

V.P.20 Strategies for Probing Nanometer-Scale Electrocatalysts: From Single Particles to Catalyst-Membrane Architectures

Carol Korzeniewski

Texas Tech University
Department of Chemistry & Biochemistry
Lubbock, TX 79409-1061
Phone: (806) 742-4181; Fax: (806) 742-1289
E-mail: carol.korzeniewski@ttu.edu

DOE Program Officer: Richard. D. Kelley

Phone: (301) 903-6051
E-mail: richard.kelley@science.doe.gov

Subcontractors: none

Objectives

Primary objectives are to prepare and elucidate the promoting properties of materials that possess high activity for the conversion of H₂ and related small molecules (H₂O, O₂, CO and CH₃OH) in polymer electrolyte fuel cells. One area of research focuses on the study of catalyst materials. Protocols are being developed for probing the structure and benchmarking the activity of Pt and Pt bimetallic nanometer-scale catalyst against Pt single crystal electrode standards. A second area targets fuel cell membrane and the advancement of simple methods based on infrared spectroscopy that can be applied broadly in the study of membrane structure and transport properties.

Technical Barriers

Research aims to identify and overcome factors that limit the stability and performance of polymer electrolyte fuel cell catalyst and membrane materials. Methods are being developed to assess effects of catalyst composition and structure on the rate of electrocatalytic reactions. Techniques are under investigation to assist the design of robust, proton conductive membranes, which resist reactant crossover.

Abstract, Progress Report and Future Directions

A. Fuel Cell Membrane and Catalyst-Membrane Architectures Probed by Vibrational Spectroscopy: Infrared and Raman spectroscopy were investigated as probes of structures within proton conductive materials that limit or enhance performance in polymer electrolyte fuel cells. The following were primary accomplishments: (a) least squares modeling in conjunction with infrared spectroscopy was demonstrated as a useful approach

to detect differences in the response of hydrophilic and more hydrophobic functional groups in ionomer materials undergoing changes in hydration state [1]; (b) strategies developed during the project through studies of model Nafion membranes [2-4] were adapted to investigate new bis(perfluoroalkylsulfonyl) imide [5] and fluoroalkyl phosphonate [6] ionomer materials; (c) the capabilities of Raman spectroscopy were explored for its potential to enable depth profiling of practical fuel cell membrane and *in situ* studies of fuel cell catalyst-membrane architectures.

In initial work, transmission infrared measurements were performed on thin (~1 μm) Nafion® films [1,3] and freestanding (~50 μm) Nafion® 112 fuel cell membrane [2,4]. Effects of hydration on polymer functional groups [1] and water molecules inside membrane pores and channels [2] were examined. Figure 1 shows a series of infrared spectra recorded during the hydration of a thin Nafion® membrane. The region that encompasses the fundamental ionomer vibrations is displayed. The arrows indicate the shifts in band position and intensity that accompany water uptake. The spectra were examined by applying a least squares approach [7,8]. A diffusion equation that describes molecular transport within a cylindrical pore [9-11] was used to predict the time dependent uptake of water into the membrane [1,3]. The analysis revealed bands for vibrational modes for the more hydrophobic polymer functional

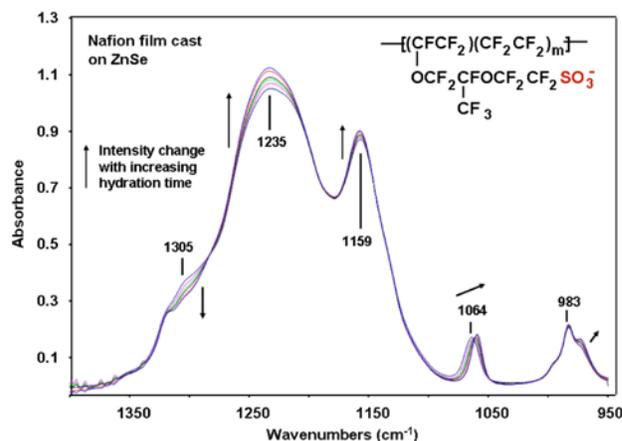


FIGURE 1. Infrared spectra of a Nafion® film cast onto a ZnSe optical window recorded during hydration in 100 % relative humidity air starting from a dry state. Spectra were recorded at times of 0 min, 0.75 min, 1.5 min, 2.25 min, 6.75 min and 28 min after exposure to humid air. The arrows indicate the direction of band intensity change with increasing hydration. The inset shows the Nafion® polymer structure. See Ref. 1 for details.

groups ($-\text{CF}_2$ and $-\text{C}-\text{O}-\text{C}-$) changed as predicted by the diffusion equation, whereas the response of the prominent band for the asymmetric S-O stretching mode of the hydrophilic $-\text{SO}_3^-$ group (near 1064 cm^{-1} (Fig. 1)) was more complicated. The deviations exhibited by the $-\text{SO}_3^-$ group vibrations were similar to those that we found for the O-H stretching modes of water inside membrane pores and channels [3]. The different responses observed for the hydrophilic and more hydrophobic ionomer functional groups were ascribed to the more complicated water structures that form in the vicinity of $-\text{SO}_3^-$ groups, due to neighboring solvated cations. Full details of the study are presented in Ref 1.

Subsequent efforts focused on extending strategies developed for the study of Nafion[®] membrane to new bis(perfluoroalkylsulfonyl) imide [5] and perfluoroalkyl phosphate [6] ionomer materials. Studies showed the vibrations of the side chain ether groups are sensitive to the nature of the charged end group. In hydrated Nafion[®], the symmetric $-\text{C}-\text{O}-\text{C}-$ stretching mode of the ether closest to the $-\text{SO}_3^-$ group appears as a low energy shoulder on the band for the ether closest to the ionomer backbone at 983 cm^{-1} (Fig. 1) [12]. The splitting of $-\text{C}-\text{O}-\text{C}-$ modes has been attributed to the different environments experienced by the two side chain groups in hydrated Nafion[®] [12]. We observed that substitution of the $-\text{SO}_3^-$ group by a bis(sulfonyl) imide ($-\text{SO}_2\text{NSO}_2\text{CF}_3$) moiety lifts the apparent splitting of ether group modes leaving only the 983 cm^{-1} band [5]. Similar effects are being detected with different types of phosphonate end group substitutions [6]. In accord with earlier studies [12], the spectral perturbations are being examined with consideration of the possible differences in the solvent environment in the vicinity of the charged end group.

The project also investigated Raman spectroscopy for applications in the study of ionomer materials. Raman spectra that were recorded from Nafion[®] materials are displayed in Fig. 2. Ongoing experiments are exploring effects of the Raman excitation wavelength on the spectral signals. The long-term benefits of Raman spectroscopy are its potential to enable depth profiling within fuel cell membrane via confocal measurements and *in situ* studies of fuel cell membrane-electrode assemblies.

B. Catalyst particle properties and electrochemical activity:

A second effort investigated Pt and Pt bimetallic fuel cell catalyst [13-15]. Emphasis was on the use of Pt single crystal electrodes as standards to benchmark catalyst activity [14, 15]. Pt single crystal electrodes were grown in the PI's laboratory, and building on the group's earlier investigations of vibrational coupling in CO adlayers on Pt(s)-[4(111) x (100)] and related surfaces [16-18], initial experiments focused on kinetic measurements of CO oxidation. Quantitative electrochemical techniques for determining CO coverage on Pt were applied. Following

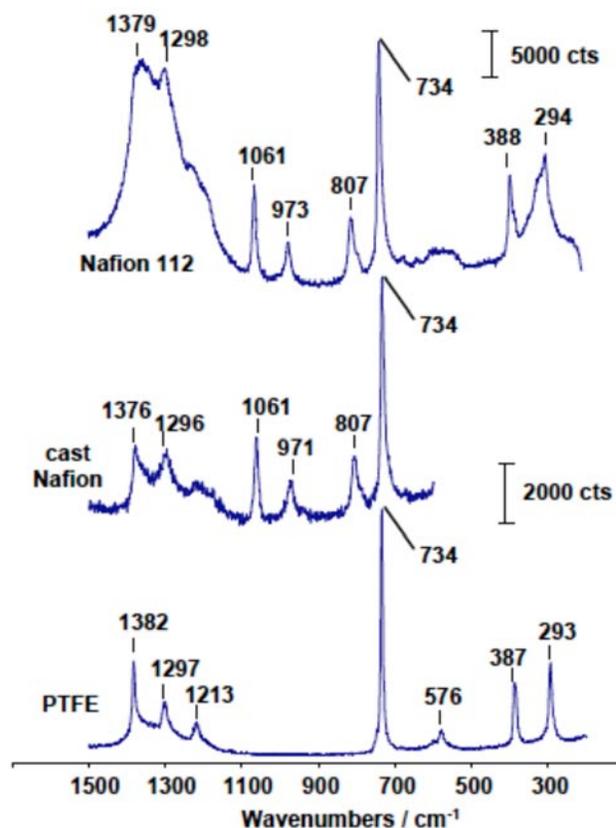


FIGURE 2. Raman spectra recorded with the use of 785 nm excitation.

studies that employed low index Pt surface planes [14], techniques were extended to the stepped Pt(s)-[4(111) x (100)] surface [15]. The saturation coverage for CO on a Pt(s)-[4(111) x (100)] electrode was determined for the first time and found to be consistent with expectations based on ultra high vacuum surface science experiments on the system [19-21]. Our study also included the first kinetic measurements of sub-saturation coverage CO monolayer oxidation. Current-time transients recorded in potential step experiments could be fit by numerically solving the rate equations [22] to the Langmuir-Hinshelwood model of adsorbed CO electrochemical oxidation. Fig. 3 shows the changes that occur in experimental current-time transients as initial CO monolayer coverage is lowered. The comparison to the current-time transients determined by solving the reaction rate equations for CO monolayer electrochemical oxidation is detailed in Ref 15. The experiments laid groundwork for our subsequent benchmarking in kinetic studies of electrochemical reactions for small molecules (O_2 , CO, CH_3OH) over practical catalyst materials.

References

1. Korzeniewski, C.; Adams, E.; Liu, D., *Appl. Spectrosc.* **2008**, *62*, 634.

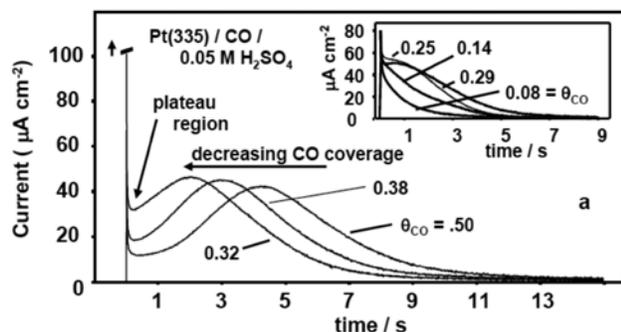


FIGURE 3. Current-time transients recorded during CO electrochemical oxidation at 0.7 V_{RHE} on Pt(s)-[4(111) × (100)] ≡ Pt(335) for the initial coverages indicated. Full details are given in Ref 15.

2. Basnayake, R. Peterson, G.R. Casadonte, D.J., Jr. and Korzeniewski, C. *J. Phys. Chem. B* **2006**, *110*, 23938.
3. Korzeniewski, C.; Snow, D. Basnayake, R., *Appl. Spectrosc.* **2006**, *60*, 599.
4. Basnayake, R.; Wever, W.; Korzeniewski, C. *Electrochim. Acta* **2007**, *53*, 1259.
5. Byun, C.K.; Sharif, I.; DesMarteau, D.D.; Creager, S.E.; Korzeniewski, C. *J. Phys. Chem. B* **2009**, *113*, 6299.
6. Byun, C.K.; Korzeniewski, C. *Anal. Chem.* (in preparation).
7. Rivera, D.; Peterson, P.E.; Uibel, R.H.; Harris, J.M. *Anal. Chem.* **2000**, *72*, 1543.
8. Rivera, D.; Harris, J.M. *Anal. Chem.* **2001**, *73*, 411.
9. Goswami, A.; Acharya, A.; Pandey, A.K. *J. Phys. Chem. B* **2001**, *105*, 9196.
10. Suresh, G.; Scindia, Y.M.; Pandey, A.K.; Goswami, A. *J. Membr. Sci.* **2005**, *250*, 39.
11. Suresh, G.; Scindia, Y.M.; Pandey, A.K.; Goswami, A. *J. Phys. Chem. B* **2004**, *108*, 4104.
12. Cable, K.M.; Mauritz, K.A.; Moore, R.B. *J. Polym. Sci.: Part B: Polym. Phys.* **1995**, *33*, 1065.
13. Stoupin, S., *et al.*, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6430.
14. Inkaew, P. and Korzeniewski, C. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3655.
15. Inkaew, P.; Zhou, W.; Korzeniewski, C., *J. Electroanal. Chem.* **2008**, *614*, 93.
16. Kim, C.S.; Korzeniewski, C. *Anal. Chem.* **1997**, *69*, 2349.
17. Kim, C.S.; Tornquist, W.J.; Korzeniewski, C. *J. Chem. Phys.* **1994**, *101*, 9113.
18. Kim, C.S.; Korzeniewski, C.; Tornquist, W.J. *J. Chem. Phys.* **1994**, *100*, 628.
19. Xu, J.; Yates, J.T., Jr. *J. Chem. Phys.* **1993**, *99*, 725.
20. Xu, J.; Henriksen, P.; Yates, J.T., Jr. *J. Chem. Phys.* **1992**, *97*, 5250.
21. Lambert, D.K.; Tobin, R.G. *Surf. Sci.* **1990**, *232*, 149.
22. Koper, M.T.M., *et al.*, *J. Chem. Phys.* **1998**, *109*, 6051.

Publications (including patents) acknowledging the grant or contract

1. Byun, C.K.; Sharif, I.; DesMarteau, D.D.; Creager, S.E.; Korzeniewski, C. "Infrared Spectroscopy of Bis(perfluoroalkylsulfonyl) Imide Ionomer Membrane Materials" *J. Phys. Chem. B* **2009**, *113*, 6299.
2. Stoupin, S.; Rivera, H.; Li, Z.; Segre, C.U.; Korzeniewski, C.; Casadonte, D.J., Jr.; Smotkin, E.S. "Structural analysis of sonochemically prepared PtRu versus Johnson Matthey PtRu in operating direct methanol fuel cells" *Phys. Chem. Chem. Phys.* **2008**, *10*, 6430.
3. Inkaew, P. and Korzeniewski, C. "Kinetic Studies of Adsorbed CO Electrochemical Oxidation on Pt(335) at Full and Sub-Saturation Coverages", *Phys. Chem. Chem. Phys.* **2008**, *10*, 3655.
4. Korzeniewski, C.; Adams, E.; Liu, D. "Responses of Hydrophobic and Hydrophilic Groups in Nafion Differentiated By Least Squares Modeling of Infrared Spectra Recorded During Thin Film Hydration" *Applied Spectroscopy* **2008**, *62*, 634.
5. Inkaew, P.; Zhou, W.; Korzeniewski, C. "CO monolayer oxidation at Pt(100) probed by potential step measurements in comparison to Pt(111) and Pt nanoparticle catalyst" *J. Electroanal. Chem.* **2008**, *614*, 93.
6. Basnayake, R.; Wever, W.; Korzeniewski, C. "Hydration of Freestanding Nafion Membrane in Proton and Sodium Ion Exchanged Forms Probed by Infrared Spectroscopy" *Electrochim. Acta* (Special Issue on Select Papers from 2006 ISE Meeting) **2007**, *53*, 1259.
7. Korzeniewski, C.; Snow, D. Basnayake, R.; "Transmission IR Spectroscopy as a Probe of Nafion Film Structure: Identification and Resolution of Complex Spectral Regions Fundamental to Understanding Hydration Effects" *Applied Spectroscopy* **2006**, *60*, 599.
8. Basnayake, R. Peterson, G.R. Casadonte, D.J., Jr. and Korzeniewski, C. "Hydration and Interfacial Water in Nafion Membrane Probed by Transmission Infrared Spectroscopy" *J. Phys. Chem. B* **2006**, *110*, 23938.
9. Korzeniewski, C. "Vibrational Spectroscopy for the Characterization of PEM Fuel Cell Membrane Materials" In *Fuel Cell Science: Theory, Fundamentals, and Bio-Catalysis*, Norskov, J. and Wieckowski, A., Eds. Wiley (in press).