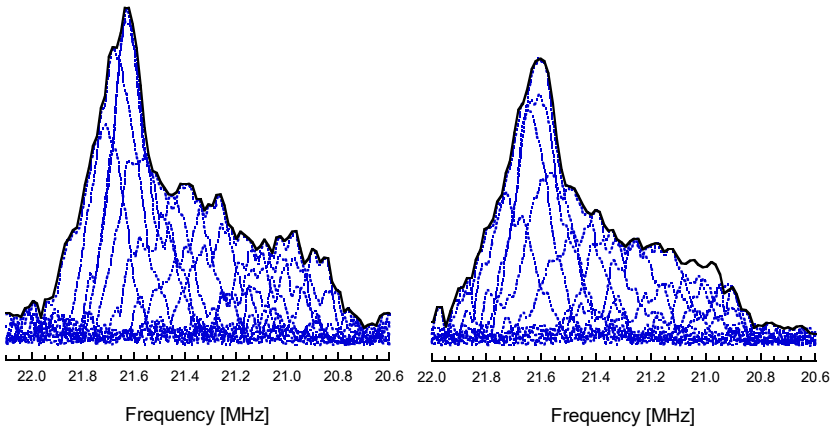

Figure 7: ^{195}Pt NMR spectra obtained for commercial supported catalysts using automated method.

Klug formed a collaboration with Eunkeu Oh (Code 5611). Taking advantage of Code 6122's optimized low field NMR spectrometer, Klug obtained ^{195}Pt NMR spectra for two Pt cluster samples where the average size is 1.0 and 2.5 nm respectively. While the smaller particles appear non-metallic in the NMR studies both in terms of their spectra and relaxation, the larger particles yield an NMR spectrum consistent with their size—Reference 7.

Sean A. Fischer joined Code 6189 and became more involved in this project. Dunlap continued to develop density perturbation theory, a tool with applicability to the modeling of metal clusters relevant to electrocatalysis. A focus of the work remained metalloid clusters, atom-precise metal clusters that are big enough to have interior atoms bound only to other metal atoms, but are protected with organic ligands. A collaboration with Professor Eichhorn at the University of Maryland began in FY16 began in FY16 with variational fitting DFT calculations to understand the magnitude of Jahn-Teller distortions from the icosahedral 3-minus to lower-symmetry 4-minus states of $Sb_{21}Pd_{12}$—Reference 6. Dunlap and Michael Conroy (Code 6185) used density functional theory to calculate NMR properties for aluminum clusters while Klug obtained ^{7}Li, ^{13}C and ^{27}Al NMR data for the materials—in preparation Reference 1. (Several of these measurements were performed at low field where the results were far superior in terms of information content relative to the high field results. Indeed, the advantages of low field NMR became one of the themes of this project and some of these results were presented in January 2017 at an NMR symposium at Washington University in Saint Louis.) Density perturbation theory for the Jahn-Teller effect was begun.

Technical Progress—Year 4

During FY18, Hangarter continued to make improvements in the design of the electrochemical cell to eliminate leaks and optimize electrical connections. This led to a significant improvement in the long-term stability of the electrochemical cell. Active potentiostatic control was introduced and cyclic voltammetry measurements were performed. As was anticipated, significant RF noise was observed in the in-situ NMR experiments. Hangarter and Klug worked closely to minimize the RF noise pickup by introducing robust low pass filters and improving the RF shielding and grounding of all the electrical cables. They demonstrated ^{195}Pt NMR signal

detection under active potentiostatic control. Additional work was focused on eliminating a background ^{63}Cu NMR signal which arises at high frequency and low field.

Hangarter also developed a cell that allows electrochemical control of electrocatalysts and simultaneous X-ray absorption spectroscopy (XAS) measurements. This cell was utilized to conduct XAS measurements of commercial Pt nanoparticles as function of electrochemical conditions and particle size on beamline 8-ID at National Synchrotron Light Source II (NSLS II). An additional general user proposal and beamtime request was awarded for the fourth quarter of calendar year 2018. As part of this visit an electrochemical cell array and associated fluidics were designed and constructed for automation of XAS measurement with electrochemical experiments. In that visit, Hangarter look specifically at an electrochemical monolayer deposition system, trying to capture the mechanism of Pt deposition termination by examination of Pt on Au nanoparticles. The extreme deposition deposition conditions suffered from iR drop not relevant at normal electrochemical operating conditions and are still being analyzed as sufficient care must be taken to deconvolve Pt and Au spectra.

The automated technique for detection of broad NMR spectra developed in this project was applied to a collaboration with Savannah River National Laboratory: Characterization of the Environmentally Induced Chemical Transformations of Uranium Tetrafluoride. The ^{19}F NMR spectrum for this material is broad due to the paramagnetic U^{4+} species. Using a specially designed glassware apparatus, the ^{19}F NMR spectra were followed as a function of time under constant humidity conditions. Significant chemical changes were observed to occur over the time period of days.

During FY18, the collaboration with Professor Eichhorn at the University of Maryland to study metalloid clusters continued. Additional ^{27}Al NMR spectra for aluminum clusters were obtained with the goal of obtaining a clear spectrum for the Al_5 cluster.

Expanding on the earlier metalloid cluster work, Fischer has collaborated with Andrew Purdy (Code 6123), Raymond Butcher (Howard University), James Yesinowski (Code 6122), Daniel Gunlycke (Code 6189), and Brian Chaloux (Code 6123) in the synthesis and characterization of the largest reported Sn cluster with all Sn atoms 4-coordinate. Fischer used density functional theory to calculate the NMR properties of the newly synthesized Sn cluster. The theoretical calculations helped in confirming that the core of the cluster is qualitatively similar to α-Sn. This work was published—Reference 7.

Technical Progress—Year 5

The primary goal of FY19 was to complete the testing of the in situ NMR electrochemical cell and to begin acquiring ^{195}Pt NMR spectra as a function of applied potential. While initial results were promising, it was soon discovered that the NMR spectra did not match the expected ^{195}Pt NMR spectra for supported catalysts. In particular, NMR signals were observed for resonance frequencies well outside the typical frequency range from 20.8 to 21.8 MHz—see Figures 1 and 7. This led to extensive work to determine the source of these signals and to eliminate them. During the course of this investigation numerous effects were observed. For example, magneto-acoustic ringing of the relatively large RF coil used with the electrochemical cell led to large false signals which could overwhelm the smaller real signals. To reduce or eliminate this effects,

the RF coil was coated with epoxy. Another modification introduced was a copper metal shield between the RF coil and the cell which reduces the electric field within the cell due to the RF pulses and significantly reduces heating of the electrodes. Furthermore, perhaps the largest effect was the observation of non-linear magneto-acoustic ringing effects from some of the RF connectors. The magnitude of this effect varied considerably from connector to connector, even within the same group. To reduce or eliminate this effects, all of the connectors were carefully screened. Ultimately, a combined system was achieve with a minimal false signal. It was not feasible to completely eliminate the false signal. It was decided that the best approach was to maximize the true signal either via increasing the RF power to the NMR probe or by introducing alternate excitation schemes.

The high power RF amplifiers used in the program were made by Amplifier Research and although they were initially able to deliver in excess of 1 kW power when procured over 20 years ago, their outputs had reduced to only a few hundred watts. Every effort was made to optimize the output of the best amplifier, but it was concluded that only a refurbishing by Amplifier Research would solve the problem. Code 6122 has a 10 kW RF amplifier, also made by Amplifier Research. Unfortunately this amplifier had not been used in over 20 years. After getting the amplifier's power core directly attached, the amplifier was tested, but the coolant leaked. After repairing the lines, more coolant was ordered, but still hasn't arrived.

An alternate excitation mechanism involves using low power swept pulses. Late in FY19 this method was implemented at low field for a test sample—Figure 8. Application to the ^{195}Pt NMR is ongoing.

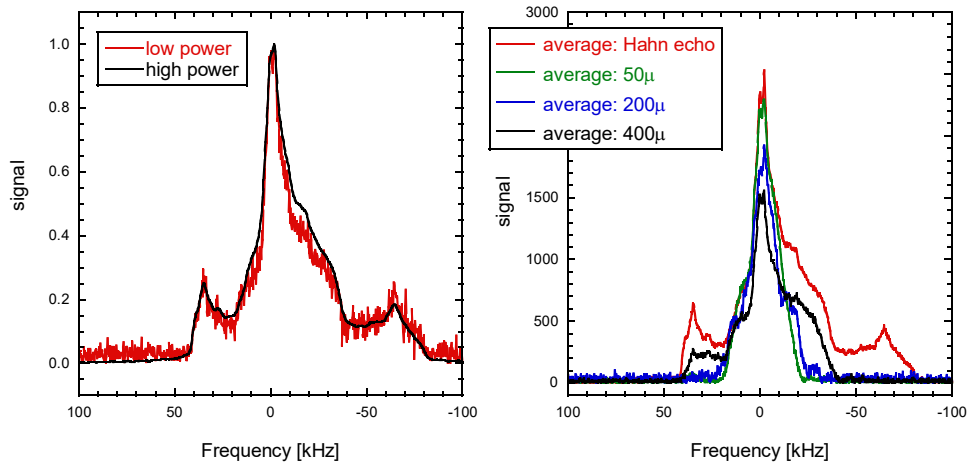

Figure 8: ^{87}Rb NMR spectra at 2.35 T for $RbSO_4$ demonstrating the ability to obtain spectra using low power swept pulses.

Ultimately, optimization of the in situ electrochemical NMR experiment will require improved signal size, particularly

A description of the Jahn-Teller effect specific to DFT was developed that bridges the gap between the original work of Jahn and Teller and the degenerate density functional perturbation theory of Palenik and Dunlap. The theory that was developed for this description also led to the development of a computational model whereby an artificially closed-shell molecule can be computed in symmetry and perturbed into the correct, symmetry-breaking ground state.

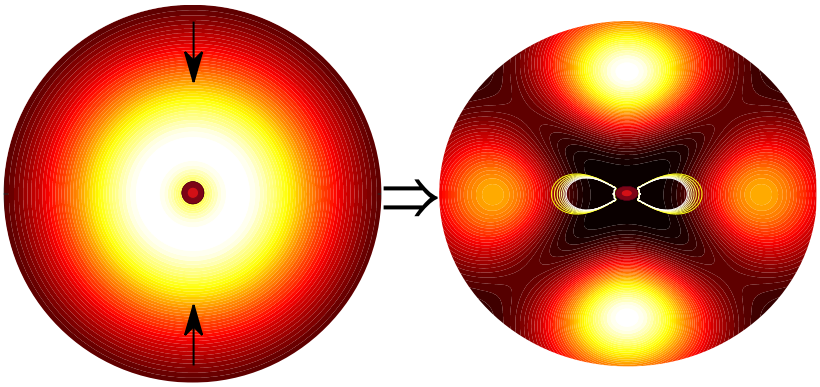

Figure 9: A jellium model of a superatom with a hole in the center undergoing a Jahn-Teller distortion as computed by the method of Palenik and Dunlap. Change in electron density superimposed over change in geometry.

We have begun studying the role of Jahn-Teller distortions in Cs doped $Sb_{21}Pd_{12}$ crystals. The Eichhorn group has found that the clusters in these molecular crystals can exist in a variety of charge states, which should correspond to different conducting properties. We are beginning to study

Additional density functional calculations were performed on $LiAlH_4$, $LiAlPh_4$, and crystals to obtain structures and NMR parameters for comparison to experimental work performed by Klug. Samples of $[(Bu_2O)_2Li][Li_4Al_5Ph_{12}]$ crystals were produced by the Eichhorn group that were not of sufficient quality for experimental NMR, but from which crystallographic structures were obtained that were used in theoretical NMR calculations.

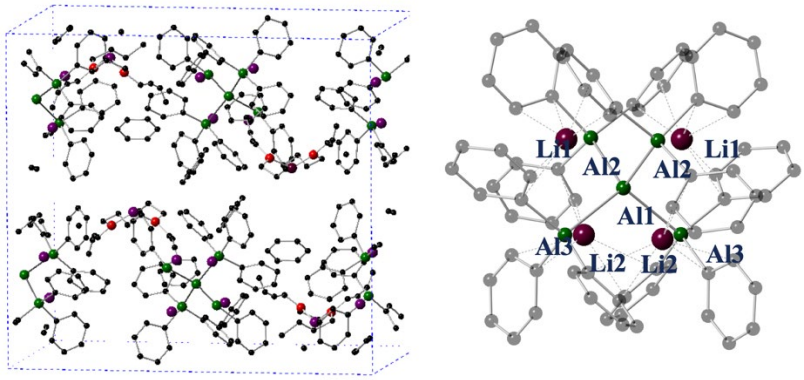

Figure 10: The $[(Bu_2O)_2Li][Li_4Al_5Ph_{12}]$ unit cell (left) and central cluster (right). Hydrogens are hidden for clarity.

Conclusions

While at the time of this writing we are now just beginning to achieve our goal of true in situ electrochemical nuclear magnetic resonance and therefore are unable to include significant new insights from this approach, we nevertheless have made considerable fundamental scientific progress during this program. Furthermore, all the knowledge gained and techniques developed in this program will be applicable to the new program beginning in FY20: "Electrical Energy Storage Electrode Materials Based on Metal-Organic Frameworks".

Nuclear magnetic resonance methods optimized for low field detection of broad spectra were developed. These methods have already led to new collaborative opportunities and will prove useful for a wide range of materials characterizations.

XAS was demonstrated to be in important complementary tool, both in measurement time scale and data analysis, for in-situ electrode characterization with NMR systems. Although nuclei dependent, the combined use of these XAS and NMR show significant promise for long term electrode characterization including material/device degradation

Density perturbation theory was defined and developed toward practical quantum chemical calculations of chemical perturbations such as those occurring during NMR experiments.

Publications

Peer review publications (published, in review, submitted)

1. "*Dopant Clustering and Correlated Oxygen Migration in Conditionally Stabilized Zirconia Electrolytes*", S. P. Miller, **B. I. Dunlap**, and A. S. Fleischer, J. Fuel Cell Tech. 12, 021003 (2015)
2. "*Density Perturbation Theory*", **M. C. Palenik** and **B. I. Dunlap**, J. Chem. Phys. 143, 044115 (2015)
3. "*Variationally fitting the total electron-electron interaction*", **Brett I. Dunlap** and **Mark C. Palenik**, Phys. Rev. B 93, 195162 (2016).
4. "*Degenerate density perturbation theory*", **M. C. Palenik** and **B. I. Dunlap**, *Phys. Rev B.* **94**, 115108 (2016).
5. "*Orbital angular momentum eigenfunctions for fast and numerically stable evaluations of closed-form pseudopotential matrix elements*", A. Hu, N. W. C. Chan, and **B. I. Dunlap**, Journal of Chemical Physics 147, 074102 (2017)
6. "*$Sb@Ni_{12}@Sb_{20}^{-/+}$ and $Sb@Pd_{12}@Sb_{20}^{n}$ Cluster Anions, Where n = +1, −1, −3, −4: Multi-Oxidation-State Clusters of Interpenetrating Platonic Solids*", Y. Wang, M. Moses-DeBusk, L. Stevens, J. Hu, P. Zavalij, K. Bowen, **B. I. Dunlap**, E. R. Glaser, and B. Eichhorn, J. Am. Chem. Soc. 139, 619-622 (2017)
7. "*Utility of PEGylated dithiolane ligands for direct synthesis of water-soluble Au, Ag, Pt, Pd, Cu and AuPt nanoparticles*", E. Oh, J. B. Delehanty, **C. A. Klug**, K. Susumu., W. R. Algar, R. Goswami, and I. L. Medintz, Chemical Communications (Cambridge, United Kingdom), 54(16), 1956-1959 (2018).
8. "*Synthesis and Structure of $Sn_{14}Cl_6(CH_2SiMe_3)_{12}$: Towards Nanoclusters of 4-Coordinate a-Sn*", A. P. Purdy, R. J. Butcher, J. P. Yesinowski , **S. A. Fischer**, D. Gunlycke and B. L. Chaloux, Inorg. Chem., 57, 4921−4925 (2018).
9. *"Automated detection of broad NMR spectra at low field: ^{19}F NMR of paramagnetic UF_4 and ^{195}Pt NMR of supported Pt catalysts at 2.3T"*, **C. A. Klug** and J. B. Miller, Solid State Nuclear Magnetic Resonance, 92, 14-18 (2018).
10. "*Jahn-Teller effect in density-functional theory*", **M. C. Palenik**, **B. I. Dunlap** and D. Gunlycke, Physical Review A, **99**, 022502 (2019).

Manuscript in preparation:

1. "*Experimental and theoretical comparison of ^{27}Al, ^{7}Li, and ^{13}C magic-angle-spinning NMR spectra for $LiAlH_4$ and $LiAlPh_4$ crystals with rotational symmetry in their unit cells*", **M. C. Palenik**, **C. A. Klug**, M. W. Conroy, **B. I .Dunlap**, **S. A. Fischer**, L. D. Gunlycke, L. Stevens, P. Zavalij, and B. Eichhorn, in preparation for Physical Review B.
2. *"Dynamic potential effects on Pt/C electrode structure with QXAFS"*, **C. M. Hangarter**, R. Anderson and **P. Natishan**, in preparation for Journal of Electrochemical Society

Presentations

Presentations (Poster)

1. "*Experimental and theoretical comparison of ^{27}Al, ^{7}Li, and ^{13}C magic-angle-spinning NMR spectra for $LiAlH_4$ and $LiAlPh_4$ crystals with rotational symmetry in their unit cells*", **C. A. Klug**, M. W. Conroy, **B. I .Dunlap**, **S. A. Fischer**, L. D. Gunlycke, L. Stevens, P. Zavalij, and B. Eichhorn. Presented at 20th Meeting of the International Society of Magnetic Resonance, Québec City, Canada, July 23-28, 2017.

Presentations (Oral)

1. "*Density Perturbation Theory*", **M. C. Palenik** and **B. I Dunlap**, 250th ACS Fall Meeting, Boston, MA, 16-20 August 2015
2. "*Density Perturbation Theory*", **M. C. Palenik** and **B. I Dunlap**, 2016 APS March Meeting, Baltimore, MD, Mar 14–18, 2016
3. "*Taking Advantage of Low Field NMR*", **C. A. Klug**, Presented at Symposium to honor Professor Jacob Schaefer, Department of Chemistry, Washington, University, Saint Louis, MO, January 6, 2017.
4. "*Nuclear Magnetic Resonance at NRL*", **C. A. Klug**, Presented at NMR group meeting hosted by Professor Alexej Jerschow, Department of Chemistry, New York University, New York City, New York, September 27, 2017.