Final Technical Report for ER46239 DOE, "Surface-Directed Fabrication of Integrated Membrane-Electrode Interfaces"

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I. **Introduction.** The cathodic triple interface in a proton exchange membrane (PEM) fuel cell is the region where oxygen, protons, and electrons converge for the production of water. The preparation of this essential interface is often accomplished through classical coating and processing methods that yield poor control over uniformity and weak physical interactions between ionomer and electrode.[1,2] As an example of a common integration of catalyst layers within a fuel cell, a microscopically ill-defined mixture of catalyst and ionomer is sprayed or brushed onto a Nafion® membrane, and the resulting structure is pressed against a carbon cloth.[2] Due to the poor control of this method, a significantly thicker catalyst layer must be prepared to assure complete coating of the membrane, leading to poor utilization and waste of expensive materials.[3] Poor interfacial wiring of these key components undoubtedly contributes to the common identification of the oxygen reduction reaction and related reagent mass transfer as the predominate source of voltage losses in PEM fuel cells.[4-6]

The use of 3-D interfaces with controlled porosity can provide a boost in power[7] due to additional surface area for catalysis to support higher mass transfer rates.[8] The few prior investigations of porous interfaces in PEM fuel cells have been prepared by catalyst deposition within nanoporous supports[7] or through texturing of membrane surfaces.[9] These studies have not addressed the spatial definition or uniformity of materials (catalyst, ionomer, diffusion pathways) within this 3-D framework nor the direct chemical wiring of ionomer to the electrode surface. Methods to precisely control materials composition, structure, and dimensions at these 3-D interfaces could have a profound impact on the power, cost, and efficiency of alternative fuel cell architectures. Further, a detailed understanding of how the depth-dependent structure of ionomer films affects both proton and oxygen transport, as well as a means to tailor that structure for enhanced performance in PEM fuel cells, are presently lacking.

Nafion and similar perfluorosulfonate polymers provide very high proton conductivities when used as membranes, but these materials have serious drawbacks when applied to

interfaces. Due to their complex syntheses, these materials cannot be grown from surfaces to ensure uniform, chemically anchored coatings, which becomes more pronounced for porous electrodes that are instrumental in boosting the power at fuel cell interfaces. Simply forcing bulk polymers such as Nafion into small pores is unlikely to provide good uniformity.

In the past five years, we have established a research program to investigate the integration of electrode/catalyst support, gas diffusion pathways, and ionomer into a single network based on a bottom-up, surface-directed approach.[10-14] Here, the porous electrode surface provides the common foundation for both catalyst deposition and ionomer growth to develop a highly controlled process. Our efforts have focused on (1) the preparation of surface-initiated ionomer that can be grown from electrodes of essentially any geometry and is chemisorbed to the active electrode surface, and (2) the integration of this ionomer with both planar and 3-D electrodes that are atomically modified by Pt catalysts. Figure 1 shows a schematic of a single pore of such an integrated cathode where a catalytic Pt atomic layer is supported along the pores of a nanoporous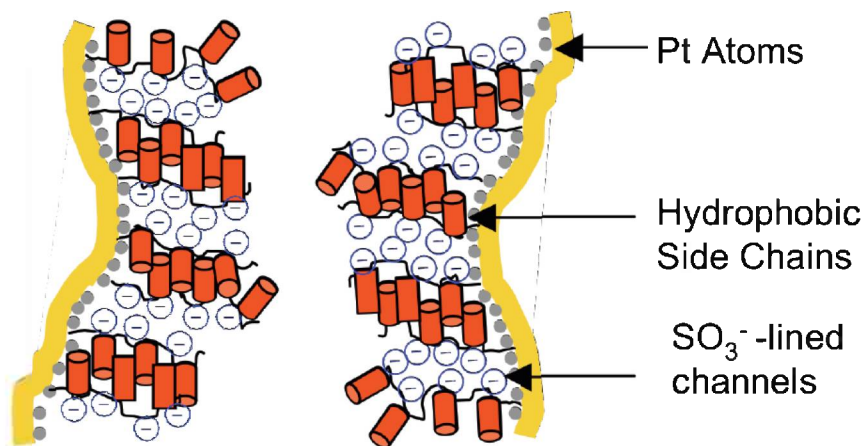 gold electrode. The catalyst layer is electronically accessible from the metal cathode and in contact with proton-conducting ionomer to yield extremely high utilization efficiencies of the catalyst (approaching 100%) with the ultralow loadings expected from atomic overlayers. We

Figure 1. Schematic illustration of a single pore within a porous gold cathode containing an atomic monolayer of a Pt and surface-initiated ionomer chains.

have introduced a new class of ionomer film that is grown from the catalyst/electrode interface to develop proton conducting pathways throughout the 3-D electrode and to the adsorbed catalyst particles. This ionomer is a comb polymer designed to contain sulfonate-lined channels for rapid proton conduction as well as hydrophobic domains (fluorocarbon or hydrocarbon) to

promote O_2 solubility and transfer. This interfacial ionomer is designed to interface with a bulk membrane (such as Nafion) and an anode that could be engineered in a similar way. A key conclusion thus far is that ionomer and Pt catalyst can be integrated at a single interface (both 2-D and 3-D) to provide a high level of control over the construction of electrodes.

To expand our efforts to date, we seek to utilize the materials chemistry we have developed to investigate how the depth-dependent structure of an ionomer film affects its performance in transferring protons and oxygen to accelerate the rate of the oxygen reduction reaction. By correlating structure and composition to performance and identifying barriers that limit efficiency, we seek to design ultra high performance ionomer films that are customized for the oxygen reduction reaction. Specifically, we will examine how the following factors impact structure and performance:

- the fluorocarbon volume fraction within the ionomer film, which is tailored by adjusting the chain length of the fluorocarbon side chains
- fluorocarbon versus hydrocarbon hydrophobic component
- the level of sulfonation, varied based on concentration and reaction time
- pore volume occupied by ionomer (versus that left open)

II. Progress Report.

By integrating catalyst, ionomer, and gas diffusion layer into a porous electrode architecture, we are developing a molecularly transformed cathodic interface of a proton exchange membrane fuel cell. The targeted cathode consists of a thin porous gold support (costs only 6 cents/cm^2) that is atomically modified by a Pt monolayer for ultra-low catalyst loadings and is integrated with fluorocarbon/hydrocarbon comb ionomer (Figure 2) through surface-initiated polymerization (SIP) from surface sites within the pores. The ionomer consists of sulfonated poly(*n*-alkylnorbornenes) (pNBHn-sulf) and poly((5-perfluoro-*n*-alkyl)norbornenes) (pNBFn-sulf), where n indicates the chain
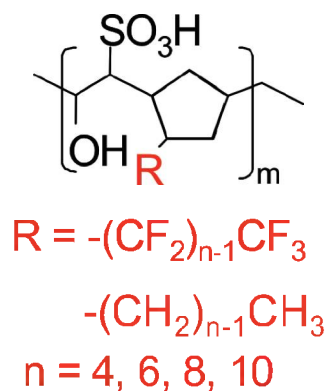
$$R = -(CF_2)_{n-1}CF_3$$
$$-(CH_2)_{n-1}CH_3$$
$$n = 4, 6, 8, 10$$

Figure 2. Schematic of ionomer repeat structure for pNBFn-sulf and pNBHn-sulf. The polymers are grown from electrodes via surface-initiated ROMP.

length of the fluorocarbon or hydrocarbon side chain. The surface-directed deposition of catalyst and ionomer enables high control over the composition within nanoporous electrodes and should enable high utilization of key materials. The combined higher interfacial area and utilization should boost the power and efficiency of proton exchange membrane fuel cells. Below, we briefly describe the milestones of this project.

II.1. Surface-Initiated Growth of Poly(n-Alkylnorbornene) Thin Films

We reported the first surface-initiated polymer film composed of poly(n-alkylnorbornene)s,[10] which contain internal olefin bonds to enable subsequent sulfonation (vide infra) to yield a structure as shown in Figure 2.

Figure 3. Schematic illustration of the gold surface preparation by attachment of allyl mercaptan and Grubbs' catalyst, denoted as [Ru], and the ring-opening metathesis polymerization of alkylnorbornenes.

Our approach (Figure 3) begins by preparing a vinyl-terminated monolayer on a surface by exposure to allyl mercaptan. The terminal vinyl group is reacted with a metathesis catalyst, immobilizing the catalyst on the substrate. The bound catalyst is then reacted with the desired monomer through ring-opening metathesis polymerization (ROMP) for 15 min to create a surface-tethered poly(n-alkylnorbornene) film. Importantly, the entire processing of this film can be accomplished within 30 min, allowing 10 min for the SAM, 5 min for Grubbs' catalyst attachment, and 15 min for the polymerization.[10]

Figure 4. RAIR spectra of a 50-nm polynorbornene film before (bottom) and after (top) sulfonation with acetyl sulfate. High conversion is indicated by the strong diminution of the out of plane C=CH bending peak at 968 cm^{-1}.

Films with longer alkyl chains exhibit greater hydrophobic structuring, as evidenced by surface IR spectroscopy. This increased hydrophobicity and alkyl structuring is critical to maintain hydrophobic domains for gas transfer once the film is sulfonated.
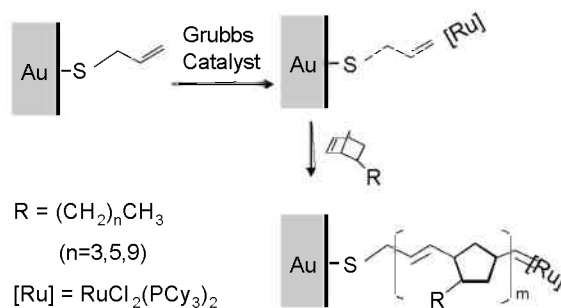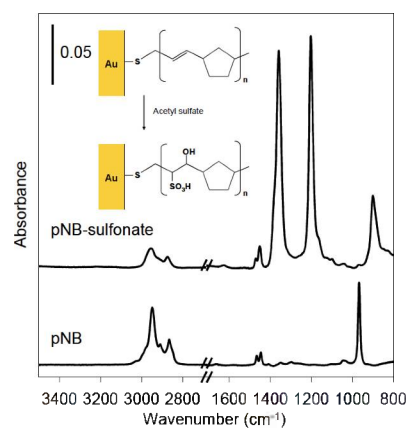
II.2. Sulfonation of Surface-Initiated Films

Upon exposure of a 60 nm pNB film to 0.1 M acetyl sulfate in dichloromethane for 5 min, the RAIR spectrum (Figure 4) indicates ~98% diminution of the trans C=CH out of plane bending peak (968 cm^{-1}) and reduction of all peaks associated with olefin functionality.[11] The introduction of sulfonate functionality is observed through the appearance of asymmetric and symmetric S=O stretching (~1359 and ~1204 cm^{-1}, respectively) and S-OH stretching (903 cm^{-1}) modes. The final sulfonated film is highly stable as evidenced by its stability in a good solvent (DMSO) under ultrasonic conditions.[11] In a procedure identical to that described above, we have sulfonated the pNBH4 and pNBH6 films via a 5 min reaction with 0.1 M acetyl sulfate and achieved analogous results with yields greater than 95%.[11] Sulfonation of these films reduces their resistance against proton transfer from $> 10^{6.5}$ $\Omega \bullet cm^2$ to < 10 $\Omega \bullet cm^2$. The factor of ~10^6 change in resistance is consistent with the combined hydrophilicity and ion transport capability of the additional sulfonate and hydroxyl functionality. The exceptionally low charge transfer resistance of the sulfonated film and its surface-initiate growth are promising for application as interfacial ionomers.[15]

II.3. Integration of Ionomer Films with Catalyst

We have shown that surface-initiated ionomer films are easily integrated with Pt catalyst at an electrode surface. We have used the method of Adzic and co-workers[16] to underpotentially deposit a monolayer of copper onto the gold surface followed by exposure to a solution of K$_2$PtCl$_4$ to electrolessly replace the adsorbed copper with Pt according to the following reaction:

$$Cu^0/Au + PtCl_4{}^{2-}(aq) \rightarrow Pt^0/Au + Cu^{2+}(aq) + 4\,Cl^-(aq)$$
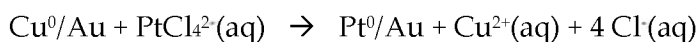
The resulting monolayer of Pt on gold is known to exhibit catalysis for oxygen reduction that

rivals pure Pt surfaces.[17] As shown in Figure 5, a polycrystalline gold electrode with a complete Pt monolayer, as quantified by X-ray photoelectron spectroscopy (XPS), exhibits high currents for the oxygen reduction reaction (~600 μA/cm^2) and a peak potential that is ~400 mV
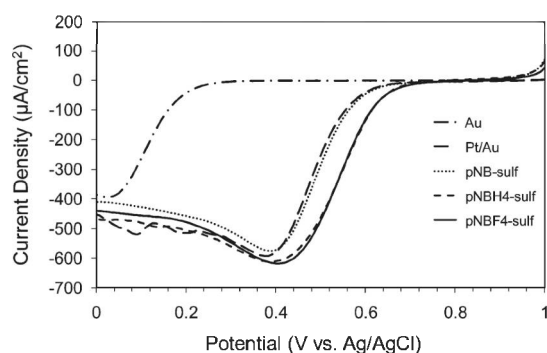
Figure 5. Voltammetric scans for oxygen reduction in O$_2$-saturated, 0.1 M H$_2$SO$_4$ (aq) for Au, Pt/Au, and sulfonated films of pNB, pNBH4, and pNBF4 that were grown from Pt/Au.

more anodic than the unfunctionalized gold surface. After deposition of the Pt monolayer, we grew ionomer from the surface as described above and demonstrated that molecular groups on the surface (SAM components) that do not anchor polymer could be electrochemically desorbed without affecting the ionomer film to effectively clean the interface and promote reactions at the electrode surface.[18] The use of an atomic Pt layer was instrumental here in showing that the catalyst was not destroyed or negatively impacted in the processing of the ionomer. Figure 5 also shows that the sulfonated films with hydrophobic structuring exhibit oxygen reduction at a potential that is ~80 mV more noble and higher currents than either the bare Pt monolayer or the pNB-sulf-coated Pt surface. The higher potential and current for these ionomer-modified electrodes are consistent with greater, sustainable O_2 concentration in the vicinity of the catalyst, most likely through effective partitioning of O_2 from solution into the hydrophobic domains of the ionomer. The purpose of this manuscript was to demonstrate that the surface-directed deposition of catalyst and ionomer are integral on a planar electrode surface.

II.4. Partially Fluorinated Polymer Films

While our earliest manuscripts from this project demonstrated the controlled growth and sulfonation of hydrocarbon polymer films by SI-ROMP and their integration with Pt catalyst at an electrode surface, we have more recently demonstrated the first SI-ROMP of partially fluorinated polymer films prepared from (5-perfluoro-n-alkyl)norbornenes (pNBFn; where n = 4, 6, 8, 10 fluorinated carbons)[13] with sulfonated repeat structure shown in Figure 2. These fluorocarbon films are advantageous as ionomers over hydrocarbons due to the stronger hydrophobic structuring of the fluorocarbon groups within the film and the enhanced solubility of oxygen within fluorocarbon structures.[19] By varying the fluorocarbon chain length, we are able to control the fluorocarbon volume fraction in the polymer and the critical surface tension.[13] The fluorocarbon side chains orient mostly parallel to the surface in the bulk of the film and almost normal to the surface at the polymer/air interface. The thicknesses of these films are controlled between a few nm and a few μm by varying the concentration of the monomer, and all the films can be grown rapidly through SI-ROMP (within 5 min).[13] Sulfonation of the film follows a similar method as for hydrocarbon films.[12]

II.5. Fluorocarbon Polymer Growth from Carbon Paper

We have used SI-ROMP of 5-(perfluoro-n-hexyl)norbornene (NBF6) to grow partially fluorinated polymer films (pNBF6) from the surface of carbon fibers within carbon paper.[14] By initial exposure of the carbon paper to O_2 plasma for a sufficient time, we were able to generate enough reactive groups on the surface to initiate the growth of a uniform polymer coating as evidenced by EIS and SEM images (Figure 6d). The advantage of a surface-initiated approach here is that only a very low percentage (< 5%) of reactive sites are required on the surface to nucleate the growth of the polymer. The films

Figure 6. Scanning electron micrographs of: (a) unmodified carbon paper, and pNBF6 grown on carbon paper treated in O_2 plasma for (b) 0 s, (c) 10 s, and (d) 45 s. The scale bar indicates 500 nm.

prepared here provide improved performance in wettability and coverage as compared to a commercially available Teflon®-coated carbon paper. Aside from a demonstration of feasibility to extend SI-ROMP to 3-D substrates, this approach could have practical applications to improve the hydrophobicity of the fibrous mat,[14] which should minimize the chances of flooding during fuel cell operation, and to provide a key step toward the bottom-up integration of partially fluorinated ionomer and catalyst on carbon paper electrodes.
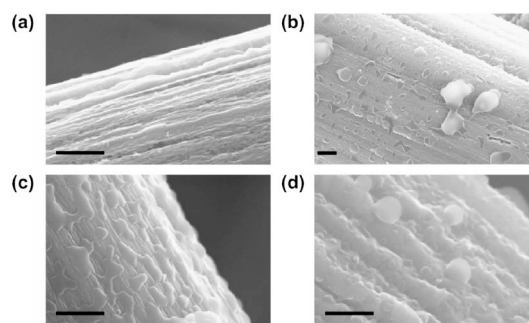
II.6. Ionomer Growth in Nanoporous Electrode Architectures

A key feature of the electroless catalyst and surface-initiated ionomer processing described above is that it can readily be extended into most 3-D architectures to achieve effective proton conduction over a large interfacial area. As a model 3-D electrode, we have selected the nanoporous gold leaf (NPGL) reported by Erlebacher and co-workers[20] but with a few key modifications to integrate more seamlessly into our processing.[21] As shown in Figure 7, this nanoporous substrate is prepared by floating a

Figure 7. Method for dealloying a 100-nm sheet of Ag/Au alloy to create nanoporous gold leaf (NPGL) films (top). The NPGL is then transferred to an aqueous solution directly above a pre-modified porous support (bottom left), and the water is gradually removed to allow the NPGL to chemically bind to and coat the porous support (alumina, in this case, bottom right), creating a thin functionalizable skin.

~100 nm ultrathin sheet of commercially available Ag/Au alloy (50%/50%) on concentrated nitric acid to etch away the silver and generate porosity. After transfer to the surface of water for rinsing, the NPGL can be collected and chemically anchored to a solid substrate, as we have previously shown,[22] but for fuel cell applications, collection of the NPGL onto a porous support is desirable to enable oxygen transfer from the backside while interfacing the top face with a suitable proton-conducting membrane, such as Nafion. To accomplish this latter goal, the rinsed NPGL is placed on the surface of water and positioned directly above a porous alumina or O_2-plasma-treated carbon paper support that is pre-modified with $(MeO)_3Si(CH_2)_3SH$ as a molecular adhesive to bond to both the porous support and the NPGL. The water is then removed from the container gradually so that the NPGL deposits directly onto the porous support. Figure 7 shows pictures of NPGL deposited onto nanoporous alumina. Using this approach, we can generate a robust
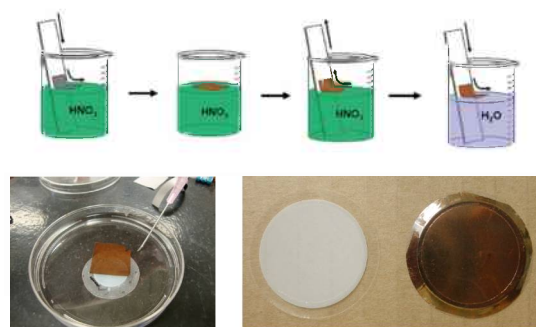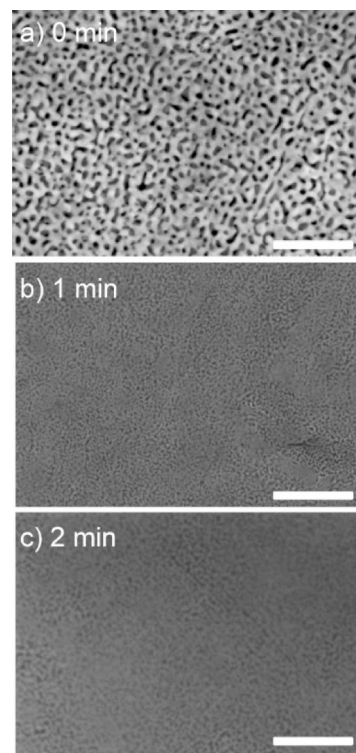

Figure 8. Scanning electron micrographs of pNBF6 films grown from a 0.05 M monomer solution on NPGL-coated alumina after different polymerization times. The scale bar indicates 1 μm.

ultrathin layer of gold (~100 nm) with pore sizes, which are controllable by the dealloying time,[22] ranging from 20 – 100 nm and up to a 20-fold enhancement in electrochemically accessible surface area as compared to a flat gold electrode. We have also shown that a Pt monolayer can be deposited throughout this structure.[23] SI-ROMP of NBF6 within this pore structure is evidenced by SEM images in Figure 8 that show shrinking and eventual filling of pores as time of exposure to the NBF6 monomer solution is increased, and by EIS, which shows that the electrode area is effectively blocked before sulfonation of the polymer but accessible after sulfonation.[21] We also demonstrate that the polymer can be grown selectively in the nanoporous gold or in both the nanoporous gold and porous alumina structures (Figure 9). Interestingly, the growing polymer also pushes the gold and alumina apart at an average rate of 0.6 nm/s as it grows in between them.[21]
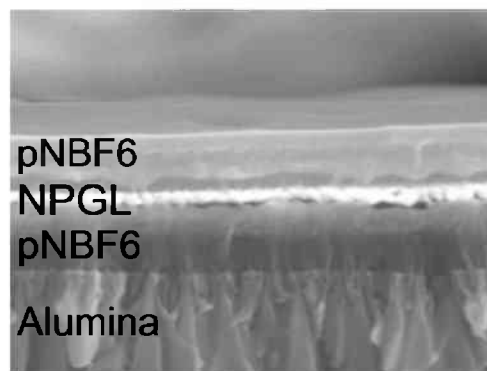

Figure 9. Scanning electron micrograph showing the cross section of a NPGL/alumina membrane in which pNBF6 was grown in both the porous gold and alumina sections and served as a "nano forklift" to raise the NPGL from the alumina surface.

II.7. Summary. Our accomplishments in this project represent a new way to engineer the triple interface of PEM fuel cell cathodes using the electrode surface to direct the deposition of key components. By exploiting bottom-up, surface-directed deposition of catalyst and ionomer, we have introduced an innately higher level of interfacial control that has tremendous potential to increase catalyst utilization through improved wiring to ionomer while minimizing loading.

II.8. List of Published Papers in which DOE Support is Acknowledged.

B. J. Berron, E. P. Graybill, and G. K. Jennings, "Growth and Structure of Surface-Initiated Poly(n-alkylnorbornene) Films," *Langmuir, 23,* 11651-11655, **2007.**

Berron, B. J.; Payne, P. A.; Jennings, G. K.; "Sulfonation of Surface-Initiated Polynorbornene Films," *Ind. Eng. Chem. Res., 47,* 7707 - 7714, **2008.**

B. J. Berron, C. J. Faulkner, R. E. Fischer, P. A. Payne, and G. K. Jennings, "Surface-Initiated Growth of Ionomer Films from Pt-Modified Gold Electrodes," *Langmuir, 25,* 12721-12728, **2009.**

C. J. Faulkner, R. E. Fischer, and G. K. Jennings, "Surface-Initiated Polymerization of 5-(Perfluoro-n-alkyl)norbornenes from Gold Substrates," *Macromolecules, 43,* 1203-1209, **2010.**

C. J. Faulkner, P. A. Payne, and G. K. Jennings, "Surface-Initiated Ring-Opening Metathesis Polymerization of 5-(perfluorohexyl)norbornene on Carbon Paper Electrodes," *Journal of Colloid and Interface Science, 351,* 248-253, **2010.**

P. N. Ciesielski, C. J. Faulkner, M. Irwin, J. Gregory, D. E. Cliffel, N. H. Tolk, and G. K. Jennings, "Enhanced Photocurrent Production by Photosystem I Multilayer Assemblies," *Advanced Functional Materials, 20,* 4048-4054, **2010.**

C. A. Escobar, A. R. Zulkifli, C. J. Faulkner, A. Trzeciak, and G. K. Jennings, "Composite Fluorocarbon Membranes by Surface-Initiated Polymerization from Nanoporous Gold-Coated Alumina," *ACS Applied Materials & Interfaces* **2012,** 4, 906-915.

II.9. Career Development of Supported Students. This project has funded one Ph.D. student per year and one undergraduate per summer. Brad Berron finished his Ph.D. with funding from this project in 2008 and is now an Assistant Professor of Chemical Engineering at the University of Kentucky. Chris Faulkner, who was funded for 1.5 years on this grant, completed his Ph.D in January, 2010, and is now employed by ClearEdge Power in Oregon for the development of fuel cells. Current Ph.D. student Carlos Escobar was funded on this project for one year and is set to receive his Ph.D. in January of 2014. He has accepted a job with Dow Chemical. Of the six undergraduate students trained on this project, three (Evan Graybill, Andrew Payne, and Remington Fischer) each finished in the top 2 (with Graybill 1st) nationwide each year at the American Institute for Chemical Engineers Undergraduate Poster Session in the Energy/Fuels Division. All the undergraduates are either gainfully employed or in professional school.

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