



Exploring substrate/ionomer interaction under oxidizing and reducing environments



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ABSTRACT

Local gas transport limitation attributed to the ionomer thin-film in the catalyst layer is a major deterrent to widespread commercialization of polymer-electrolyte fuel cells. So far functionality and limitations of these thin-films have been assumed identical in the anode and cathode. In this study, Nafion ionomer thin-films on platinum(Pt) support were exposed to H₂ and air as model schemes, mimicking anode and cathode catalyst layers. Findings indicate decreased swelling, increased densification of ionomer matrix, and increased humidity-induced aging rates in reducing environment, compared to oxidizing and inert environments. Observed phenomenon could be related to underlying Pt-gas interaction dictating Pt-ionomer behavior. Presented results could have significant implications about the disparate behavior of ionomer thin-film in anode and cathode catalyst layers.

1. Introduction

As polymer-electrolyte fuel cells (PEFCs) gain traction in the energy-device landscape, they face a major hurdle from significant mass-transport losses associated with the ionomer/catalyst interface [1, 2]. Sources of mass-transport losses include: confinement driven gas transport losses in ionomer thin-film coating carbon-supported platinum, interfacial resistances caused by structural changes at local ionomer-platinum boundary, and partial electrochemical deactivation of platinum surfaces [3–6]. The latter can impact overall kinetics on platinum(Pt) surfaces [7, 8], however such effects on ionomer mass-transport and the interplay with reducing atmospheres are unknown. As a result, explicit understanding of losses at the ionomer/Pt interface is required for optimal electrode-ionomer design and accelerating market penetration of PEFCs.

Ionomer thin-films cast onto a Pt surface can serve as model systems providing a focused glimpse into the catalyst layer. Although bulk, continuous polycrystalline Pt does not fully describe Pt nanoparticle phenomenon present in real catalyst layers, it can still elucidate surface specific interactions that impact ionomer properties and morphology [9, 10]. While impact of Pt substrate on ionomer performance have been shown [8, 11], efforts to clarify the source of this impact have been contradictory, especially in elucidating the role of water on oxidized and unoxidized Pt surfaces [12, 13]. Additionally, the extent of Pt

surface influence on ionomer during exposure to oxidative/reductive environments remains unexplored. In this study, water-vapor-sorption dynamics of dispersion-cast Nafion thin-films under reducing (H₂), oxidizing (Air), and inert (Ar, N₂) environments are investigated in order to understand the Pt/ionomer interaction in anode and cathode catalyst layers.

2. Material and methods

2.1. Thin-film preparation

Nafion dispersions (5 wt%, 1100 g/mol SO₃⁻ equivalent-weight, Sigma Aldrich) were diluted in isopropanol, spin cast onto Pt-coated Si, and Si/SiO₂ wafers to form ~50 nm films. Pt substrates were prepared via e-beam evaporation of 5 nm Ti adhesion layer followed by 60 nm of Pt. Pt substrates were cleaned with benchtop Ar plasma for 6 min prior to casting. Thin-films were annealed at 150 °C under vacuum for 1 h before measurement.

2.2. Water-uptake measurement

Thickness change of Nafion films was monitored using in-situ spectroscopic ellipsometry (J.A. Woollam) as detailed in Ref [14]. Measurements shown are the average of at least two separate samples

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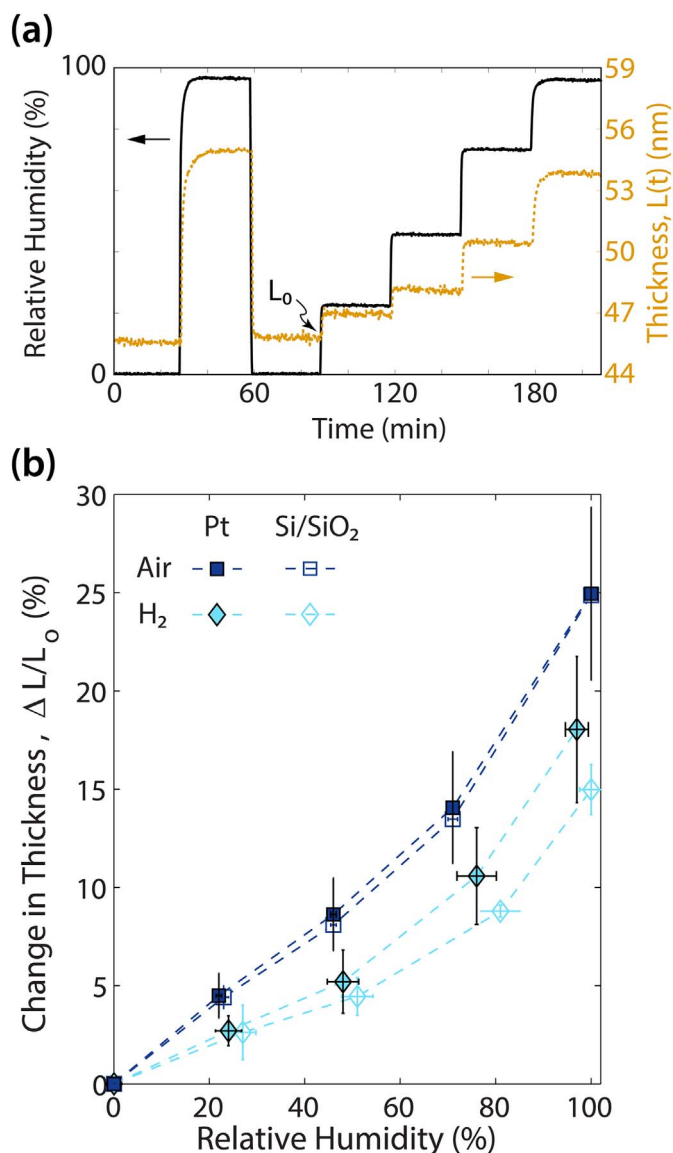


Fig. 1. (a) Humidity protocol applied during in-situ tracking of spin-cast Nafion thin-films (~50 nm) (b) % Change in Nafion thickness on Pt and Si/SiO₂ substrate under H₂ and Air environments as a function of relative-humidity.

measured < 15 min after annealing. To create a consistent water history, all measurements were preceded with an hour exposure to dry (0%) and saturated (96%) relative humidity (RH) (See Fig. 1a for hydration protocol). Humidity-dependent thickness ($L(t, RH)$) was an average of the last 10 min of set humidity. The % change from dry (L_0) is given by:

$$\text{Change in Thickness (\%)} = 100 \times \frac{L(t, RH) - L_0}{L_0} \quad (1)$$

2.3. Grazing incidence small angle scattering (GISAXS) measurements

Pt-coated Nafion films were placed into an in-house built environmental chamber with X-ray transparent Kapton windows as in Ref [6]. The sample was equilibrated in dry H₂ and N₂ gas at room temperature and GISAXS patterns were collected after multiple purges for 5 to 10 min in each gas, at varying incidence angles (α_i).

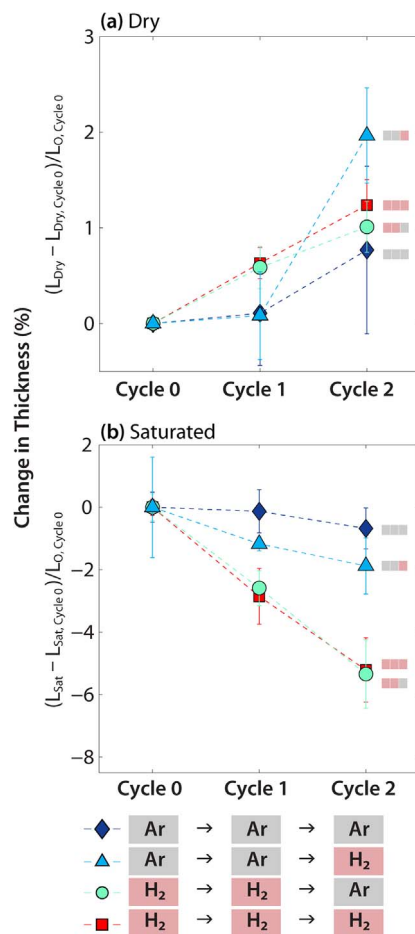


Fig. 2. Humidity-cycling of Pt-supported Nafion thin-films (~50 nm) with alternating inert and reducing gas. Comparison of Cycle 1 in gas 1 and Cycle 2 in alternative gas 2. Thickness change of Nafion in (a) Dry and (b) Saturated (96% RH) relative to dry and saturated thickness in Cycle 0 exposed to gas 1, respectively.

2.4. Mechanical-property measurement

100 nm Nafion films were prepared on Pt-coated thin Si cantilever wafers (105 μm thickness by approximately 0.5 cm \times 4 cm). Sample was clamped in an environmental cell with humidified gas feeds. Constrained swelling due to the substrate results in a compressive force, which bends the Si cantilever. Using a laser array reflected off the backside of sample, change in curvature of the cantilever was measured and related to stress-thickness via Stoney's equation, see Ref [15]. Humidity-induced stress-strain curves were generated by combining stress and strain (from ellipsometry, see Eq. (1)) under the same humidity conditions, and the deformation energy density was calculated by integrating the area under the curve.

3. Results and discussion

Fig. 1b compares swelling of ionomer films on Pt and Si/SiO₂ under different humidified gas feeds. Swelling values demonstrate a depression in swelling for ionomer thin-films exposed to H₂. Values reported here fall between previous studies [13, 16]. Differences in swelling values between studies are ascribed to different ageing, conditioning, and annealing protocols.

The reversibility and persisting impact of the gaseous environment on ionomer swelling was explored using humidity-cycling by alternating inert and reducing gas exposure. In-situ ionomer thickness change on Pt was monitored over three hydration cycles: first, a single step of dry to 96% RH gas exposure (Cycle 0, gas 1); second, in the same

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