

V.D.6 Strategies for Probing Nanometer-Scale Electrocatalysts: From Single Particles to Catalyst-Membrane Architectures

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Objectives

Primary objectives are to prepare and elucidate the promoting properties of materials that possess high activity for the conversion of H_2 and related small molecules (H_2O , O_2 , CO and CH_3OH) 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 Infrared Spectroscopy: One area under investigation is the use of least squares modeling in conjunction with infrared spectroscopy to gain greater understanding of structures within proton conductive materials that limit or enhance performance in polymer electrolyte fuel cells. Initial work is focusing on Nafion[®] [1-3] and aims to produce guidelines for application to new membrane materials.

To lay groundwork, transmission infrared measurements were performed on thin ($\sim 1 \mu m$) Nafion[®] films [1] and freestanding ($\sim 50 \mu m$) Nafion[®] 112 fuel cell membrane [2]. Effects of hydration on the polymer [1] and water molecules inside membrane pores and channels [2] were examined. Of particular interest was the appearance of interfacial water vibrational bands. The features were investigated in detail for Nafion[®] 112 under controlled humidity [2-3].

Figure 1 shows a sequence of infrared spectra that follow water uptake into Na^+ exchanged Nafion[®] 112 in air at approximately 10 % relative humidity. The O-H stretching region is highlighted. The band assignments have been discussed in detail (see Refs 1-3, and references therein). The features arise from condensed water inside the membrane and show evidence of water-polymer interactions. The broad feature near 3525 cm^{-1} is associated with water O-H stretching and appears at higher energy compared to the ν_1 (3200 cm^{-1}) and ν_3 (3400 cm^{-1}) modes of bulk liquid water, indicating the hydrogen bonding interactions among the water molecules inside the Nafion[®] pores and channels are weaker than in the bulk [4-7]. The peaks labeled 3674 cm^{-1} and 3712 cm^{-1} are due to O-H stretching modes of interfacial water [4-7] and have been observed previously in infrared spectra of Nafion[®] in a variety of cation exchanged forms [4,5]. The 3674 cm^{-1} band has been assigned to stretching of the free-OH group of water molecules that extend one O-H into fluorocarbon-rich regions of Nafion[®] [2,4,5]. The 3712 cm^{-1} band has been ascribed to water molecules that neighbor

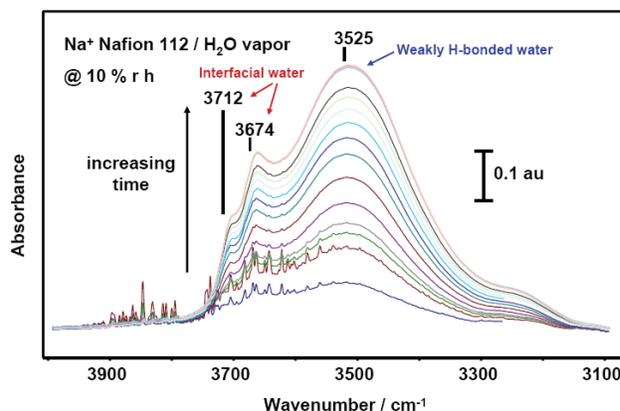


FIGURE 1. Transmission infrared spectra of Na^+ exchanged Nafion[®] 112 membrane after initial drying (bottom) and following subsequent exposure to atmosphere above LiCl saturated H_2O (ca. 10 % relative humidity) for 2 min, 5 min, 8 min, 15 min, 30 min, 45 min, 1 hr, 1.25 hr, 1.5 hr, 1.75 hr, 2 hr, 3 hr, and 5 hr (in order from the next to bottom spectrum to the top).

ionic groups [2,4,5], or possibly straddle water-vapor interfaces inside Nafion[®] membrane [2]. In addition to the prior literature on the vibrational spectroscopy of hydrated Nafion[®], we also draw upon recent results from sum frequency vibrational spectroscopy (SFVS) studies of water/organic [6,7] and salt-solution/air interfaces [8] in making spectral band assignments [2].

To gain deeper insight into environments within hydrated Nafion[®] and related proton conductive materials, multivariate analysis techniques are being explored with emphasis on adapting the least squares modeling strategy applied by Rivera and Harris [9,10] to studies of site heterogeneity in sol-gel films. Initial tests of a program that encodes the algorithm used by Rivera and Harris [9] were discussed in the spring 2006 progress report. In the present report, results are presented that show water sorption into Nafion[®] 112 membrane follows a pore-diffusion model. In ongoing work, the pore-diffusion model is being applied to determine component spectra from least squares analysis of infrared spectral data.

Figure 2 shows the variation in peak intensity at 3525 cm⁻¹ versus time during water uptake into Nafion[®] 112. The points are average values determined from the data in Figure 1 and two replicate experiments. The solid line in Figure 2 is the fit of the data points to the pore diffusion model [11-13] according to Eq. 1:

$$\frac{A}{A_{\max}} = \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{D}{L^2} (2n+1)^2 \pi^2 t\right) \right] \quad [1]$$

where D is a diffusion coefficient, L is the pore length, A is the band absorbance and A_{max} is the maximum absorbance attained at long times. The sum in Eq. 1 was carried out to n = 3. We achieved similar fits for the integrated intensities of the bands at 3525 cm⁻¹ and 3674 cm⁻¹ [3]. The correspondence between the experimental time dependent absorbance data and the pore diffusion equation is consistent with proposed structures of Nafion[®] as consisting of a network of hydrophilic pores and channels. Isotope exchange kinetics facilitated by diffusion of water [12] and cations [11,13] into water swollen Nafion[®] have also been shown to be in accord with Eq. 1.

As mentioned above, Eq. 1 is being applied to the determination of component spectra derived through least squares modeling of spectral data sets. Subsequent work will look for similar behavior in Nafion[®] 112 exchanged by H⁺ [2]. Our recent experiments on H⁺ exchanged Nafion[®] 112 revealed the rich spectra of solvated H₃O⁺ species in Nafion[®] [2] and the more rapid time for water sorption compared to metal cation exchanged Nafion[®] [3]. A long range goal is to extend understanding to the study of membrane-catalyst architectures probed through the use of attenuated total reflection sampling.

Prior to spectral acquisition, samples of Nafion[®] 112 were cleaned and ion exchanged using procedures developed for measurements on Nafion[®] 112 and related membrane in preparation for fuel cell use [14].

B. Catalyst particle properties and electrochemical activity: A second area under investigation is the activity and stability of Pt and Pt bimetallic fuel cell catalyst. Special emphasis is on materials for O₂ reduction. Pt single crystal electrodes are being employed as standards to benchmark catalyst activity. Earlier approaches of Markovic [15] and Feliu [16] are serving as a guide. Figure 3 shows cyclic voltammograms for a Pt(100) electrode in a rotating

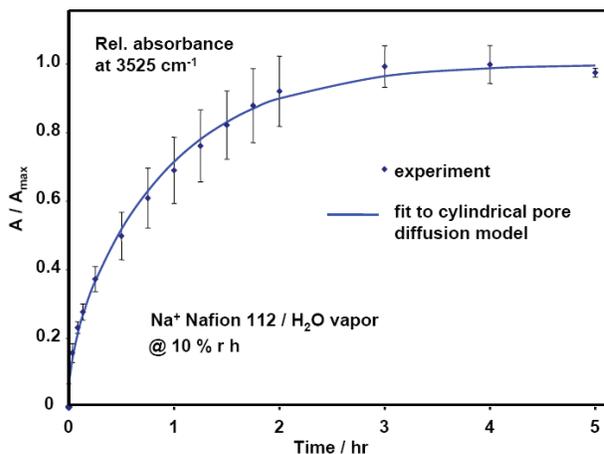


FIGURE 2. Plot showing peak absorbance at 3525 cm⁻¹ versus time following the addition of LiCl saturated H₂O to the humectant chamber in a cell holding a Na⁺ exchanged Nafion[®] 112 membrane. See Figure 1 legend for other details. The error bars give the standard deviations on the average of triplicate measurements. The absorbance values were normalized to the maximum absorbance attained at times > 3 hr. The solid line shows the fit to the pore diffusion model in Eq. 1 with L²/D = 3.41 x 10⁴ s (τ/π² = 0.96 hrs).

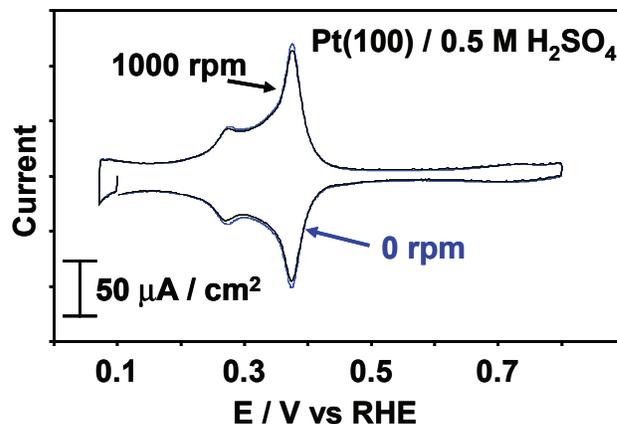


FIGURE 3. Cyclic voltammograms of a Pt(100) electrode in a rotating disk electrode assembly, with and without rotation, as indicated. Scan rate = 50 mV/s.

disk electrode assembly. The voltammetry is benchmark for Pt(100) [15,16], and the near identical responses with and without rotation demonstrate the cleanliness of the system [15,16]. Ongoing experiments are investigating O₂ reduction kinetics at nanoscale PtCo, using Pt crystals to establish the baseline performance and monitor cleanliness of the system. PtCo samples are provided by Dr. Timothy J. Boyle in the Advanced Materials Laboratory at Sandia National Laboratories. A long term goal is to correlate the electrochemical responses with catalyst structure through the use of high resolution electron microscope techniques in collaboration with the Boyle group.

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Publications (Including Patents) Acknowledging the Grant or Contract

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