OPERANDO SPECTROSCOPY OF ELECTROCHEMICAL ENERGY CONVERSION DEVICES

A thesis presented

by

Emily Anne Lewis

to

The Department of Chemistry and Chemical Biology

In partial fulfillment of the requirements for the degree of Masters of Science in the field of Chemistry

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ABSTRACT OF THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry in the Graduate School of Arts and Sciences of Northeastern University, April, 2009
ABSTRACT

A fuel cell for operando FTIR and x-ray absorption spectroscopy (XAS) was designed and constructed. The cell is based on the combination of operando cells previously developed in the Smotkin group. Special consideration was put into the design to enable both transmission XAS, fluorescence XAS, and diffuse reflectance FTIR spectroscopy. Operando x-ray fluorescence spectroscopy of the Pt cathode was accomplished at Argonne national labs.

The x-ray absorption near edge structure (XANES) region of the fluorescence XAS spectra was analyzed by subtractive normalization (Δ-XANES). Using this technique, the trends in the data became apparent: there were both time- and potential-dependence in the reduction of surface and sub-surface Pt-oxides. The time constant for the reduction of these oxides was greater than two hours at 530 mV, much longer than previously expected.

Theoretical Δ-XANES (Δ-XANES signatures) of oxygen adsorbates on Pt clusters were modeled using FEFF8 software. Two new models were developed to generate the Δ-XANES signatures: the isolated all-atoms Janin cluster, and the embedded all-atoms Janin cluster. The progressive development of these models provides insight concerning the relative charge depletion of surface and subsurface atoms, and the compensation of charge transfer by platinum-reservoir electron density.

Future directions of the operando spectroscopy cell include using electrochemical promotion of organic chemistry (EPOCH) to assist epoxide ring-opening reactions for pharmaceutical building blocks, and the study of fuel cell poisoning by common atmospheric pollutants.
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<tr>
<td>Δ-XANES</td>
<td>subtractively normalized XANES</td>
</tr>
<tr>
<td>ATR-SEIRAS</td>
<td>attenuated total reflection surface enhanced infrared reflection absorption spectroscopy</td>
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<td>DMFC</td>
<td>direct methanol fuel cell</td>
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<td>DRIFTS</td>
<td>diffuse reflectance infrared Fourier transform spectroscopy</td>
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<td>EPOCH</td>
<td>electrochemical promotion of organic chemistry</td>
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<tr>
<td>EXAFS</td>
<td>extended x-ray absorption fine structure</td>
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<tr>
<td>fcc</td>
<td>face centered cubic</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>GDL</td>
<td>gas diffusion layer</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal close packed</td>
</tr>
<tr>
<td>ICE</td>
<td>internal combustion engine</td>
</tr>
<tr>
<td>IRAS</td>
<td>infrared reflection absorption spectroscopy</td>
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<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
</tr>
<tr>
<td>MFTIRS</td>
<td>microscopy Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>NASA</td>
<td>national aeronautics and space administration</td>
</tr>
<tr>
<td>NEMCA</td>
<td>non-Faradaic electrochemical modification of catalytic activity</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal hydrogen electrode</td>
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<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
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<tr>
<td>PEM</td>
<td>polymer electrolyte membrane</td>
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<td>PEMFC</td>
<td>polymer electrolyte membrane fuel cell</td>
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<tr>
<td>SAXS</td>
<td>small angle x-ray scattering</td>
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XANES – x-ray absorption near edge structure

XAS – x-ray absorption spectroscopy
1.1 PEM Fuel Cells

There is an immediate need for alternative (renewable, non-fossil fuel) energy sources due to the unprecedented amount of anthropomorphic carbon dioxide in the Earth’s atmosphere. Fuel cells are emerging as a key component of an economy based on renewable energy. A fuel cell is a galvanic electrochemical cell that takes chemical energy (in the form of a fuel) and converts it into usable electrical energy. This process of electrochemical conversion is more efficient than the conversion of fuels to mechanical energy through combustion; an average combustion engine runs at about 1/3 efficiency due to Carnot cycle limitations. Fuel cells that use hydrogen and oxygen (denoted H₂/air fuel cells) are of particular interest because the only product formed through the electrochemical conversion is water. Because they operate at low temperatures, the electrochemical combustion of fuels does not generate greenhouse gases or atmospheric pollutants typical of internal combustion engines.

All electrochemical cells work through the coupling of complimentary oxidation-reduction reactions via an electrolyte. In a H₂/air fuel cell, hydrogen is oxidized into two protons and two electrons at the anode. The protons migrate through the electrolyte to the cathode, while the electrons travel through the external circuit where they can power an electrical load on the way to the cathode. The protons, electrons and oxygen from air combine at the cathode to form water. The combination of the half reactions leads to the overall cell reaction (equation 1).
Equation 1:

\[
\begin{align*}
2\text{H}_2 & \rightarrow 4\text{H}^+ + 4\text{e}^- & E^0 = 0 \text{ V} \\
4\text{e}^- + 4\text{H}^+ + \text{O}_2 & \rightarrow 2\text{H}_2\text{O} & E^0 = 1.23 \text{ V} \\
2\text{H}_2 + \text{O}_2 & \rightarrow 2\text{H}_2\text{O} & V_{\text{cell}} = 1.23 \text{ V}^2
\end{align*}
\]

The energy associated with the overall cell reaction is 1.23 V. This is the theoretical maximum potential the fuel cell can achieve.

One of the most promising types of H\textsubscript{2}/air fuel cells is the polymer electrolyte membrane fuel cell (PEMFC). PEMFCs had their major debut as auxiliary power sources aboard NASA’s Gemini space flights. Today, they are involved in about 90\% of all fuel cell research.\(^3\) H\textsubscript{2}/air PEMFCs have a number of advantages over other fuel cells: they run at low temperatures, they are relatively lightweight, and they have very high power densities. These properties make them excellent candidates for portable power applications, automotive use, and stationary power sources. PEMFCs are unique because of their polymer electrolyte or proton exchange membrane (PEM). When the hydrogen is split into two protons at the anode, the protons cross a proton conductive membrane, usually a sulfonated fluoropolymer such as Nafion, via the Grotthuss hopping mechanism.\(^4\) The Grotthuss hopping mechanism explains the unusually fast diffusion of protons through a PEM compared that of Brownian motion, which is one reason PEMFCs are so viable. A fuel cell schematic is shown in Figure 1.1.
The Nafion PEM is sandwiched between the anode and cathode catalysts. Outside of the catalysts are the GDLs and flow fields.

To lower the activation energy of the cell reaction, catalysts are required. The standard catalyst for both the anode and the cathode in a H₂/air fuel cells is carbon supported platinum (Pt/C), which has platinum nanoparticles dispersed onto activated carbon particles. The active surface area of Pt/C varies with the amount of platinum, but with nanometer particle size and good dispersion, it can be as high as 120 m²/g. When the particle diameter is greater than 2 nm, the active surface area is directly proportional to the reactivity of the catalyst.³ On average, Pt/C has about three times the specific activity of unsupported catalysts.⁶ The disadvantage of platinum as a catalyst is that it is a very expensive noble metal. Even with the sub-mg/cm² platinum loadings achievable with supported catalysts, the cost of a platinum MEA is prohibitive to fuel cell marketability. The platinum loadings at the cathode side tend to be much larger than the

---

³活性表面積はプラチナの量に関わるが、ナノメートルサイズの粒子を用いることで高い値を示すことが知られている。プラチナの粒子径が2 nmを超えると、活性表面積は触媒の活性に直接比例することが知られている。⁶平均値では、Pt/Cは非支承触媒の約三倍の活性を示す。プラチナのコストは非常に高く、特に触媒の表面積が小さい場合に影響を与える。耐久性を損なわぬように、支持型触媒の使用が推奨される。しかし、プラチナのメタル界面は非常に高価である。それによって、プラチナメタルのコストは燃料電池の市場化を阻害する。カソード側のプラチナの粒子径は、支持型触媒のそれよりも大きくなる傾向がある。
loadings at the anode because of the sluggish electrode kinetics of the oxygen reduction reaction (ORR). Thus the greatest impact on catalyst loading would result from improving the ORR kinetics on Pt based catalysts, or finding non precious metal group catalysts. Thus the primary focus of Department of Energy fuel cell R&D is cathode catalysis.

Equation 1 shows that the ideal cell voltage of a H₂/air fuel cell is 1.23 V; however, the expected potential is about 1 V at best. Kinetic, ohmic, and mass transport losses keep the cell from reaching its ideal potential. Most of the polarization losses are attributed to the cathode (> 400 mV) because the hydrogen oxidation overpotential is in the 10s of millivolts even during high performance. Ohmic losses are due primarily to the resistance protons encounter as they migrate through the MEA. These losses are usually associated with imperfect water management. Kinetic losses are due to the activity of the catalyst, and its activation overpotential. Mass transport limitations are due to the availability of the catalyst active sites, which can be blocked by cathode flooding or by persistent adsorbates (poisons). Therefore, in addition to researching cost-effective catalysts, new catalysts that circumvent kinetic and mass transport limitations are also being explored.

1.2 Operando Spectroscopy

Although many spectroscopy techniques have been applied to the study of fuel cell electrocatalysts, our approach emphasizes performing spectroscopy under entirely realistic operating conditions. We call this approach “operando” spectroscopy. Operando spectroscopy of catalysts is important because it examines the active state of the catalyst,
which only exists during catalysis. In fuel cells, operando spectroscopy differs from in situ spectroscopy because it requires entirely realistic operating conditions, including typical catalyst loadings. High loadings are avoided because they can cause a $z$-dependence (normal to the plane of the catalyst layer) in the current and potential profiles. Additionally, the fuel cell is run with normal reactant flow conditions, in the absence of additional acidic electrolytes (e.g., $\text{H}_2\text{SO}_4$ or $\text{HClO}_4$), which is essential if typical fuel cell operating temperatures are required, and if poisoning by mobile ions is to be avoided. Although these prerequisites make operando spectroscopy substantially more challenging than in situ spectroscopy, it allows for the most realistic examination of the solid-gas catalytic interfaces.

Operando spectroscopy of the solid-gas interface is ideal for examining catalyst adsorbates. Adsorbates effect dynamic changes on the catalyst surface such as surface restructuring where surface atoms can be entirely displaced in order to make stronger surface-adsorbate bonds. These changes can be observed, in operando and in situ spectroscopy, as changes in the vibrational modes of either the surface or the adsorbate atoms. For example, Shao et al. were able to study the potential dependence of the ORR intermediates via in situ attenuated total reflection surface enhanced infrared reflection absorption spectroscopy (ATR-SEIRAS). Smith et al. were able to observe potential-dependent platinum particle growth due to oxide formation and Ostwald ripening with in situ small-angle x-ray scattering (SAXS). More common techniques such as Fourier transform infrared spectroscopy (FTIR) and XAS are also emerging as powerful tools for in situ and operando spectroscopy of electrochemical systems.
The biggest challenge in performing operando spectroscopy of fuel cells is cell design. There are restrictions as to what components can be metallic because they can interfere with XAS if their work function is close to that of the catalyst. The cell should accommodate both transmission and glancing angle measurements. Fluorescence measurements obtained at glancing angles mitigate interference due to the other cell components. In the IR region, most fuel cell materials are completely non-transmissive, so the operando cell must accommodate special windows to enable reflection techniques. IR spectroscopy is also sensitive to MEA materials such as the carbon GDL, which necessitates fabrication of MEA with gas diffusion layers modified to provide access of the beam to the catalytic surface. Operando spectroscopy of fuel cells requires careful water management because variable flooding causes fluctuations in the overall system absorption coefficient. This reduces the amount of data available for signal averaging. Finally, the cell geometry must accommodate the configuration of the optical components of the spectrometry system.

1.2.1 Operando XAS

X-ray absorption spectroscopy has grown from a relatively esoteric technique to a widely used analytical method over the last few decades. This is partially because of the advancements in x-ray absorption near edge structure (XANES), which began in the 1970s. The first of these advancements was the development of synchrotron radiation that has the ability to provide high intensity, polarized radiation with a wide spectral range, predictable fluctuations, and small beam divergence. Another advancement was the development of x-ray fluorescence techniques, which occurred after the development
of detectors sensitive to this energy range.\textsuperscript{17} Other advancements include the advent of computer processing, which enables XAS spectra to be taken in minutes (as opposed to hours), and the ability to model experimental data theoretically using full multiple scattering software.\textsuperscript{16}

To perform XAS spectroscopy, x-rays are tuned with a crystalline monochromator to the work function of the sample. When these x-rays impinge on the metal surface, a core electron is excited, and ejected as a photoelectron either into the valence band of the metal (XANES) or into the continuum (EXAFS – x-ray absorption fine structure).\textsuperscript{18} This wave is scattered by surrounding atoms creating the XAS spectrum. The XANES region, within 50 eV of the work function, is most sensitive to changes in oxidation state of the metal because it looks at multiple scattering events (Fig. 1.2a). The EXAFS region of the spectrum is a powerful analytical technique that can be used to determine the atomic spacing of a crystal lattice (Fig. 1.2b).\textsuperscript{19} For H\textsubscript{2}/air fuel cells, the x-rays are commonly tuned with a Si (111) crystal monochromator to the platinum L\textsubscript{II-III} edges at 13.731 and 11.92 keV, respectively.\textsuperscript{20} These transitions correspond to 2p\textsubscript{1/2} or 2p\textsubscript{2/3} to 5d transition.\textsuperscript{21, 22}
Many studies have been done using in situ XAS and operando XAS techniques to study catalyst properties. A few studies were done to look at the oxidation state of the catalyst metals. All determined that at fuel cell operating potentials conditions, platinum is purely metallic. The oxidation of CO was studied both on Pt and PtRu (the anode catalyst of a direct methanol PEMFC), and the electronic benefits of ruthenium were exemplified. Finally, adsorption of ORR intermediates was studied on fuel cell catalysts, and it was found that adsorption is both potential-dependent and site-specific.

Subtractively normalized XANES (Δ-XANES) is emerging as a new technique for XANES analysis. Delta XANES takes the XANES of the substrate under adsorbate-free conditions and uses it as a spectroscopic blank for XANES obtained under conditions conducive to adsorption (e.g., by altering the potential or the chemical environment). Although the quantitative assessment of these signatures is under debate, they are excellent for qualitative analysis. The Δ-XANES signatures provide easy-to-
interpret spectral features that show smooth variations in intensity as a function of the desired variable. Using computational software, theoretical $\Delta$-XANES spectra can be calculated, and used to interpret experimental data.

1.2.2 Operando FTIR

Unlike XAS, which observes the spectra of the catalyst, operando IR studies the spectra of adsorbates. Operando FTIR allows for the unique properties of adsorbed species to be clearly observed. Stark tuning is induced by the electrical field formed at the electrode surface. It can allow forbidden vibrations to be seen in the IR spectra by inducing a dipole moment in the adsorbed molecule.$^{38,39}$ The study of CO adsorption is particularly important to fuel cells because of its persistence and its detrimental effects on the catalyst. FTIR allows the site specificity of CO on the crystalline catalyst surface to be observed via the change in vibrational frequency of the molecule.$^{40-45}$ CO binds preferentially to catalyst step sites because the platinum atoms are under coordinated, and therefore, electron deficient. The terrace sites are only filled after so much CO is adsorbed that the step sites are full. Finally the potential-dependence this site-specificity as well as the potential dependence of adsorption configuration (e.g., atop, or bridge) and total coverage can be seen using in situ FTIR.$^{46-51}$

The characteristic IR vibrational bands of molecules can also be used to study fuel cells in situ and in operando. Studies of direct methanol fuel cell (DMFC) anodes have been done to look at the methanol oxidation reaction.$^{52-63}$ Using FTIR techniques, it is easy to distinguish between adsorbed methanol, gaseous methanol, and intermediates of the reduction reaction. In situ FTIR can also be used to study the effects of atmospheric
pollutants on the catalytic surface. Quijada et al. used in situ infrared reflection adsorption spectroscopy (FR-IRRAS) to study the irreversible adsorption of SO$_2$ on platinum electrodes by looking at its characteristic band at 1220 cm$^{-1}$. Another use of operando FTIR is to study organic reactions promoted by non-Faradaic electrochemical modification of catalytic activity (NEMCA) in a fuel cell environment.

Reflectance FTIR techniques must be used to acquire operando spectra because an IR beam cannot be transmitted through the components of the membrane electrode assembly housing. A few techniques including diffuse reflectance FTIR (sometimes referred to as DRIFTS), IR reflection absorption spectroscopy (IRAS or IRRAS), microscope FTIR reflection spectroscopy (MFTIRS), attenuated total reflectance (ATR), and surface-enhanced IR absorption spectroscopy (SEIRAS). Diffuse reflectance FTIR uses a special accessory to the usual FTIR spectrometer. The accessory directs the IR beam to the sample through a series of mirrors. The beam is then scattered by the sample and re-combined with an integrating mirror and sent to the detector. Diffuse reflectance spectra exhibit the same peaks as regular absorbance spectra, but some of the more minor peaks observed in the absorbance spectra are magnified.

### 1.3 Research Objectives

The objectives of this research include development of a versatile operando spectroscopy fuel cell that enables FTIR and XAS analysis of fuel cell catalytic surfaces to study the time and potential dependent dynamics of fuel cell catalyst structures. Chapter 2 discusses the design of the multi-spectroscopic operando fuel cell. Special considerations were made to design a cell that could be interrogated by transmission
XAS, fluorescence XAS and FTIR spectroscopy. Chapter 3 discusses operando XANES acquired with the new cell. The platinum L_{II-III} edges were examined for changes in oxidation state. The XANES data were analyzed by Δ-XANES technique for ease of data trend observations. Chapter 4 discusses theoretical modeling of the operando Δ-XANES using the full multiple scattering software FEFF8. Two models of platinum cluster adsorbates were given special attention to show how charge transfer selectively depletes charge from near neighbor atoms, and how this charge depletion is compensated for by embedding the cluster into a larger reservoir of Pt atoms. Chapter 5 discusses the future prospects for operando spectroscopy.
CHAPTER 2: OPERANDO CELL DESIGN

2.1 Introduction

Previous operando spectroscopy fuel cells have been reported for FTIR and XAS. There is an advantage to combining the form and functions of the two types of operando spectroscopic cells. The multi-spectroscopic cell was designed to accommodate FTIR and XAS studies of the electrode surface of operating fuel cells membrane electrode assemblies. The advantage of a multi-spectroscopic cell is that reaction conditions can be duplicated using the exact same electrode surface in either the FTIR or XAS mode. This enables the acquisition of a diverse range of spectroscopic information while minimizing the effects of sample variation. The complex humidity- and air-sensitive parameters required of the fuel cell environment makes this feature particularly attractive.

Another consideration in the design of the multi-spectroscopic cell was easy interfacing to the commercially available diffuse reflection accessories for FTIR systems, and orientation independent operation for easy manipulation in the cramped environment of synchrotron beamline hutchs.

2.1.1 Legacy Cells

Operando spectroscopy cells for fuel cell analysis, developed in the Smotkin lab, have been extensively reported. Fan et al. designed an operando diffuse IR cell (Fig. 2.1a), and Viswanathan et al. designed an operando XAS cell (Fig. 2.1b). The Fan cell was designed to fit into a 1990’s model Harrick Praying Mantis (Pleasantville, NY)
The cell had a number of useful design elements that were helpful in developing the new cell: the IR window, the flow field design, and the gas inlet/outlet features.

The Viswanathan cell incorporated a graphite lower flow field with a posterior cavity to eliminate signal attenuation in transmission XAS. This feature was integrated into the new design. The new cell design was also built to optimize the fluorescence XAS mode in addition to transmission mode, which would eliminate signal attenuation due to travel length entirely. The new cell incorporated many design features from the legacy cells, building upon their strengths, and improving their weaknesses.
2.2 Multi-Spectroscopic Cell Design Features

The new cell, shown in Figure 2.2, enables operando diffuse reflectance FTIR, transmission XAS, and fluorescence XAS (Fig. 2.3) of fuel cell catalytic layers. In fluorescence XAS mode, the top plate can be removed so that only the windowed graphite

![Figure 2.2: New multi-spectroscopic cell for operando spectroscopy. Top photo: Cell disassembled. The top piece is the housing slider. The middle row from left to right contains the lower flow field, upper flow field, and the top plate. The bottom row contains an MEA. Bottom photo: Assembled cell.](image)

upper flow field is between the beam and the MEA. This is advantageous because the stainless steel top contains iron, nickel and chromium, which fluoresce at energies that are similar to the edge energies of the catalyst components. The advantage of fluorescence XAS is that beam intensity is not attenuated by the lower flow field graphite material. The use of graphite flow fields (black plates in Figure 2.3), and recessing the lower flow field beneath the MEA (in a similar fashion to the Viswanathan cell), enables either mode of operation. To accommodate transmission XAS, the slider has a wide bevel on the underside to allow for transmission XAS to be recorded at an optimum angle (Fig. 2.4).
A compact cell design is required because the beamline hutch is densely packed with equipment. In the air-breathing fluorescence XAS mode, the cell is operated on its side (Fig. 2.4), which can cause water droplets to form and pool at the bottom of the flow field. Wicking material is used on the upper flow field to remove water formed at the cathode by the ORR. Although the flow fields have no set polarity, these studies have used the upper flow field as the cathode, which is most prone to the effects of flooding.

Figure 2.3: Illustrated exploded view of the cell. The red arrow represents the beam path of reflectance FTIR or fluorescence XAS modes. The yellow arrow represents transmission XAS mode.

Figure 2.4: Photo of the cell in line at Argonne National Laboratory. The cell must be operated on its side to accommodate the x-ray beam path.
For FTIR, the slider design allows for easy alignment below the integrating mirrors of a Pike Technologies (Madison, WI) diffusIR accessory (Fig. 2.6). The original accessory was designed so that the sample holder slides into position under the integrating mirror. The cell design integrated this feature by including a housing slider that easily aligned the cell in the accessory. The slider assembly incorporates wiring for temperature and potentiostatic control, as well as manifolding for the reactant gases. Swagelok fittings for gas entry and exhaust, and a DE9 plug for potentiostatic and temperature control are positioned at a terminal end of the slider for ease of insertion into the commercially available diffuse reflection accessory. The wide bevel angle of 158° on the top plate maximizes the collection of the scattered signal. The upper flow field employs a pins style-flow field to optimize flow distribution around the CaF$_2$ window inset. The wicking is still effective at controlling flooding in the upright operation mode for FTIR, which is especially important in the water-sensitive IR region.

Figure 2.5: Photo of the cell interface with an FTIR. The cell is aligned within the Pike diffusIR accessory, which connects to a Bruker (Billerica, MA) Vertex 70 FTIR Spectrometer.
2.3 Experimental

Polarization curves were obtained with an EZstat potentiostat/galvanostat (NuVant Systems, Inc. Crown Point, IN). The cell was operated as a H$_2$/air fuel cell with an air-breathing cathode at 50 °C with humidified gases. The membrane electrode assembly (MEA) was prepared using standard procedures.$^7$ The cathode side was loaded with 30% PtNi/C acid washed E-Tek catalyst (special made E1030523) at 0.9 mg/cm$^2$. The anode side was prepared with Pd/C Alfa Aesar catalyst (stock # 38309, lot # C02R014) using a 1.0 mg/cm$^2$ loading. Palladium was used on the anode because its L edge energy is much lower than that of Pt and its K edge is twice as large as the Pt L$_{II-III}$ edge that was being studied. The Ni K edge is so low that it enables separate examination of Pt and Ni atoms.

The operando XAS were acquired at Advanced Photon Source (Argonne National Laboratory, IL) at the MRCAT beamline 10-ID-B. The cell was aligned for fluorescence mode between the source and the Lytle detector (Fig. 2.3). The operando spectra were collected by tuning the beamline undulator to the Pt L$_{III}$ edge energy range using the 2$^{nd}$ harmonic of a Si (111) crystal monochromator. Higher harmonics were rejected using a Rh reflection mirror. The incident ion chamber was filled with N$_2$ gas.

2.4 Results and Discussion

A polarization curve was acquired after conditioning the cell for about an hour (Fig. 2.6). The sweep shows hysteresis that is commonly observed during fuel cell cyclic voltammetry. The return anodic sweep shows that cell performance is regained after surface oxides are reduced.
Figure 2.6: Polarization curve obtained with the multi-spectroscopic cell.

Operando fluorescence XAS acquired with the new cell showed a step improvement in signal-to-noise over the Viswanathan cell in transmission mode with similar catalyst loadings, as exemplified by the Ni and Pt edge data of a PtNi catalyst (Fig. 2.7). The nickel edge data shows a much cleaner EXAFS spectral region and the absence of observable pre-edge noise. At the Pt edge, the difference in signal-to-noise ratio is not as distinct, but there is less fluctuation in the EXAFS region. The improved spectral quality is due to the use of the new fuel cell’s fluorescence-mode.
Figure 2.7: Comparison of XAS data acquired with the Viswanathan cell (red line) and data acquired with the new multi-spectroscopic cell (green line). a.) Ni K edge of the Pt$_3$Ni cathode. b.) Pt L$_{III}$ edge Pt$_3$Ni cathode.
2.5 Conclusions

This work has demonstrated a new operando multi-spectroscopic fuel cell capable of diffuse reflectance FTIR, fluorescence XAS, and transmission XAS. The cell was operated under normal operating conditions and a standard polarization curve was acquired. Fluorescence XAS data shows a significant decrease in signal noise compared to the previous operando transmission XAS cell. The Ni K edge demonstrates that the increased signal-to-noise ratio is more dramatic at lower energies. More operando catalyst studies with this cell are sure to come.
CHAPTER 3: TIME- AND POTENTIAL-DEPENDENT Δ-XANES

3.1 Introduction

Fuel cell degradation can be ascribed to short-term and long-term degradation modes. Our previous work has shown that in both cases, adsorption plays a key role. For example in the case of direct methanol fuel cells, it has been shown that the anode is highly susceptible to adverse adsorbates such as CO. The poisoning of an electrode surface by CO occurs on a very short time scale. Recovery has been effected by fuel starvation of the anode, which causes a positive excursion of the electrode potential that oxidatively cleans the surface. There are also longer term degradation modes that occur over periods of hours to hundreds of hours. The degradation of direct methanol fuel cell cathodes exemplifies long term degradation modes. This includes time-dependent poisoning of the cathode by Ru crossover from the anode, and deep oxide formation and passivation of the cathode. The study of time-dependent degradation processes can most effectively be studied by operando spectroscopy.

The ability to monitor the time- and potential-dependence of oxygen adsorbates on cathode catalysts is important because of their inevitable formation over the life of the cell. Oxides cause detrimental kinetic and mass transfer losses, thus an understanding of their persistence is essential to better catalyst design. Smith et al. recently studied Pt growth due to oxides and Ostwald ripening with in situ SAXS. A number of other studies have been done using in situ XAS and operando XAS techniques to study fuel cell catalysts. Towards this end, the multi-spectroscopic cell was taken to a synchrotron source to acquire high-quality operando fluorescence XAS data.
These spectra were analyzed by the $\Delta$-XANES technique for the easiest observation of oxide trends.

### 3.2 Experimental

The cell was operated as an air-breathing $\text{H}_2$/air cell. The membrane electrode assembly (MEA) was prepared using standard procedures. The cathode side was loaded with 20% Pt/C Alfa Aesar catalyst (HiSpec 3000 stock # 35849, lot # A305023) at 1.2 mg/cm$^2$. The anode side was prepared with Pd/C Alfa Aesar catalyst (stock # 38309, lot # C02R014) using a 1.0 mg/cm$^2$ loading. The cell was operated at 50 °C with humidified gases. Polarization curves were obtained with an EZstat potentiostat (NuVant Systems, Inc. Crown Point, IN). The cathode was left open to enable the collection of high quality XAS in fluorescence mode with no signal attenuation.

Pt L$_{\text{III}}$ edge XAS data were collected at the MRCAT 10-ID-B beamline at the Advanced Photon Source (Argonne National Laboratory, IL). The beamline undulator was tuned to the Pt L$_{\text{III}}$ edge energy range using the 2$^{\text{nd}}$ harmonic of the Si (111) monochromator crystal. A Rh reflection mirror was used to reject higher harmonics. The incident ion chamber was filled with $\text{N}_2$. XAS data were collected at different fuel cell potentials: 0 mV (short circuit), 530, 600, 710, 780, 820, 900 mV vs. NHE, and at open circuit voltage (OCV). The cell was held at each potential for about 2 hours while 32 scans were run. In addition, ex situ XAS data were collected on a similarly prepared dry MEA unexposed to the fuel cell humidified environment.
3.3 Results and Discussion

3.3.1 Time-dependent $\Delta$-XANES

After the cell is conditioned$^{29,35}$ for 1 hour, a reference XANES was obtained at 0 volts versus a normal hydrogen electrode (NHE). Time-dependent XAS were then acquired and subtractively normalized to the reference spectrum to yield $\Delta\mu$ fingerprints. Figure 3.1 shows time dependent fingerprints acquired at 530 mV. The fingerprints are the running average of three consecutive scans (Fig. 3.1). These initial cathode spectra demonstrate the time-dependence of a peak at about 11568 eV. The time dependence is likely related to a variety of time constants, including surface and sub-surface catalyst restructuring induced by adsorption/desorption of oxygen. The fingerprint peak is observed to decrease in magnitude as the potential is held constant. This is coincident with the fact that 530 mV is a reducing potential for platinum oxide. The observed time constant is on the order of hours, which is much longer than expected for simple surface oxide reduction. The reduction of sub-surface oxygen species, which have been incorporated into the platinum lattice, may be responsible for the long time constant. To our knowledge, this is the first instance of time-dependent operando XAS of a fuel cell.
Figure 3.1 Time-dependent operando fluorescence XAS fingerprints highlighting an oxide peak at 11568 eV.

3.3.2 Potential-dependent $\Delta$-XANES

The fingerprint obtained at 204 minutes was used as the lowest potential plot in the potential dependent data of Fig. 3.2. The rest of the potential-dependent signatures are running averages of 30 scans taken at the given voltages. The peak shown at 11568 eV is the same oxide peak shown in the time-dependent signatures (Fig. 3.1). As the potential was increased from 600 – 900 mV, the signature oxide peak increased. At OCV, the peak intensity increased dramatically. The ex situ dry MEA signature shows that the cathode is completely oxidized before exposure to the fuel cell environment, consistent with the results of Stoupin et al.\textsuperscript{80}
Figure 3.2: Potential-dependent operando fluorescence XAS fingerprints highlighting an oxide peak at 11568 eV.

The potential-dependent data shows a negative dip at about 11564 eV that evolves at 780, 820, and 900 mV. This negative dip has been hypothesized to be a manifestation of the ligand effect, which is the withdrawal of electron density from nearby atoms due to adsorption of an electronegative atom or molecule.\textsuperscript{81} Charge transfer can shift a XANES edge to higher energy if there is charge depletion. Therefore, when a reference spectrum is subtracted from a blue-shifted spectrum, the result is a negative dip in the $\Delta$-XANES signatures.

However, this negative dip should be interpreted with caution. There are inherent errors in creating accurate $\Delta \mu$ fingerprints. To create reproducible fingerprints, the reference and sample spectra need to be reproducibly aligned within 0.01 eV. Furthermore, the Si (111) crystal monochromator that controls the beam frequency is only accurate to $\pm$ 0.01 eV. Consequently, even if two experimental spectra could be accurately and reproducibly aligned to 0.01 eV, the error inherent in the data is too large.
The manifestation of this error is not equally distributed through the whole spectrum, the greatest impact is in the lower energy region of the signatures (Fig. 3.3).

Figure 3.3: The error distribution through a $\Delta \mu$ fingerprint. Error is represented by the shaded area.

3.4 Conclusions

Excellent quality operando fluorescence XAS has been acquired with high signal-to-noise ratios using a new operando spectroscopy cell. The time-dependent data, obtained with the cell, elucidates a time constant for surface and sub-surface oxide removal that is on the order of hours. XAS taken at increasing potentials exhibit an increase in the magnitude of the oxide peak. The potential-dependent spectra also exhibit a negative dip prior to the oxide peak, which could be the manifestation of the ligand effect. However, alignment errors in XANES and instrumental uncertainty in XAS instrumentation make the analysis of fine structure fingerprint features challenging.
4.1 Introduction

The potential-dependence of adsorbate coverages on a distribution of sites is likely the most important determining factor in electrocatalysis. An important example is the ORR. The sluggishness of the ORR kinetics is the primary barrier to the commercialization of PEMFCs. Diffusing dioxygen must compete with mobile anions and tenaciously adsorbed oxygen for free Pt sites. The competition with mobile anions can be mitigated by using electrolytes with anchored anions, such as Nafion.\(^82\) The competition with tenaciously adsorbed oxygen is a more difficult issue. A strategy for improving ORR catalysts is the alteration of the electronic band structure (by alloying) to increase the Pt oxidation potential.\(^83\)-\(^88\) A number of mixed metal catalysts have been studied as alloys and more recently as core shell structures. Model systems such as Pt skin alloys suggest that the key issue is electronic structure, with no need for alloying components on the surface.\(^89\)-\(^91\) De-alloying of Pt alloys is another strategy.\(^92\)-\(^97\) The experimental ORR work has been complemented with computational modeling based primarily on cluster or periodic density functional theory (DFT).\(^98\)-\(^111\)

Oxygen adsorption is an elementary step in anode fuel cell reactions as well. In DMFCs, oxygen adsorption is required for the bifunctional methanol oxidation mechanism.\(^112\)-\(^114\) Although Pt, a good C-H activator, oxidatively adsorbs methanol to yield adsorbed CO, it cannot provide the oxygen required for complete oxidation to CO\(_2\) within the practical DMFC anode potential window (200 – 350 mV vs. NHE). Thus practical DMFC anode catalysts are binary or ternary alloy systems where the alloying
components chemisorb oxygen at lower potentials (e.g., Os, Ru, W, etc).\textsuperscript{47, 112-118} In spite of a massive collective effort, the improvements in both anode and cathode kinetics over the past few decades have been incremental. Much of the improvements can be attributed to better preparative methods for MEAs.

The ability analyze adsorption site coverage dependencies is fundamental to understanding electrocatalysis. Towards that end subtractively normalized x-ray absorption near edge spectroscopy (\(\Delta\)-XANES) has been under development for analysis of site-specific adsorption in a variety of electrochemical systems.\textsuperscript{24-27, 33, 34, 119} The XANES of the substrate under adsorbate-free conditions is used as a subtraction standard for XANES obtained under conditions conducive to adsorption (e.g., by altering the potential or chemical environment). The challenge is interpretation of the experimental \(\Delta\)-XANES (\(\Delta\mu\) fingerprints). Ramaker uses theoretical XANES of model clusters such as the Pt\(_6\) Janin cluster\textsuperscript{120}(Fig. 4.1), with and without adsorbates, to calculate theoretical \(\Delta\mu\) fingerprints (\(\Delta\mu\) signatures).\textsuperscript{24-27, 33, 34, 119}

Figure 4.1: Janin cluster with adsorbed oxygen. Clockwise from top left: atop adsorption, bridged adsorption, hexagonal close-packed (hcp) adsorption, and face-centered cubic (fcc) adsorption.
The 6-atom Janin cluster is an ideal model because it can accommodate all four oxygen absorption sites: atop, bridged, fcc, and hcp.\textsuperscript{120} The $\Delta \mu$ signatures are calculated using FEFF8, a full multiple scattering code that employs self-consistent-field calculations of local electronic structure.\textsuperscript{121, 122} To date, the Ramaker $\Delta \mu$ signatures for oxygen adsorption have been limited to the scattering of photoelectrons originating from only one adsorbing Pt atom (atom-0 in Fig. 4.1?).\textsuperscript{24, 26, 33} However, Ankudinov et al.\textsuperscript{123} showed that changes in the near neighbor Pt-scattering potentials due to adsorbate-Pt bonds (i.e., changes in the Pt electronic structure) are sometimes more important than the effect of Pt-adsorbate photoelectron multiple scattering. For example, the Pauling electronegativity value for oxygen is 1.3 units larger than for Pt. Thus charge transfer from the Pt lattice to the adsorbate oxygen would be expected. The withdrawal of electrons from near neighbor Pt atoms should cause a blue shift in their respective XANES spectra. Such blue shifts would be manifested as a negative dip at the low energy side of the $\Delta$-XANES. In order to account for the ligand effect,\textsuperscript{81, 124} our first iteration in the development of a more meaningful signature involved the inclusion of x-ray absorption events from all of the atoms of the Janin cluster. These signatures are referred to as all-atoms signatures.

The metallic cluster has delocalized electrons that can participate in charge transfer during modification of the cluster chemical environment (e.g., adsorption processes) (Fig. 4.2).
Figure 4.2 A Janin cluster with oxygen adsorbed in the atop configuration. The orange arrows represent the direction of charge transfer through the cluster.

Since XAS probes all atoms in the cluster, the photoelectrons from all of the adsorbate-free Pt atoms and adsorbing atoms, should be included in the $\Delta \mu$ calculations (i.e., all-atoms model). However, the use of isolated Janin cluster atoms for an all-atoms model of oxygen adsorption overemphasizes Pt charge depletion of the Janin cluster atoms because they are artificially under-coordinated. A more realistic model would result from embedding the Janin cluster within a larger reservoir of Pt atoms. This work shows how progressive improvement of the $\Delta \mu$ signatures models (i.e., from the limited-absorber model of Ramaker, to an all-atoms model, and finally to an embedded-all-atoms model) elucidates the importance of charge transfer effects induced by the adsorbate. Moreover the analysis of the isolated all-atoms model provides insights into the relative contribution to charge transfer from each Janin cluster atoms. That information is masked by charge compensation from the Pt-reservoir in the embedded-all-atoms model. Thus observations extracted from progressively increasing the number of atoms contributing
photoelectrons (i.e., from limited-absorber atom model to the embedded all-atoms-model) contribute to the understanding of the ligand effect.

4.2 Methods

4.2.1 Janin all-atoms signatures

All-atoms signatures were computed for the atop and bridged adsorption configurations using FEFF8, a full multiple scattering code. The XANES for the adsorbate-free cluster and adsorption configurations were computed on a per-atom basis (0-5 Fig. 4.1). These simulated XANES were used to calculate per-atom $\Delta \mu$ signatures, which could be averaged without weighting or configurationally averaged to yield isolated all-atoms signatures. The criteria for the method of averaging will be discussed later.

4.2.2 Embedded all-atoms signatures

When the atop-adsorbed Janin cluster is embedded into the fcc Pt reservoir, the cluster symmetry is increased to $C_{4v}$ with the Pt – O bond as the $C_4$ axis (Fig. 4.3). The $C_4$ operation creates four equivalent atom-1 sites about atom-0, and atom-2, -3, -4, and -5 (the subsurface atoms) become equivalent. The increased symmetry allows for reassignment of the six available FEFF8 potentials to accommodate atoms of the Pt reservoir. Four unique potentials are distributed between the oxygen, atom-0, the atom-1s, and the subsurface atoms. The final two potentials are assigned to the reservoir. Each of the four non-reservoir (Janin atoms) potentials yields a per-atom signature. The per-atom signatures of a cluster configuration are configurationally averaged to yield an
embedded all-atom signature. The configurational average weights the per-atom signatures by the multiplicity generated by relevant symmetry operations (i.e., the atom-1 per-atom signature and the subsurface atom signatures are both weighted by four because their rotation about the C₄ axis).

Figure 4.3: A Janin cluster embedded in an fcc Pt lattice

The bridged adsorption configuration yields a C₂ᵥ symmetry upon insertion into the Pt reservoir. The σᵥ plane bisects the oxygen, atom-3, and atom-5. The σᵥ reflection makes atom-1 and -0 equivalent. Additionally, atom-2 and -4 have equal counterparts opposite of the plane. The σᵥ' plane bisects the oxygen, atom-1, and atom-0. Reflection through the σᵥ' plane equates the atom-2s to the atom-4s, and atom-3 to atom-5. As before, per-atom signatures are generated from the unique potentials of atom-0/1s, atom-2/4s, and atom-3/5s. Configurational-averaging weights atoms-2/4 by four, atoms-3/5 by two, and atoms-1/0 by two as per the relevant symmetry operations.

4.3 Results & Discussion

Figure 4.4a shows the isolated per-atom Δμ signatures for the atop (top) and
bridged (bottom) adsorption configurations. The atom-0 $\Delta \mu$ signatures for the atop and bridged configurations (dotted blue lines) correspond to the Teliska limited-absorber signatures, which only consider x-ray photoelectrons from atom-0. The primary effect of atop oxygen adsorption is an increase in the white line of the adsorbing atom-0. There is a slight increase in edge absorption of atoms-2, -4, -3 and -5. The slight increase in absorption in the atom-1 $\Delta \mu$ signature will be discussed in the context of the embedded-atop $\Delta \mu$ signatures. The lower panel of Fig. 4.4a shows the per-atom $\Delta \mu$ signatures for bridged oxygen adsorption on the isolated Janin cluster. In the bridged configuration atoms-2, -4, -3, and -5 exhibit a negative dip on the low-energy side of the peak. This is a manifestation of the ligand effect. These atoms experience substantial charge depletion upon adsorption of oxygen over atom-0 and -1. This causes the blue-shift in the XANES that is responsible for the negative dip in the $\Delta \mu$ signature. Negative dips are a direct consequence of a ligand effect. It is noteworthy that the atom-0 and atom-1 signatures are not exactly the same. This would be better discussed in the context of the embedded clusters, where the atom-0 and atom-1 signatures are exactly identical.

Figure 4.4b compares the embedded per-atom $\Delta \mu$ signatures of the atop (top panel) and bridged (lower panel) configurations. The atop atom-0 signature intensity decreases significantly when the cluster is exposed to the Pt reservoir electron density. Atoms-2, -4, -3, and -5 exhibit no change in the XANES, relative to the clean cluster, upon atop adsorption. The embedded atom-1 atop signature is similar to that of the isolated atom-1 atop signature except that the negative dip and the high intensity region are more sharply defined. The well-defined negative dip in the embedded signature
suggests that the Pt reservoir is unable to fully charge-compensate surface atoms in proximity to the adsorbing atom. In the embedded-bridged configuration, atoms-2, -4, -3, and -5, now subsurface atoms, are almost completely charge-compensated (i.e., atoms-3/5 still shows a small negative dip) by the reservoir electron density. The signatures of atom-1 and atom-0 are now exactly the same, as would be predicted by increased symmetry of the embedded cluster.

Figure 4.4c compares the configurational averages of the embedded (solid lines) and isolated (dashed lines) signatures for both adsorption configurations. In the atop-embedded signature, peak intensity is substantially decreased relative to the isolated cluster: The subsurface-atom embedded signatures contribute no intensity to the weighted average. It is noteworthy that the atom-1 charge depletion is completely masked by the magnitude of the atom-0 signature intensity. However, the higher-energy peak in the atom-1 signature is more prominent in the configurationally averaged embedded signature. That peak appears as a shoulder in the configurationally averaged isolated-cluster signature. In the bridge configuration, all of the charge depletion that results from charge transfer from atoms-2, -3, -4, and -5, are completely compensated for when those atoms are made subsurface by embedding the cluster. The negative dip in the isolated signature disappears completely, the signature intensity is decreased, and the profile is dominated by the atom-0/1 signature.
Figure 4.4a: Isolated per-atom signatures. Top: Signatures obtained with the atop configuration; Bottom: Signatures obtained with the bridged configuration.
Figure 4.4b: Embedded per-atom signatures. Top: Signatures obtained with the atop configuration; Bottom: Signatures obtained with the bridged configuration.
Figure 4.4c: Configurational averages of the per-atom signatures – dashed lines are isolated all-atoms signatures, solid lines are embedded all-atoms. Top: Signatures obtained with the atop configuration; Bottom: Signatures obtained with the bridged configuration.
4.4 Conclusions

Limited-absorber $\Delta \mu$ modeling precludes the ability to sense charge transfer effects concomitant with adsorption. Adsorbed oxygen on a Pt$_6$ Janin cluster modifies the x-ray absorption properties of the adsorbate-free Pt atoms. $\Delta \mu$ signatures calculated on per-atom basis show that all Pt-atom photoelectrons must be included in FEFF8 simulations if charge transfer effects are to be modeled. Although the isolated Janin all-atoms signatures overemphasize charge depletion (because Janin atoms are under-coordinated relative bulk Pt atoms) they do determine the per-atom contributions to charge transfer. Overemphasis of charge depletion can be mitigated by embedding the Janin cluster into a larger reservoir of Pt atoms. The embedded per-atom $\Delta \mu$ signatures demonstrate that only the surface atom-1 in the atop configuration remains charge depleted after change compensation from the Pt reservoir. All of the charge depletion resulting from charge transfer effects from sub-surface atoms is compensated for by the Pt reservoir. Thus this work shows how the progressive improvement of the signature models, from the limited-absorber model of Ramaker, to an all-atoms model, and finally to an embedded-all-atoms model, elucidates the importance of charge transfer effects induced by the adsorbate. Moreover the analysis of the all-atoms model provides insight into the source of charge transfer from near neighbor atoms, which are masked by charge compensation from the Pt-reservoir electron density as evidenced by the embedded all-atoms model.
5.1 Poisoning Studies

5.1.1 Introduction

In order for H\textsubscript{2}/air fuel cells to be a viable option for automotive power sources, they need to be able to withstand the dynamic environment of the roadway. Assuming that fuel cells will be gradually phased into automotive power, they will simultaneously be on the road with internal combustion engines (ICEs). Consequently, even though H\textsubscript{2}/air fuel cells are clean forms of energy, they will be subject to a number of air pollutants formed by ICEs such as NO\textsubscript{x} and SO\textsubscript{x} gases.

In situ voltammetric studies have shown these pollutants to have detrimental effects on the performance of H\textsubscript{2}/air fuel cells.\textsuperscript{127-134} In situ FTIR studies show that SO\textsubscript{2} is irreversibly adsorbed onto platinum catalysts in aqueous solutions.\textsuperscript{64-66} However, the effect of these contaminants have never been studied in a fuel cell by operando techniques. These gases, and their reduction intermediates have distinct vibrational modes in the IR region,\textsuperscript{20} which make them excellent candidates for study with the multispectroscopic cell by diffuse reflectance FTIR. The fingerprints of the adsorbed species and their reduction intermediates will enable mechanistic analysis of how these poisons adversely affect fuel cell performance.

5.1.2 Hypothesis and objectives

Based on the results of operando CO adsorption studies, it is hypothesized that there will be potential and site-specific coverage dependence of these adsorbates. It will
be interesting to see if \( \text{SO}_x \) and \( \text{NO}_x \) are adsorbed preferentially to \( \text{CO} \) or other common poisons. Examination of the potential dependence of the adsorbates, in tandem with fuel cell performance analysis, will provide information as to how adsorbate coverages affect performance. An understanding of these adsorption mechanisms is required if successful mitigation strategies are to be developed.

### 5.2 Epoxide Ring Opening with EPOCH

#### 5.2.1 Introduction

The non-Faradaic electronic promotion of organic chemistry (EPOCH) is an ideal catalytic system for epoxide ring-opening reactions, which represent an ideal synthetic route to a number of pharmaceutical building blocks. EPOCH conversion of epoxides to aldehydes and ketones provides a form of “green” chemistry in that atom efficiency is enhanced compared to conventional syntheses (e.g., the oxidative cleavage of alkenes). Moreover, solid polymer electrolytes obviate the need for liquid solvent waste disposals. EPOCH occurs by a proton-spillover mechanism: hydrogen oxidized at the anode of a PEM cell yields protons that migrate through the MEA to the cathode. The protons spillover onto the cathode catalyst surface and become co-adsorbates with the target organic reactants. The spillover protons have sufficient lifetime to catalyze isomerization of the adsorbate; a transistor-like base current of spillover protons amplifies organic transformations at the cathode.\(^{67-70}\)
5.2.2 Hypothesis and objectives

The multi spectroscopy cell will be utilized to monitor EPOCH conversion of epoxide ring-opening reactions via operando FTIR. Previous studies have examined EPOCH reactions through the use of in-line spectroscopy techniques to monitor the reaction effluent. These reactions are excellent candidates to be studied via operando FTIR because the reactants are adsorbed on the surface, reduced by spillover protons and then desorbed. Each of these steps will have a unique fingerprint in the FTIR spectra. The efficiency of the reaction can then be measured as a function of potential. Furthermore, the reaction intermediates can be studied, elucidating the multi-step reduction.
REFERENCES


