Experimental report

15/09/2023

Proposal: 1-06-22 **Council:** 4/2023

Title: Interfacial transport in water electrolyzers to elucidate mass transport losses

Research area: Engineering

This proposal is a new proposal

Main proposer: Aimy BAZYLAK

Experimental team: Vasant BATTA
Chaeyoung HAM
Eric CHADWICK
Leya KOBER
Salvatore RANIERI
Aimy BAZYLAK
Lijun ZHU
Tess SEIP
Jongmin LEE
Kevin KRAUSE

Local contacts: Lukas HELFEN

Samples: Iridium Oxide catalyst coated membranes
Titanium textiles

Instrument	Requested days	Allocated days	From	To
NEXT	4	3	08/09/2023	11/09/2023

Abstract:

Polymer electrolyte membrane (PEM) electrolysis is a promising solution for chemical storage of renewable energy sources by producing clean hydrogen, which then can be paired with a fuel cell to provide on-demand electricity. However, mass transport losses must be minimized, or better yet, eliminated to make the technology viable for practical use. Unfortunately, the nature of product gas evolution in the porous transport layer (PTL) is still not well-understood, as there are highly coupled phenomena that govern the behaviour of product gas. Via past modelling work, we elucidated the strong influence of temperature on oxygen gas accumulation and importance of the catalyst layer and PTL interface. In the proposed work, we will use operando imaging of our custom electrolyzer to identify the nature of oxygen gas accumulation within the PTL and flow fields with concurrent electrochemical performance. Here, we propose to resolve the dynamic bubble transport accompanied with the explanation of how temperature impacts this oxygen gas accumulation at the interfacial regions as a function of increasing current density and temperature.

ILL Proposal #89005 – Experimental Report (Aimy Bazylak)

Motivation and Objectives: Mass transport losses in the anodic porous transport layer (PTL) of the polymer electrolyte membrane water electrolyzer (PEMWE) must be drastically improved for practical employment. Moreover, previous works have identified temperature as a key variable that impacts oxygen gas accumulation in the porous titanium PTL, but visualization of these pathways using X-ray imaging techniques is challenging due to the high X-ray attenuation of metallic materials. As such, our proposed objectives were as follows:

1. Resolve dynamic bubble transport pathways in the PTL, channels, and PTL-catalyst layer (CL) interface to elucidate the effects of increasing temperatures and current densities on oxygen bubble evacuation from the anode, using neutron radiography.
2. Quantify bubble sizes and spatial distributions throughout the PTL to identify the formation of preferential mass transport pathways, using neutron computed tomography.

PEMWE Hardware and Electrochemical Characterization: For our group's first visit to ILL (Sept 8-11, 2023; 4 days prior to the Sept 15, 2023 call for proposals), we designed custom aluminum-based cylindrical electrolyzer hardware to minimize the electrolyzer's distance to the scintillator and enable high neutron flux into the active area during tomography scans. To enable sealing of the region of interest (where the electrochemical reaction occurs) while minimizing the cross-section of the cell to prevent interference with the scintillator, the cell was clamped via a tongue and groove design, where clamping force was primarily applied at the bottom of the cell (Figure 1, left). This design gave us the flexibility to leverage either the medium or the high-resolution scintillator. Water was fed into both the anode and cathode of the electrolyzer via Al tubing with valves on both the inlets and outlets. These valves were closed during tomography scans to preserve the water and gas distributions in the porous components of the cell. To characterize the electrochemical performance of the cell, polarization curves (Figure 1, right) and electrochemical impedance spectroscopy (EIS) data was collected. The open circuit voltage of the cell was 1.5 V, and the maximum current density reached before cell failure (defined as voltages above 2.4 V) was 300 mA/cm^2. The relatively high voltages compared to other cells in literature is attributed to large ohmic resistance in the cell caused by poor contact between porous media and current collectors, potential leaks, and reactant crossover. Detailed analysis of the EIS results is in progress and will provide additional insights into the mechanisms responsible for observed cell performance.

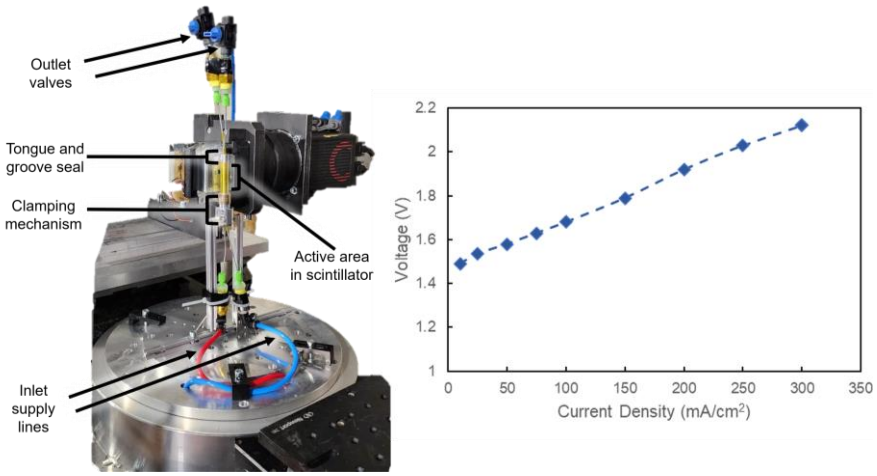

Figure 1 Custom tomography cell mounted on the NeXT beamline (left) and the cell's corresponding electrochemical performance measured via a polarization curve (right).

Preliminary Imaging Results: Neutron radiography was performed at current densities of 75 mA/cm^2, 100 mA/cm^2, and 150 mA/cm^2 at room temperature to characterize the effect of current on oxygen distributions in the PTL. Preliminary analysis at 150 mA/cm^2 (Figure 2 b) revealed that gas distributions in the PTL are heterogeneous, with local reductions in PTL water saturation due to concentration gradients resulting from product gas evolution. Oxygen bubble blockages in the PTL create variations in local current densities due to increased mass transport losses. Simultaneously, bubble blockages dehydrate the membrane, reducing ionic conductivity to further limit electrochemical performance. Both radiography and tomography datasets for 3 current densities at the room temperature were obtained for our current cell design. For our next experiments, exploring temperature effects on gas evolution in the PTL would provide valuable insights and further reveal trends between fluid properties (viscosity, density, etc.) and cell kinetics on the effects of mass transport.

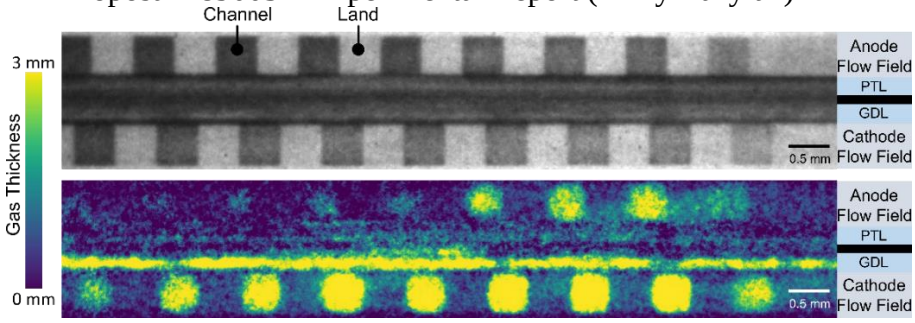

Figure 2 Raw cell radiograph (top) after 15 minutes of cell operation at 150 mA/cm^2 and room temperature, and preliminary processed radiograph (bottom) demonstrating gas thicknesses under the assumption that the only change from the reference image was the displacement of reactant water by product gases. Heterogeneous water and gas distributions are observed along the anode channels and within the anode PTL.

Liquid water has a large neutron incoherent cross-section, leading to significant overshoot error when quantified with the Beer-Lambert law. The contribution of scattering from absorption imaging can be quantified using a black body made of strong neutron absorbents based on B or Gd [1]. The transmission through the black body is theoretically lower than 1% for cold neutron beamlines; therefore, the pixel values at the positions of the black body dots are due to sample scattering. Then, scattering background can be computed by interpolating among black body dots.

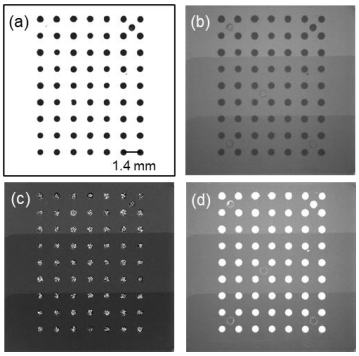

Figure 3. (a) open beam (OB) with a black body grid, (b) water in a step wedge (4.0, 4.5, and 5.0 mm from top to bottom), (c) transmission with scattered background (SBKG) correction, and (d) transmission

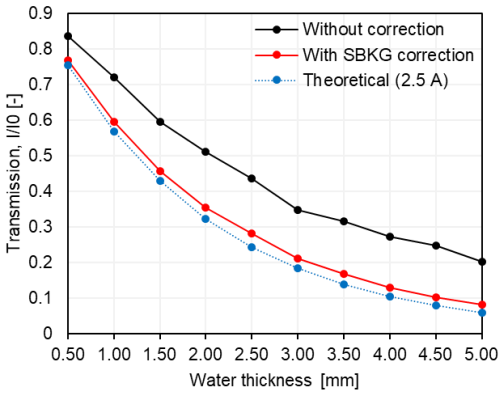

Figure 4. Transmission through varying thicknesses of water (0.50 to 5.00mm).

To enhance water quantification in our work, we investigated water in a stepwise container where the water thickness varied from 0.05 to 5.00 mm. The images were normalized by the open beam with and without the scattered background (SBKG) correction (Figure 33). We identified that transmission is strongly affected by scattering, with more than 100% for water thicknesses above 3.5mm (Figure 4). The resulting water attenuation coefficients were 3.34 and 5.14 cm^{-1} without and with SBKG correction, respectively. We will apply SBKG corrections for all future beamtimes.

Proposed Improvements: Our original cell design was tailored for the medium spatial resolution scintillator for fast temporal resolution to capture oxygen bubble dynamics. Thus, we designed an asymmetric sealing mechanism to limit the height of the hardware. The trade-off for fast temporal resolution was control over the mechanical sealing of the active area. While on site, in discussion with Dr. Lukas Heflen, we pivoted to optimize for spatial resolution rather than temporal resolution. Thus, we adjusted our experiment with the goal to produce the highest quality imaging possible. This new approach involved the vertically shorter scintillator, which would enable a symmetrical cell design. This new constraint presents a new opportunity for our work, facilitating a new cell design that radially protrudes above the height of the scintillator. We could dramatically improve our hardware for a superior experimental outcome, and if awarded more beamtime, we would focus on the following: **1) Cell Compression:** With the ability to extend the hardware in the vertical space, we will redesign our cell to seal with a minimum of two screws at both the inlet and outlet sides of the cell. We will seal the assembly more robustly and improve material contact and reduce ohmic losses. In turn, we will reach higher, more industrially relevant current densities. **2) Temperature Control:** To maintain high temperatures (80-90°C) and representative bubble distributions in the PTL during tomography scans (where heated reactant flow to the cell is paused), we will add fluid recirculation pathways outside the field of view. **3) Improved valve control:** The new design will allow us to integrate valves (e.g. direct-operated solenoid valves) to prevent water/gas from shifting during tomography and to enable remotely controlled cell purging, minimizing experimental intervention. Moreover, this will eliminate the need for the fragile Al tubing previously incorporated into the cell, reducing risk of failure.

Ref: [1] *Boillat, P. et al. Opt. Express 2018, 26 (12), 15769-15784.*