Confocal Raman Microscopy and Neutron Reflectometry Profiling of Composition at Polymer-Polymer Interfaces

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1. Overall Objectives:

✓ Adapt confocal Raman microscopy[1] for spatial profiling ion composition across the AEM-CEM (anion-exchange membrane / cation-exchange membrane) interface within bipolar polymer membranes.

✓ Develop a platform to perform neutron reflectometry (NR)[2] measurements to attain < 10 nm spatial resolution in profiling the AEM-CEM interface

✓ A long term goal is to develop quantitative spectro-electrochemical approaches for the study of structure and reactivity within catalyst-membrane architectures.

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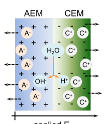
2. Background

- Bipolar membranes are composed of anion- and cation-exchange phases in adjacent layers (Scheme 1).[3]



Scheme 1. Bipolar membrane under reverse-bias showing water dissociation at the AEM-CEM interface. (See Ref 3 for details.)

- The membranes enable electrochemical devices to operate with the anode and cathode near the pH optimum of the catalytic reactions, providing a route to improved energy efficiency and cost reduction.
- In a reverse-bias configuration, water dissociation at the AEM-CEM interface can replenish H^+ consumed at the cathode (*e.g.*, during H_2 generation) and OH^- consumed at the anode (*e.g.*, O_2 generation).
- There is interest in a technique to profile the ion-depletion region under bias, and understand the voltage dependence, to guide the development of new membrane materials for improved energy efficiency.

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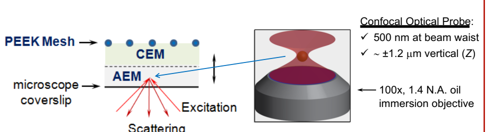
3. Experimental

Confocal Raman Microscopy. The confocal Raman microscope system is described in Ref. 1. The source was a Kr^+ laser operating at 647.1 nm. A 100x, 1.4 N.A. oil immersion objective brought the laser excitation radiation to a focus within the sample (Scheme 2). Scattered radiation was collected using the same microscope objective. Samples were excited using 3 mW (graphene) or 30 mW (polymer membrane) laser power.



Scheme 2. Confocal Raman sampling configuration of bipolar membrane and characteristics of the optical probe.

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3. Experimental (cont.)

Samples. Bipolar membrane samples (Fumasep FBM) were provided by Nate Lewis (Caltech). The delicate membranes were backed by a PEEK mesh support (Scheme 2). Prior to measurements, the membranes were exchanged in 0.5 M NaCl or 0.1 M $NaClO_4$, as indicated. Single layer graphene (SLG) deposited on glass microscope coverslips (SLG/SiO_2) were provided by Steve Creager (Clemson University).

4. Results and Discussion:

A. Confocal Raman Probe Beam Profiling

- To determine spatial resolution limits, it was necessary to measure the intensity profile along the vertical (*Z*-) axis of the confocal Raman probe beam.
- The profile was measured by stepping through a SLG/SiO_2 interface (Figs 1-2). (See Ref 1 for details)

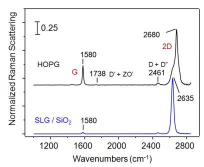

Fig. 1. Raman scattering from highly ordered pyrolytic graphite (HOPG, top) and single layer graphene (SLG) on SiO_2 (bottom) excited at 647.1 nm using 3 mW power. Peak assignments are according to Ref. 4. To aid comparison, each spectrum is normalized to its 2D peak intensity.

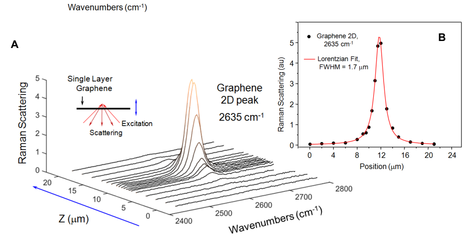

Fig. 2. (A) Raman scattering from single layer graphene on SiO_2 (microscope coverslip) recorded as a function of the confocal probe height, *Z*, relative to the graphene layer. Z = 0 μm is ~12 μm below the coverslip. The peak intensity is maximum when the confocal probe volume central region overlaps the graphene layer. (B) The 2D peak height as a function of *Z* (points). The red line shows the fit to the Lorentzian function representing the confocal probe Z-dimension profile.[1]

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D. Strategies for In-Situ Characterization

- Confocal Raman microscopy: A microscope-stage mountable in-situ spectroelectrochemical cell[6] is being tested and adapted (see below).
- NR: NIST capabilities for performing in-situ NR spectro-electrochemistry are being explored (see Panel 7).

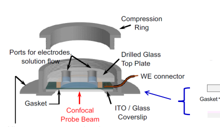

Fig. 8. Microscope-stage mountable cell for in-situ spectroelectrochemistry.[6]

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B. Application to Bipolar Membranes

- Spectra recorded during a confocal Raman depth profile are shown in Fig. 3, while Fig. 4 plots the response of the unique CEM-phase marker.
- The change in CEM-phase marker is slower than the limiting instrument response, indicating a few micron gradient in ionomer composition across the interface.
- FumaTech confirmed a few micron chemical gradient exists at the AEM-CEM interface, due to intentional roughening and addition of a water-splitting catalyst.[5]

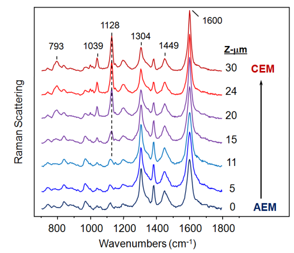

Fig. 3. Confocal Raman spectra collected at pointes in the vicinity of the AEM-CEM interface of a Fumasep FBM membrane. Spectra were recorded immediately following ion exchange in 0.5 M NaCl.

At Z = 0, the confocal probe volume is positioned within the AEM phase and ~15 μm below the AEM-CEM interface. Laser power = 30 mW.

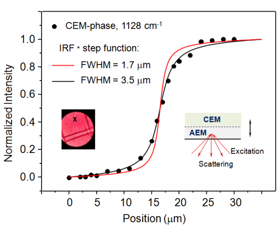

Fig. 4 Plot of the unique CEM-phase marker (1128 cm^{-1} band) in Figure 3 spectra as a function of measurement position. The solid lines are the convolution of the confocal probe volume Z-profile (IRF) with a step function representing an atomically smooth AEM-CEM junction. Responses for the limiting IRF measured with SLG (red) and IRF derived from fitting the points (black) are shown. A photo taken through the microscope eyepiece is included as an inset and shows the region of beam focus ("X") and segment of PEEK mesh.

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- Self-modeling curve resolution (SMCR) applied to a spectral dataset (Fig. 5) associates ClO_4^- with the AEM-phase (assigns the features to a single pure component).
- Traces of ClO_4^- are detected in the CEM-phase within a few micrometers of the AEM-CEM boundary, consistent with a slight gradient in polymer composition at the interface.

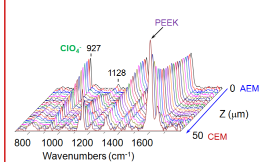

Fig. 5. Same as Fig. 3, except membrane was exchanged in 0.1 M $NaClO_4$ followed by rinsing in DI water for 48 hrs. The ClO_4^- band (927 cm^{-1}) is evident, and PEEK features begin to appear at long distances into the CEM-phase.

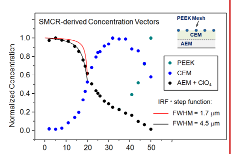

Fig. 6. Component concentrations derived from SMCR analysis of the Fig. 5 dataset. See Fig. 4 for solid line definitions.

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C. Neutron Reflectometry (NR) Characterization

- Provides ca. 1 nm spatial resolution in depth profiling.[2]
- Strategy: prepare model AEM-CEM interfaces on NR substrates (*e.g.*, Si) by sequential spin-casting of the AEM and CEM polymers; Use deuterium-labeled mobile tetraalkylammonium ions for contrast enhancement.
- Perform NR using in-situ spectroelectrochemistry capabilities at the NIST-Center for Neutron Research

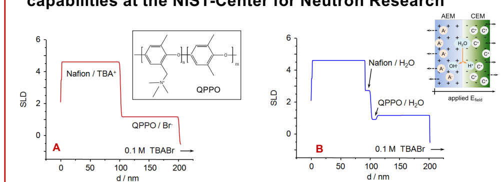

Fig. 7. Calculated scattering length density (SLD) profiles for reflection from a Nafion/QPPO interface (A) without and (B) with an electric field applied.

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5. Conclusions and Directions:

- Confocal Raman microscopy enables quantitative depth-profiling of composition within layered membrane materials when the instrument response that limits spatial resolution is known; SLG/SiO_2 provides a robust standard for IRF estimation.[1]
- In profiling composition across the bipolar membrane AEM-CEM interface, spatial resolution was limited to a few μm but was sufficient to detect the confirmed[5] component variation.
- Ongoing experiments are exploring (1) strategies for in-situ measurements at the AEM-CEM interface and (2) NR as a means to attain nanoscale (ca. 1 nm) spatial resolution.

6. References:

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