
V.H.8 Technical Assistance to Developers

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Project End Date: Project continuation and direction
determined annually by DOE

Overall Objectives

- Support fuel cell component and system developers by providing access to LANL staff scientists and state-of-art characterization techniques
- Assess and characterize fuel cell materials and components and give feedback to developers
- Assist the DOE Durability Working Group with the development of various new material durability testing protocols
- Provide support to the U.S. Council for Automotive Research (USCAR) and the USCAR/DOE Fuel Cell Technical Team
- Report findings/results to the DOE

Fiscal Year (FY) 2013 Objectives

- Support the DOE Fuel Cell Technologies Office program and working groups:
 - Provide co-chairs for the Durability, Modeling Transport and Catalyst Working Groups
 - Provide a member to the Fuel Cell Technical Team
 - Provide support on developing protocols for membrane conductivity at low relative humidity (RH)
- Characterize degradation mechanisms of components:
 - Evaluate novel microporous layer (MPL) materials
 - Compare MPL materials performance and water content

- Develop a correlation quantitating water content by in situ measurements of operating fuel cell components by small angle X-ray scattering (SAXS) and neutron imaging
- Evaluate degradation mechanism of water transport membranes
- Conduct hydrothermal ageing of membranes and characterize by Fourier transform infrared (FTIR) spectroscopy

Technical Barriers

This project addresses the following technical barriers from Section 3.4.5 of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

FY 2013 Accomplishments

- Evaluate novel compositions of MPL materials:
 - Compared/characterized traditional baseline MPL materials with those incorporating different composition of aluminosilicate or carbon nano-tube (CNT) fibers
 - Compared performance, mass transport resistance, water balance, and water content profiles
- Quantitate and compare in situ water content by neutron imaging and SAXS:
 - Performed in situ water content measurements with identical hardware utilizing neutron imaging and SAXS to quantitate the two techniques for water content
 - Defined water content at different current densities and spatially over the cell dimensions by both techniques.
- Conducted hydrothermal ageing of water transport membranes:
 - Aged different membranes at 25%, 50%, 75%, and 100% RH
 - Examining membrane processing conditions
 - Evaluated growth of membrane anhydride formation by FTIR
 - Designed new ageing sample holders for direct transfer from ageing chamber to FTIR



INTRODUCTION

This task supports the allowance of technical assistance to fuel cell component and system developers as directed by the DOE. This task includes testing of novel materials and participation in the further development and validation of single cell test protocols. This task also covers technical assistance to DOE Working Groups, USCAR, and the USCAR/DOE Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. DRIVE) Fuel Cell Technical Team. Assistance includes technical validation of new fuel cell materials and methods, single-cell fuel cell testing to support the development of targets and test protocols, and regular advisory participation in other working groups and reviews. This assistance is made available to polymer electrolyte membrane (PEM) fuel cell developers by request and upon DOE approval.

APPROACH

The LANL fuel cell team has extensive knowledge and in-house analytical capabilities which can be made available to PEM fuel cell developers to support the U.S. DOE Fuel Cell Technologies Office. These capabilities, along with the personnel, uniquely allow us to conduct thorough diagnostics and confirm results of existing and novel materials. In FY 2013, several tasks were addressed. This included testing of novel MPL materials, examination of water transport membrane durability, and conducting experiments to relate in situ water measurements by neutron imaging and by SAXS. Detailed highlights of these projects will be further discussed below. Los Alamos has extensive experimental equipment available for testing and characterizing fuel cells that includes, but is not limited to:

- Approximately 40 single-cell fuel cell test stations
- Three-dimensional material imaging by X-ray tomography
- Scanning electron microscopy/energy dispersive X-ray analysis
- X-ray fluorescence spectroscopy
- Differential scanning calorimetry
- FTIR spectroscopy
- Tapered element oscillating microbalance
- Thermogravimetric analysis
- Simultaneous thermogravimetric analysis/differential scanning calorimetry
- Differential thermal analysis

- Solid-phase and liquid-phase nuclear magnetic resonance
- Gas chromatography
- Mass spectroscopy
- X-ray diffraction
- Solid-state diffuse reflectance infrared Fourier transform spectroscopy
- Raman spectrometer

RESULTS

In FY 2013, we completed testing and analysis and provided feedback to both the collaborator and the DOE technical development managers in several different major component areas. Some selected findings were as follows:

Novel MPL Material Characterization

Scanning electron microscopy characterization showed MPLs have ‘loosely packed’ carbon black + polytetrafluoroethylene (PTFE); upon incorporation of fibers, such as CNT and aluminosilicate fibers, the carbon black particles tend to surround CNT ‘bundles,’ and fibers such as CNTs are not homogeneously distributed within the MPL. The performance of these novel MPL materials was measured in terms of fuel cell performance and their effect on mass transport limitations. Figure 1 shows the performance for the materials in terms of (a) voltage-current-resistance (VIR) in H_2/Air_2 , (b) VIR in $H_2/He/Ox$, and (c) the impedance at $1.2 A/cm^2$. 25BC is the traditional carbon black MPL mixed with PTFE binder, 25BL has hydrophilic aluminosilicate fibers in it, and 25BN has CNTs mixed into the MPL. Similar performance for three different MPL/gas diffusion layers (GDLs) is observed in $H_2/He/Ox$ up to about $2 A/cm^2$ - (O_2 diffuses 3.7x faster in He vs. N_2 – see Figure 1b); this indicates that with the He/Ox mixture, these MPLs show similar mass transport and water removal characteristics. In H_2/air , the VIR performance is best with the 25BN, followed by the 25BL, with the lowest performance for 25BC. The impedance (Figure 1c) verifies that the order of mass transport resistance is best with $25BN < 25BL < 25BC$. Rationale for better performance of the BN is likely due to less flooding in the cathode catalyst layer due to better water removal characteristics of the MPL with CNT additives.

In situ high-resolution cross-sectional water imaging was performed to correlate the performance and impedance to water content; this is shown in Figure 2. The water content in the catalyst layer and GDL follow the same trend as the transport resistance measured in the impedance: $25BN < 25BL < 25BC$.

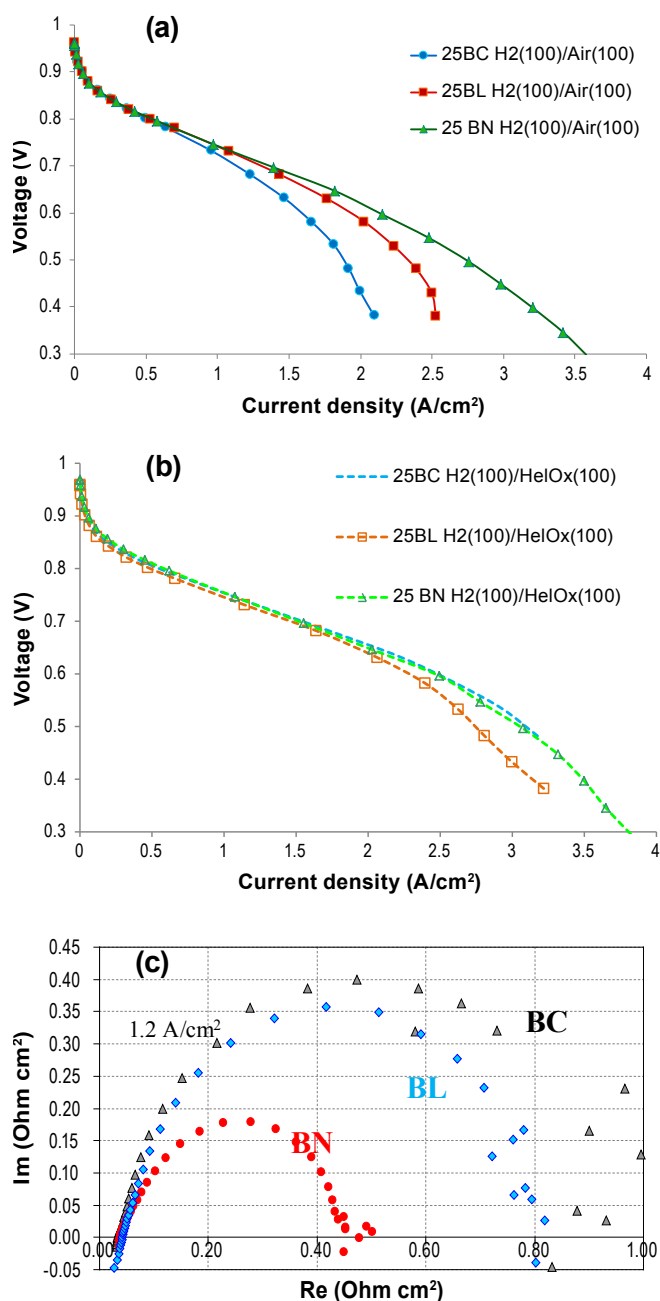


FIGURE 1. Polarization performance of 25BC, 25BL, and 25BN in (a) H₂/air, (b) H₂/He/Ox, and (c) impedance at 1.2 A/cm² in H₂/air.

Correlating In Situ Water Content by SAXS and Neutron Imaging

In situ SAXS has been used by multiple groups to characterize fuel cell membranes and the effect of water content on structure; however, to date there has not been a method to correlate the in situ SAXS measurements directly to the water content of the membranes. To correlate the water content, an identical cell was operated while conducting

SAXS and neutron imaging. The SAXS scattering profile is shown in Figure 3, showing (a) the top portion of the cell, (b) the middle portion of the cell, and (c) the lower portion of the cell when the cell was operated in a co-flow arrangement with the gas inlets at the top of the cell. The neutron imaging showing the water content for the same cell for six different current densities is illustrated in Figure 4, with the same operating geometry. The SAXS and neutron imaging both show maximum cell water content between 0.2–0.4 A/cm²; above this current density the heat generated in the cell reduces the water content. The SAXS shows that the membrane water content below the ribs is greater than that below the channels. This is consistent with higher-resolution through-plane neutron imaging. The co-flow cells have maximum water content near the outlets, and the counter flow cells have maximum water content near the middle of the cells.

Water Transport Membrane Ageing

Preliminary measurements were made of the anhydride peak formation in a number of water transport membranes subjected to different pre-treatment conditions and ageing at different RHs and temperatures. These studies were to help define the degradation mechanism and correlate the chemical differences to changing water transport properties in membranes for humidification applications. To date, the pre-treatment of the membranes shows no significant differences in anhydride formation, nor does the type of membrane. Additional measurements will be made with thinner membranes to attempt to quantitate the degradation mechanism for water transport.

CONCLUSIONS AND FUTURE DIRECTIONS

In FY 2013 LANL

- Provided support for program interaction with DOE by supplying the co-chair of the DOE Fuel Cell Technologies Durability Working Group, the co-chair of the DOE Transport Modeling Working Group, and a permanent representative to the DOE Fuel Cell Technical Team. Work on defining protocols to properly measure proton conductivity at low RHs was accomplished and presented to the Fuel Cell Technical Team.
- Specific studies were carried out on:
 - Novel MPL material characterization
 - Correlating in situ water content by SAXS and neutron imaging
 - Water transport membrane ageing

For FY 2014, we will continue to support fuel cell developers as directed by DOE by providing capabilities that exist at LANL and are not readily available to many developers.

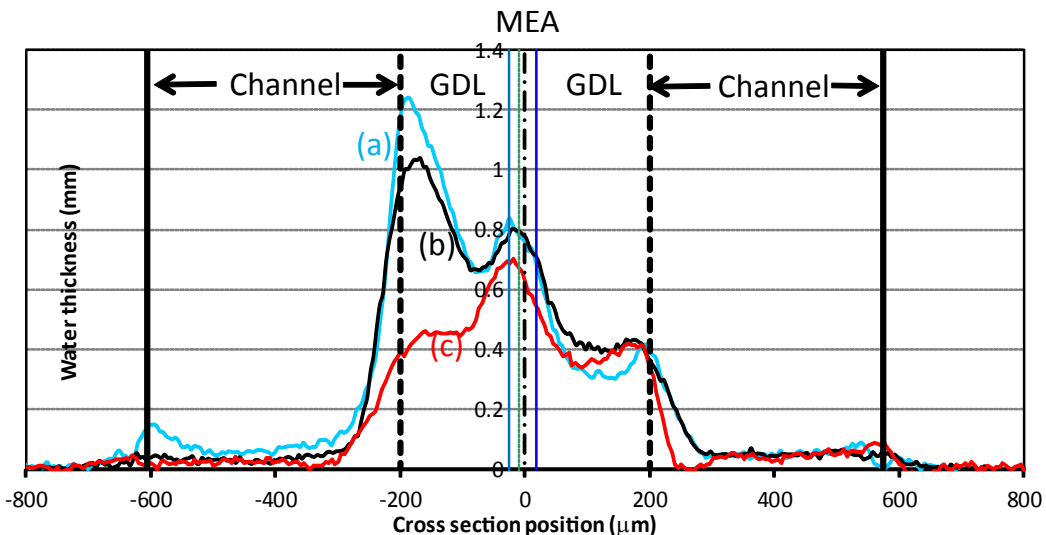
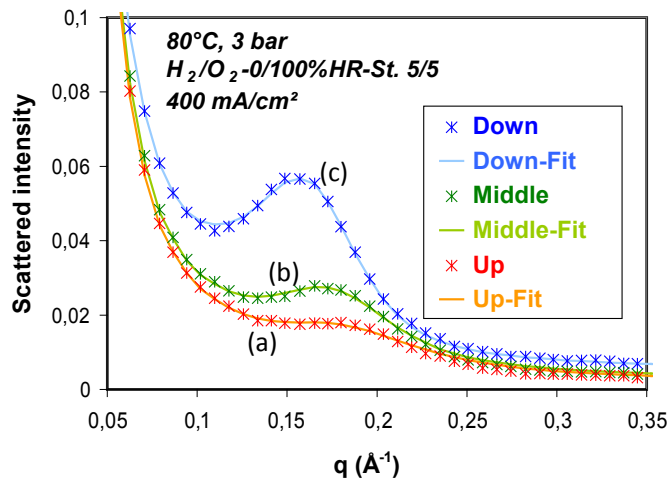


FIGURE 2. Neutron imaging water density profiles at 1.2 A/cm² of (a) 25BC, (b) 25BL, and (c) 25BN at 80°C and 100% RH.



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FIGURE 3. In situ small X-ray scattering of operating fuel cells showing average membrane water content (a) top portion, (b) middle portion, and (c) lower portion.

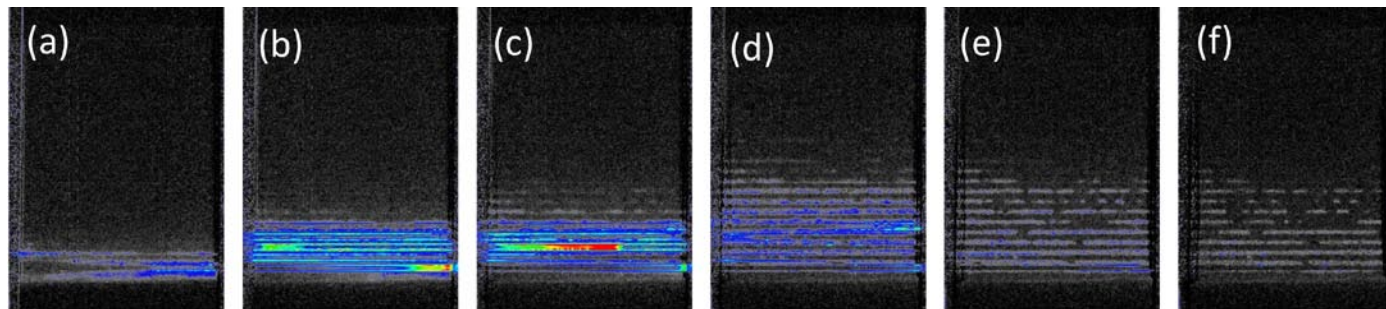


FIGURE 4. In situ water images by neutron scattering of identical cells used in Figure 3 at (a) 0.1 A/cm², (b) 0.2 A/cm², (c) 0.4 A/cm², (d) 0.6 A/cm², (e) 0.7 A/cm², (f) 0.8 A/cm².