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1   **Exploring substrate/ionomer interaction under oxidizing and**
2   **reducing environments**

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13 Graphical Abstract

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17 Keywords:

18 Hydrogen; Fuel cell; Ionomer; Confinement; Thin film; Water uptake

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21 Highlight:

- 22 • Revealed swelling of ionomer thin-film on Pt in H₂ for the 1st time.
- 23 • Demonstrated lower swelling of ionomer on both Pt and Si/SiO₂ under H₂ gas.
- 24 • Observed densification in ionomer thin-film under H₂ environment via GISAXS.
- 25 • Thin-film swelling dynamics is surface/ionomer interaction dependent.
- 26 • Polarity and hydrophilicity are key factors in Pt interface/ionomer interaction.

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 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.

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411. Introduction

42 As polymer-electrolyte fuel cells (PEFCs) gain traction in the energy-device landscape, they
43face a major hurdle from significant mass-transport losses associated with the ionomer/catalyst
44interface [1], [2]. Sources of mass-transport losses include: confinement driven gas transport
45losses in ionomer thin-film coating carbon-supported platinum, interfacial resistances caused by
46structural changes at local ionomer-platinum boundary, and partial electrochemical deactivation
47of platinum surfaces [3]–[6]. The latter can impact overall kinetics on platinum(Pt) surfaces [7],
48[8], however such effects on ionomer mass-transport and the interplay with reducing
49atmospheres are unknown. As a result, explicit understanding of losses at the ionomer/Pt
50interface is required for optimal electrode-ionomer design and accelerating market penetration of
51PEFCs.

52 Ionomer thin-films cast onto a Pt surface can serve as model systems providing a focused
53glimpse into the catalyst layer. Although bulk, continuous polycrystalline Pt does not fully
54describe Pt nanoparticle phenomenon present in real catalyst layers, it can still elucidate surface
55specific interactions that impact ionomer properties and morphology [9], [10]. While impact of
56Pt substrate on ionomer performance have been shown [8], [11], efforts to clarify the source of
57this impact have been contradictory, especially in elucidating the role of water on oxidized and
58unoxidized Pt surfaces [12], [13]. Additionally, the extent of Pt surface influence on ionomer
59during exposure to oxidative/reductive environments remains unexplored. In this study, water-
60vapor-sorption dynamics of dispersion-cast Nafion thin-films under reducing (H_2), oxidizing
61(Air), and inert (Ar, N_2) environments are investigated in order to understand the Pt/ionomer
62interaction in anode and cathode catalyst layers.

63

642. Material and Methods

652.1. Thin-film Preparation

66 Nafion dispersions (5 wt%, 1100 g/mol SO_3^- equivalent-weight, Sigma Aldrich) were diluted
67 in isopropanol, spin cast onto Pt-coated Si, and Si/SiO₂ wafers to form ~50 nm films. Pt
68 substrates were prepared via e-beam evaporation of 5nm Ti adhesion layer followed by 60nm of
69 Pt. Pt substrates were cleaned with benchtop Ar plasma for 6 minutes prior to casting. Thin-films
70 were annealed at 150°C under vacuum for 1 hr before measurement.

712.2. Water-Uptake Measurement

72 Thickness change of Nafion films was monitored using *in-situ* spectroscopic ellipsometry
73 (J.A. Woollam) as detailed in Ref [14]. Measurements shown are the average of at least two
74 separate samples measured <15 minutes after annealing. To create a consistent water history, all
75 measurements were preceded with an hour exposure to dry (0%) and saturated (96%) relative
76 humidity (RH) (See Fig 1a for hydration protocol). Humidity-dependent thickness ($L(t, RH)$) was
77 an average of the last 10 min of set humidity. The % change from dry (L_o) is given by:

$$78 \quad \text{Change in Thickness (\%)} = 100 \times \frac{L(t, RH) - L_o}{L_o} \quad (1)$$

792.3. Grazing Incidence Small Angle Scattering (GISAXS) Measurements

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

842.4. Mechanical-Property Measurement

85 100 nm Nafion films were prepared on Pt-coated thin Si cantilever wafers (105μm thickness
86 by approximately 0.5cm x 4cm). Sample was clamped in an environmental cell with humidified

87gas feeds. Constrained swelling due to the substrate results in a compressive force, which bends
88the Si cantilever. Using a laser array reflected off the backside of sample, change in curvature of
89the cantilever was measured and related to stress-thickness via Stoney's equation, see Ref [15].
90Humidity-induced stress-strain curves were generated by combining stress and strain (from
91ellipsometry, see Equation 1) under the same humidity conditions, and the deformation energy
92density was calculated by integrating the area under the curve.

93

943. Results and Discussion

95 Figure 1b compares swelling of ionomer films on Pt and Si/SiO₂ under different humidified
96gas feeds. Swelling values demonstrate a depression in swelling for ionomer thin-films exposed
97to H₂. The authors note values reported here fall between previous studies [13, 16]. Differences
98in swelling values between studies are ascribed to different ageing, conditioning, and annealing
99protocols.

100

101 Figure 1: (a) Humidity protocol applied during in-situ tracking of spin-cast Nafion thin-films

102 (~50 nm) (b) % Change in thickness on Pt and Si/SiO₂ substrate under H₂ and Air

103 environments as a function of relative-humidity.

104

105 The reversibility and persisting impact of the gaseous environment on ionomer swelling
 106 was explored using humidity-cycling by alternating inert and reducing gas exposure. *In-situ*
 107 ionomer thickness change on Pt was monitored over three hydration cycles: first, a single step of
 108 dry to 96% RH gas exposure (Cycle 0, gas 1); second, humidity was stepped down to 0% RH
 109 prior to hydration cycling (Cycle 1, gas 1); finally, gas 1 was switched and stepped RH was
 110 applied (Cycle 2, gas 2). Here, the dry reference thickness was set to the thickness from Cycle 0.
 111 Figure 2a shows difference in swelling in each gas combination under dry conditions, i.e., $(L_{\text{Dry}} -$
 112 $L_{0, \text{Cycle } 0})/L_{0, \text{Cycle } 0}$. Humidity-cycling under inert gas environment ($\text{Ar} \rightarrow \text{Ar} \rightarrow \text{Ar}$) displays
 113 minimal thickness hysteresis from start to finish. However, cycling in H_2 only ($\text{H}_2 \rightarrow \text{H}_2 \rightarrow$
 114 H_2) and H_2 then Ar ($\text{H}_2 \rightarrow \text{H}_2 \rightarrow \text{Ar}$) introduces a continual increase in dry thickness upon
 115 repeated cycling. Swelling in Ar then H_2 ($\text{Ar} \rightarrow \text{Ar} \rightarrow \text{H}_2$) demonstrates a large relative shift
 116 in dry thickness immediately after H_2 exposure. Figure 2b shows swelling under saturated (96%
 117 RH) conditions for each gas combination, i.e., $(L_{\text{Saturated}} - L_{\text{Saturated, Cycle } 0})/L_{0, \text{Cycle } 0}$. The thickness
 118 change in humid inert gas environment ($\text{Ar} \rightarrow \text{Ar} \rightarrow \text{Ar}$) is maintained despite repeated
 119 relaxation and tension introduced by changes in humidity. However, RH cycling in both H_2 only
 120 ($\text{H}_2 \rightarrow \text{H}_2 \rightarrow \text{H}_2$) and H_2 then Ar ($\text{H}_2 \rightarrow \text{H}_2 \rightarrow \text{Ar}$) reduces the maximum water-uptake
 121 capacity. A reducing environment not only diminishes water uptake successively upon cycling,
 122 but does so to a greater extent than an inert environment. Switching order of H_2 and Ar ($\text{H}_2 \rightarrow$
 123 $\text{H}_2 \rightarrow \text{Ar}$ versus $\text{Ar} \rightarrow \text{Ar} \rightarrow \text{H}_2$) exhibits a reduction in swelling under saturated

conditions at a rate that is between that of H₂- and Ar-only environments, confirming the impact of the H₂ environment.

126

Figure 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.

128

129   Thickness change in (a) Dry and (b) Saturated (96% RH) relative to dry and saturated
130   thickness in Cycle 0 exposed to gas 1, respectively.

131

132   The findings in Fig. 1 and 2 are consequences of changes at the ionomer/Pt interface
133 induced by gas/Pt interaction. Surface oxidation on Pt metal can occur via electrochemical and
134 thermochemical pathways [17]. In a thermochemically oxidized Pt surface, exposure to an
135 oxidative gaseous environment like air will enlarge oxidized metal islands on Pt, while exposure
136 to a reducing environment like H₂ can reduce the unstable passivated surface even under ambient
137 conditions [17]–[20]. Pt substrates in this study are likely to exist with some surface oxidation as
138 they are stored under ambient conditions. This oxide surface continues to grow with continued
139 exposure to an oxidizing environment or, is reduced and saturated with dissociated atomic
140 hydrogen during H₂ exposure; a phenomenon that has been reported experimentally and
141 computationally [10], [21]–[23]. As a result, during exposure to Air and H₂, Pt interface can exist
142 at varied states of oxidation and reduction resulting in sample-to-sample variability. Nonetheless,
143 adsorbed hydrogen reduces the solid-surface free energy [21], resulting in a more hydrophilic but
144 nonpolar Pt/H interface compared with that of oxidized Pt. This phenomenon was verified by
145 using bare Pt-coated crystal in a quartz-crystal microbalance, which exhibited significant
146 adsorption of H₂ on Pt surface when dry, and greater absorption of water when saturated due to
147 greater affinity for water at the Pt/H interface (data not shown). The Pt/H interface lacks strong
148 electrostatic interactions, resulting in possible ionomer restructuring to orient hydrophilic
149 sidechains towards the Pt/H interface, where water molecules are likely to gather, thereby
150 creating a dense region of hydrophobic ionomer away from the interface. In such a scenario, the
151 bulk of the ionomer behaves like a higher equivalent-weight ionomer with lower water uptake.

On the other hand, negatively charged oxygen atoms on an oxidized Pt surface, which, while comparatively less hydrophilic, induce a strong polar dipole and enhance electrostatic interactions between hydronium ions and sulfonic-acid moieties. Similar depression in water-vapor uptake in thin-films on Si/SiO₂ support under H₂ also point towards impact of oxidized surfaces. Under ambient conditions, growth of native oxide layer of 1 to 2 nm is expected on a Si substrate. Continued layer-by-layer growth of SiO₂; however, requires presence of both water and oxygen [24], [25]. Although reduction of the oxide layer is not occurring under H₂ environment on Si/SiO₂ support, oxide formation is actively being facilitated under humidified air. These interactions enhance the overall effective water uptake within the ionomer on oxidized surface, which is consistent with predictions from molecular-dynamics simulations [26]. Figure 3 schematically portrays the balancing impacts of polarity and hydrophilicity in reducing and oxidizing environment.

Figure 3: Schematic representation of platinum(Pt)/ionomer thin-film interface impact in oxidizing and reducing environment resulting from differences in polarity and hydrophilicity.

The above hypothesis is supported by morphological changes tracked by GISAXS and mechanical response of Nafion thin-film on Pt exposed to H₂ and N₂ gases. When α_i of x-ray

170 beam is below the critical angle of the polymer film, $\alpha_{c, film}$, total external reflection occurs
 171 with a surface-sensitive scattering [27], whereas above $\alpha_{c, film}$, the x-ray beam penetrates
 172 through the entire film and scattering from the paracrystalline Pt surface is observed. As shown
 173 in Figure 4a, the paracrystalline peak is present at $\alpha_i = 0.16$ in dry N₂, but does not appear
 174 until $\alpha_i = 0.18$ in dry H₂, indicating an increase in the ionomer's critical angle, which is a
 175 function of chemical structure and density. This positive shift in α_c points to restructuring of
 176 the ionomer, including possible rearrangement of the hydrogen bonding of sidechains near the
 177 Pt/H interface, resulting in a more effectively packed, dense, hydrophobic ionomer structure. In
 178 addition, mechanical stress generated in thin film during its humidification in H₂ and N₂ is
 179 measured on a cantilever beam. When this stress is plotted against thickness swelling measured
 180 separately at the same RHs, shown in Fig 4b, a curve is generated, the area under which
 181 demonstrates lower deformation energy density accumulated in the film in H₂ than N₂ (539
 182 versus 680 kJ/m³). This provides further evidence to the more hydrophilic but weakly-interacting
 183 Pt/H interface induced by H₂, creating a water-rich layer (see Figure 3), thereby resulting in a
 184 reduced translation of ionomer deformation onto the substrate.

(a) Grazing Incidence X-ray Scattering (GISAXS) of Nafion thin films

185

186 Figure 4: (a) 2D GISAXS pattern of Pt-supported Nafion thin-films (~50 nm) equilibrated in dry

187 N₂ and H₂ gas. The paracrystalline peak visibility shifts from $\alpha_i \geq 0.16$ in N₂ to188 $\alpha_i \geq 0.18$ in H₂. (b) Swelling-induced stress in the thin film measured via cantilever

189 method during humidification in N₂ and H₂ plotted against the thickness swelling of
190 the film.

191

192 Despite being the least understood component, the gas/ionomer/Pt interface in the
193catalyst layer bears the utmost duty for PEFC performance. Thus, there is need for greater
194understanding of pairwise interaction between gas/ionomer, ionomer/Pt, and gas/Pt interfaces to
195reduce critical transport losses and improve electrode design. To that effect, this study focused on
196how gas/Pt interaction impacts Pt surface and ionomer thin-film morphology and properties.
197Unexpectedly, a reduced swelling, increased densification, decreased deformation energy density
198and continual reduction in effective water uptake in the ionomer during cycling were observed
199under H₂ relative to oxidizing or inert environment. These observations demonstrate the coupled
200impact of gas/substrate and ionomer/substrate interactions on ionomer thin-film's behavior and
201ultimately it's transport properties [28]. Therefore, there is a need for increased electrode-specific
202investigations and separate ionomer design for anode and cathode catalyst layers. The impact of
203electronic potential going from oxidation to reduction potentials can also affect the surface-state
204identity and ionomer thin-film morphology, which is a focus of current research. Furthermore,
205existence of a water-rich phase at the Pt/ionomer interface in a reducing environment can impact
206surface conductivity significantly, which may not occur in an oxidizing environment. The
207findings herein also indicate heightened vulnerability to delamination of ultra-thin ionomer films
208in the anode due to increased water-layer thickness and reduced deformation energy density.

209

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