Operando infrared spectroscopy of the fuel cell membrane electrode assembly Nafion–platinum interface

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ABSTRACT

The Nafion–Pt interfaces in membrane electrode assemblies of operating fuel cells were studied by operando infrared spectroscopy. The potential dependence of atop adsorbed CO peak frequencies were measured over the potential range of 0–600 mV (vs. NHE) at 60 °C. Complex Stark tuning of peak frequencies arise from a combination of potential dependent coverage effects, and changes in the extent of back-donation from the metal d-band to the renormalized $2\pi^*$ MO of CO_{ads}. The Nafion–Pt interface was studied at higher potentials (initiating at open circuit) by examining platinum reflectivity as a function of electrode potential. The oxygen reduction onset-current is coincident with the observance of a 2% step-increase in Pt reflectivity and emergence of Nafion–Pt interface spectra.

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1. Introduction

The ionomer-catalyst interface is the site of chemical transformation in a polymer electrolyte fuel cell membrane electrode assembly (MEA). The MEA is a polymer electrolyte membrane sandwiched between anode and cathode catalytic layers. The electrocatalytic layers are contacted to porous carbon paper or cloth that serve both as current collectors and gas diffusion layers (GDLs). The GDLs facilitate transport of reactants and products between the fuel cell flow fields and the ionomer-catalyst interfaces. Catalysts are dispersed in alcoholic solutions of a solubilized version of the polymer electrolyte to form an ink that is deposited on the membrane directly (catalyst-coated-membrane), or deposited directly onto the GDL to form a gas diffusion electrode. The final form of the electrocatalytic layers have carbon supported metal or metal-black surfaces [1] wetted by the ionomer electrolyte.

The ionomer facilitates proton transport and enhances electrocatalysis [2].

MEAs have applications in organic synthesis [3–10], environmental remediation [11,12] energy conversion [13] and storage devices [14–17]. Each application requires an ionomer-catalyst interface that is optimized for the required chemical reaction. Optimization requires methods for characterization under *relevant* conditions. Because the active state of the ionomer-catalyst interface exists only during electrocatalysis [18], characterization is best done at normal operating temperatures with typical reactant stream flow (*i.e.*, Operando). Operando methods preclude the use of supplemental electrolytes (e.g., H_2SO_4 or $HClO_4$) that contribute mobile anion adsorbates and dehydrate at the high end of relevant temperatures (e.g. 70–90 °C). Infrared (IR) spectroscopy, ideally suited for the characterization of ionomer-catalyst interfaces, elucidates potential and temperature

dependent reaction intermediates and competitive adsorbates [19−22]. Such information is required for optimization of ionomer-catalyst interfaces for rapidly emerging applications.

We introduced operando IR spectroscopy of fuel cells [23] for study of mechanistic methanol electro-oxidation on Pt and Pt alloys as well as X-ray absorption spectroscopy of the active phases of alloy catalysts in hydrogen−air [24] and direct methanol fuel cells [25]. More recently we applied operando IR spectroscopy to Nafion−Pt interfaces to better understand the self-assembly of Nafion onto metal surfaces [26−28]. This work focuses on operando spectroscopy of the Nafion−Pt interface in fuel cell MEAs.

2. Experimental

2.1. Membrane electrode assembly preparation

As received Nafion 117 is immersed in boiling 8 M HNO_3 (20 min), rinsed with Nanopure™ water and then immersed in boiling water (20 min). Catalyst inks are prepared by the method of Wilson [29]. Briefly, Pt black (Johnson Matthey) and 5 wt.% Nafion ionomer solution (Sigma Aldrich, Milwaukee, WI) are dispersed in Nanopure™ water. Catalyst coated membranes (CCMs) are prepared by brush painting (Red Sable marking brush size #1, Tanis Inc., Delafield, WI) the ink on 5 cm^2 of Nafion immobilized on a heated vacuum table (NuVant Systems, Crown Point, IN) at 70 °C. The CCM is sandwiched between sheets of carbon paper gas diffusion layers (Toray Industries, Tokyo, Japan) and then installed into the operando spectroscopy fuel cell. The catalyst loadings at both electrodes are 4 mg/cm^2 of Pt black. MEAs were conditioned in the fuel cell at 50 °C by scanning the potential (5 cycles) between 800 mV and 600 mV (40 mV/min) with humidified hydrogen (50 sccm) and air (200 sccm), both at ∼0 gauge pressure, delivered to the anode and cathode, respectively. The working electrode is conditioned immediately before obtaining reference spectra by cycling the potential from 0 V to 1.2 V at 100 mV/s, 50 times in the presence of humidified N_2 (200 sccm).
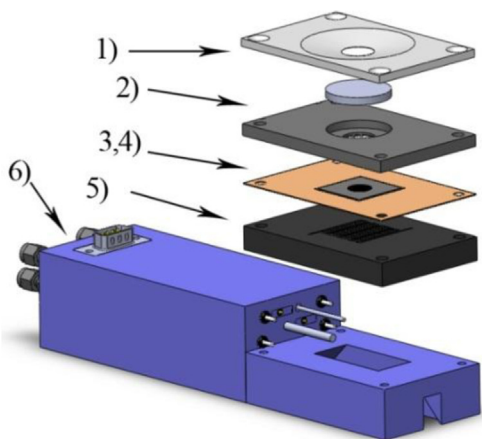
Fig. 1 − Exploded diagram of the IR-XAS cell and components: 1) Top plate, 2) Top flow field, 3) Membrane electrode assembly gasket, 4) Membrane electrode assembly, 5) Lower flow field, and 6) Slider housing.

2.2. Operando spectroscopy

Reflectance IR spectra were obtained using the cell described by Lewis and coworkers (Fig. 1) [27]. The cell is interfaced to a diffuse reflectance stage (Pike Technologies, Madison, WI) and installed in a Vertex 70 spectrometer (Bruker, Billerica, MA). The IR beam accesses the MEA catalytic layer through a CaF_2 window inserted into the upper flow field via a slit cut into the gas diffusion layer. The cell (50 °C) is fed humidified H_2 (50 sccm) and N_2 (200 sccm) to the counter/reference and working electrodes, respectively. After obtaining a reference spectrum at 1.2 V, spectra were acquired from 1.2 V to 0 V at decreasing 0.1 V increments. Spectra were obtained by averaging 100 scans at 4 cm^{-1} resolution using a liquid N_2 cooled MCT detector[1]. Operando interferogram amplitudes were obtained after acquiring each potential dependent FTIR spectra using the Opus 6.5 (Bruker).

Potential dependent IR spectra of linear bound CO (CO_{ads}) were obtained at 60 °C. The small CO oxidation currents do not measurably polarize the counter electrode which is also used as a hydrogen reference electrode [30]. The reference spectrum was acquired at 0 mV. At 300 mV the working electrode feed was switched to CO (40 sccm) for 15 min prior to purging the working electrode with N_2 (15 min). Four signal-averaged (250 scans) spectra were acquired at 100 mV and at increasing 50 mV increments, until the CO vibrational bands were no longer observable. Spectra were obtained at resolution of 4 cm^{-1} using a DLaTGS detector.

3. Results and discussion

Fig. 2 (left) shows the potential dependent spectra of CO_{ads} at the Nafion−Pt interface with the fuel cell at 60 °C. The corresponding Stark tuning curve of $\bar{u}_{CO}$ vs. potential (Fig. 2 right) is similar to previously reported curves on arc-melted [31] and Pt(111) [32] exposed to 0.5 M H_2SO_4, and on Nafion−platinum interfaces of operating MEAs [23,26,33,34]. Anderson explained Stark tuning in terms of metal-to-adsorbate orbital overlap (i.e., Blyholder mechanism) [35], first with cyanide on Ag [36] and later CO_{ads} on Pt [37]. Norskov provides a detailed description of the π bonding of CO to Pt in two steps [38,39]. In the first step, the $2\pi^*$ and the 5σ CO MOs shift to lower energy and broaden due to coupling with the Pt s,p electrons. The renormalized CO orbitals then mix with the Pt d-band bonding orbitals resulting in the splitting of the $2\pi^*$ MOs into antibonding and bonding orbitals. Thus, a shift of the surface d-band center to more positive potentials decreases the overlap between the surface d-band and the renormalized $2\pi^*$ CO MOs, increasing the carbon−oxygen bond order, and thus increasing the $\bar{u}_{CO}$. An alternative explanation has been provided by Dimakis et al. [40−44]. Cluster and periodic DFT calculations for CO_{ads} on Pt of pure Pt and Pt-based alloys show that shifts in the binding of the CO to the Pt surface are primarily due to changes in the charges and polarizations of the σ and π metal−CO hybrid

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[1] The wavelength precision of an FTIR is determined by the stability of the reference HeNe laser. Virtually all FTIR spectrometers manufactured today are capable of 0.1 cm^{-1} or better precision on the wavelength axis.