

NEUTRON REFLECTOMETRY INVESTIGATION OF NEAR IONOMER/CATALYST INTERFACE STRUCTURE IN POLYMER ELECTROLYTE BASED ENERGY DEVICES

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Concerns of effects of climate change on human life [1] and of urban air pollution on human mortality [2] is pushing the transition to low-carbon energy systems, as seen by a rapid growth in renewable energy sources such as wind and solar. However, the intermittency of renewables has created a critical need for affordable, robust and application-matched electrical energy conversion and storage (ECS) systems [3]. Of particular interest are polymer electrolytes (PE) based ECS devices such as fuel cells, batteries, electrolyzers and artificial photosynthesis. Canada is a world leader in PE-based fuel cells (PEFC) and electrolyzers for generating hydrogen from water. Automotive Fuel Cells Cooperation (Burnaby) is developing PEFC stacks for vehicles. Ballard Power Systems (Burnaby) is developing them for a variety of other applications in transportation (bus, rail), materials handling (forklifts), defence, and backup power. Hydrogenics Corporation (Mississauga) is the world leader in PE electrolyzers and also develops PEFC stacks. These companies aim to develop ECS systems that are highly efficient, low-cost and durable. Development of new materials to support engineering of devices is critical to meeting these goals.

PE-BASED ECS DEVICES

In PE-based ECS devices, the PE is an ion-conducting polymeric membrane that separates the two electrodes. In the porous electrodes of these devices, charge is transferred from sub-micron thin films of ion-conducting polymer (the “ionomer”) to an electron-conducting material, which in the case of a PEFC is an electrocatalyst, such as Pt, or in the case of PE supercapacitors, carbon. The total active interfacial area controls the amount of electrical current, while the composition of the electrochemical interface controls the efficiency of the charge-transfer process. Thus, the physical and

chemical characteristics of the electrochemical interface is a topic of intense research. While our discussion focuses on the ionomer-catalyst interface in a PEFC, the scientific aspects are pertinent to electrochemical interfaces in all PE-based devices.

In a PEFC, illustrated in Fig. 1a, hydrogen and oxygen/air are supplied to the anode and cathode, respectively. These reactant gases diffuse from the respective flow channel through a porous carbon layer (~300 μm) called the gas diffusion layer (GDL) to a few-microns-thick catalyst layer (CL); this is depicted for the cathode side in Fig. 1b. The CL is comprised of aggregates of ~30 nm carbon supporting 2-5 nm Pt nanoparticles covered by 3-10 nm thin ionomer films. For the occurrence of oxygen reduction reaction (ORR) at the PEFC cathode, the reactants – electrons, protons and oxygen gas – must arrive simultaneously via Pt/Carbon, hydrophilic channels of the ionomer, and pores, respectively to the Pt/ionomer interface. The product water generated on the Pt surface must exit through or around the ionomer film.

RESEARCH QUESTIONS

Understanding the hot bed of activity around the Pt-ionomer interface, especially with respect to water distribution is critical to designing high performance PE-based devices. Proton conduction in these ionomers occurs via a connected network of water-filled hydrophilic domains distributed within a hydrophobic matrix. Nafion, a DuPont product, is the most commonly used ionomer and belongs to the perfluorosulfonated acid (PFSA) class of materials. In bulk membranes of Nafion, SAXS data indicate the characteristic dimension of the proton-conducting hydrophilic domains as 2-4 nm [4-5]. Recent TEM images indicate that ionomers in PEFC catalyst layers are of comparable thickness, 3-10 nm [6], raising the question, can hydrophilic domains exist in ultra-thin ionomer films in PEFC's? If not, how do protons conduct in such thin films?

Furthermore, when confined to thicknesses below 50 nm, ionomers exhibit remarkably different properties (such as proton conductivity, water uptake, swelling, and possibly oxygen diffusion) compared to bulk membranes [7-8].



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SUMMARY

The neutrons' ability to non-destructively probe structures of polymer films shines new light on the platinum-ionomer electrochemical interfaces in energy conversion and storage devices.

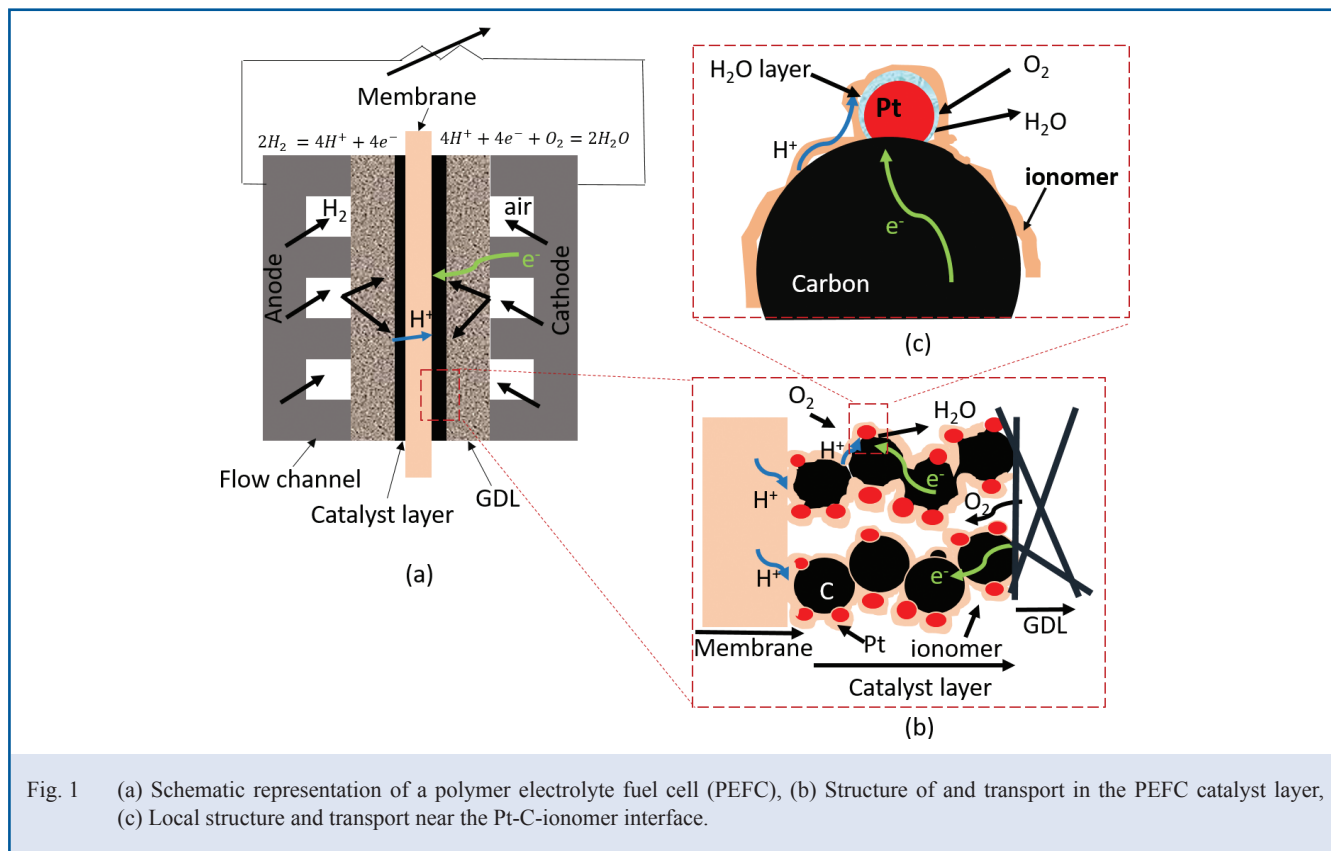


Fig. 1 (a) Schematic representation of a polymer electrolyte fuel cell (PEFC), (b) Structure of and transport in the PEFC catalyst layer, (c) Local structure and transport near the Pt-C-ionomer interface.

The density of ionomers may increase near the Pt-ionomer interface [9]. There is evidence that the hydrophilic sulfonic groups of Nafion are coordinated with the Pt [10-11]. However, it is not known how such interactions affect the formation of hydrophilic domains responsible for water-mediated proton transport. Is there interfacial water at the ionomer-catalyst interface? And, does it contribute to interfacial proton transport?

NEUTRON REFLECTOMETRY (NR) INVESTIGATIONS OF IONOMER THIN FILMS

NR is an ideal tool for probing the interfacial and bulk structures of polymer thin films [12]. The sensitivity of neutrons to light elements and the ability to penetrate most materials enables the in-situ investigation of water at the buried Pt-ionomer interface as well as in the ionomer film. The weak interaction of neutrons with matter do not change the sample under investigation, unlike x-rays and electrons, and there is no need to keep the sample in a vacuum.

Principle of NR: The scattering geometry for a typical reflectometry experiment is shown in Fig. 2. An incoming neutron beam, with wave-like properties, hits the surface of a specimen at a grazing angle θ_i and is partly reflected specularly at an angle θ_r and partly transmitted (refracted) into the specimen at an angle θ_t with respect to the sample surface.

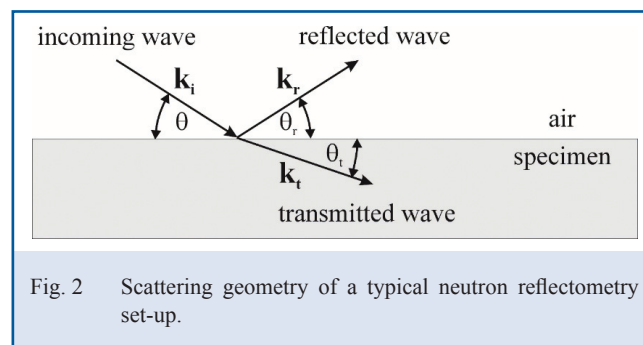


Fig. 2 Scattering geometry of a typical neutron reflectometry set-up.

The intensity of the reflected and transmitted wave can be described with an index of refraction n , identical to classical optics: $n = k_i/k_t$, with the wavevector $k_i = 2\pi / \lambda$ in air, the wavevector k_t in the specimen, and the neutron wavelength λ , respectively. The wavelength is calculated from the de Broglie relationship. The index of refraction can be written as

$$n = \sqrt{1 - \frac{\lambda^2}{\pi} Nb} \quad (1)$$

with N being the atomic density and b being the nuclear scattering length. The product $N \times b$ is called scattering length density (SLD), which varies randomly from element to element and isotope to isotope but their values are well known [13].

NR is highly sensitive to water uptake because the SLDs of water and dry Nafion differ in sign and magnitude, $-0.56 \times 10^{-6} \text{ \AA}^{-2}$ and $4 \times 10^{-6} \text{ \AA}^{-2}$ respectively; the slightest water uptake leads to a decrease in the net SLD.

The neutron refractive index and the Fresnel reflectivity arising at interfaces can be calculated based on the Parratt recursion algorithm and Eq. (1) [14]. In a typical NR experiment, the reflectivity, which is the specularly reflected intensity divided by the incident intensity, is obtained as a function of incidence angle (θ), and is commonly presented as a function of the scattering vector (Q), where Q is given by $Q = 4\pi/\lambda \cdot \sin\theta$. For thin films, reflectivity is fit to a layered model where the SLD, layer thickness, and, if needed, interface roughness of each layer are variables [15].

Pioneering work on NR of ionomer thin films have been carried out by Dura and co-workers at NIST, USA. Their study examined 60 nm Nafion thin films on gold or SiO_2 substrates under high relative humidity (RH) [16] conditions. For SiO_2 , they observed a multi-lamellar structure near the interface, comprising of alternating 3 nm thick water-rich and water-lean layers but for Au, only a single polymer layer was observed with a water rich layer at the interface. Wood *et al.* performed an NR study at Los Alamos on ~60 nm Nafion films on Pt, PtO, and hydrophilic glass carbon (GC) substrates at room temperature and 97% RH [17]. The interfacial layer for films on Pt was water lean but for PtO and GC was water-rich compared to bulk ionomer layers. Upon hydrophobizing the SiO_2 substrate, Page *et al.* [18] at NIST observed the multi-lamellar structure of the ionomer

change to a single bulk layer containing water. Recently, Kalisvaart *et al.* applied NR at Canadian Nuclear Laboratories to study the hysteresis effect of temperature from 25 °C to 60 °C and RH up to 97% for a 15 nm Nafion film on SiO_2 [19]. The films showed increased water absorption and hygro-expansion with temperature, but after cooling to the original temperature at 97% RH, the film demonstrated hysteresis by retaining some of the water.

OUR NR STUDIES OF THE IONOMER-PT INTERFACE

We are investigating ultra-thin ionomer films (50 nm and less) on a Pt substrate. Interpretation of NR data requires a careful choice of a layer model [20]. Instead of relying on statistical measures only, we employ complementary techniques such as quartz crystal microbalance (for water mass uptake) and ellipsometry (for swelling) to cross-correlate or constrain the NR model. The substrate is characterized by x-ray reflectometry and atomic force microscopy.

Preliminary Experiments: Here, we discuss NR for a 17 nm film of Nafion (EW1100) ionomer spin-coated on a 10 nm Pt film with a 4 nm Cr buffer layer sputter-coated on a Si wafer (with native oxide). NR measurements were carried out in dry (8% RH) and humid (97% RH) conditions at 30 °C using a humidity and temperature controlled cell [21]. The reflectivity measured over 12 hours from $Q = 0.006 \text{ \AA}^{-1}$ to 0.14 \AA^{-1} is shown in Fig. 3a. The fit using a three-layer model — an interfacial layer at the Pt-ionomer interface, a bulk ionomer layer, and a roughness

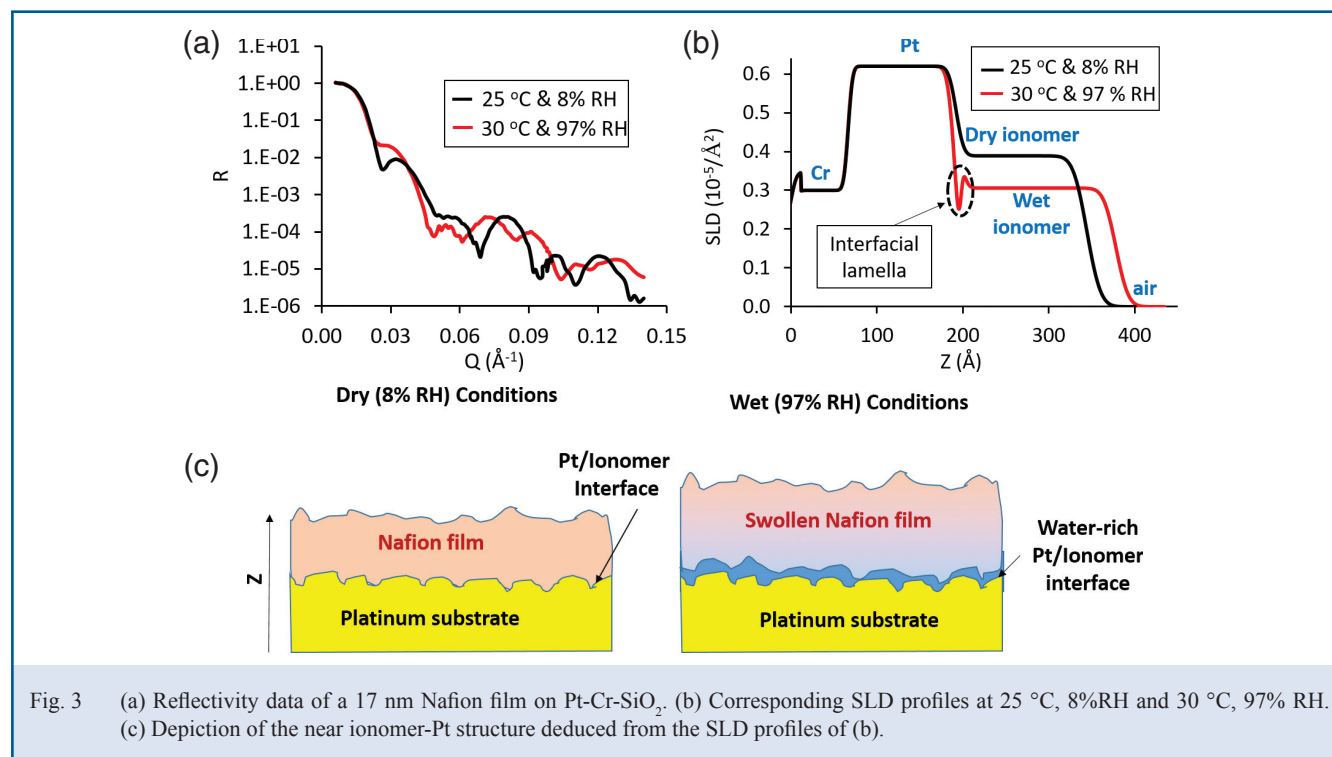


Fig. 3 (a) Reflectivity data of a 17 nm Nafion film on Pt-Cr- SiO_2 . (b) Corresponding SLD profiles at 25 °C, 8%RH and 30 °C, 97% RH. (c) Depiction of the near ionomer-Pt structure deduced from the SLD profiles of (b).

layer — is depicted in Fig. 3b in terms of the SLD profiles. The dip in SLD at the Pt-ionomer interface corresponds to a 6 Å thick, 90% water interfacial layer, which was critical in the fit of all the NR data at high RH. Dura's previous work on ionomer-metal film presents similar findings [16]. The water uptake (λ = number of water molecules per SO_3^- group) determined from the SLD using Dura's approach was found to be 8.9 and a swelling ($\Delta L/L$) of 23% is consistent with ellipsometry data.

OUTLOOK

NR is a critical and powerful tool for studying the physical structure of the ionomer-catalyst interface for PE-based ECS devices. NR allows a quantitative assessment of the distribution

of water at the electrochemical active ionomer-catalyst interface and within the ionomer films covering the catalytic surface. NR is unique in its ability to provide nm-scale resolution on spatial distribution of water at this critical interface of ECS devices. As the nature of this interfacial region is poorly understood, there is a tremendous opportunity to explore the unknowns for this system using NR, to determine the effect of ionomer architecture or molecular structure on near ionomer-Pt interface structure, to investigate ionomer films of thickness relevant to fuel cell electrodes (4-10 nm), and to study the structure under operational conditions of electrical potential. Although NR relies on a model, experiments can be designed to remove artifacts by characterizing substrates separately, exchanging D_2O for H_2O , and cross-correlating with data obtained from other techniques.

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