1. Overview Objectives:

- Adapt confocal Raman microscopy for spatial profiling ion concentration across the AEM-CEM (anion-exchange membrane / cation-exchange membrane) interface within bipolar polymer membranes.
- Develop a platform to perform neutron reflectometry 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.

2. Background

- Bipolar membranes are composed of anion- and cation-exchange phases in adjacent layers (Scheme 1).
- 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 H₂ generation) and OH⁻ consumed at the anode (e.g., O₂ production).
- 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.

3. Experimental (cont.)

- 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 was utilized for laser excitation radiation to a focus within the sample (Scheme 2). Scattered radiation was collected using the same microscopy objective. Samples were excited using 30 mW (graphene) or 30 mW (polymer membrane) laser power.

D. Strategies for In-Situ Characterization

- Confocal Raman microscopy: A microscope-stage mountable in-situ spectroelectrochemical cell is being tested and adapted (see below).
- NR: NIST capabilities for performing in-situ NR spectroelectrochemistry are being explored (see Panel B).

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 lower 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.

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/SiO₂ interface (Figs 1-2). (See Ref 1 for details)

C. Neutron Reflectometry (NR) Characterization

- Provides ca. 1 nm spatial resolution in depth profiling.

- Neutron reflectometry NR provides a robust standard for IRF estimation.
- 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 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.

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/SiO₂ provides a robust standard for IRF estimation.
- 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 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:
5. Bauer, B. FumaTech, BRT GmbH.

Acknowledgements:
Joel M. Harris, Shelley McIntyre, and Jay Kilt (Utah)
Steve Creager and Saheed Bukola (Clemson U).
Ke Sun and Nate Lewis (Caltech)
TTU Faculty Development Leave Program, NSF (CBET-1922956), NIST (NR beamtime award)