Neutron imaging of water transport in polymer-electrolyte membranes and membrane-electrode assemblies

D.S. Hussey and D.L. Jacobson
National Institute of Standards and Technology
100 Bureau Dr., M.S. 8461, Gaithersburg, MD USA
20886-8461
D. Liu and B. Khaykovich
Massachusetts Institute of Technology
138 Albany Street, Cambridge, MA0 2139, USA
M.V. Gubarev
Marshall Space Flight Center, NASA,
VP62, Huntsville, AL 35812, USA
D. Spernjak, G. Wu, J. Fairweather, R. Mukundan, R. Lujan, P. Zelenay, and R.L. Borup
Los Alamos National Laboratory
Los Alamos, NM 87545

Neutron imaging is a powerful tool to measure and visualize water transport phenomena in proton exchange membrane fuel cells. This is owing to the fact that neutrons have high transmission through materials commonly used in fuel cell construction, yet still have high sensitivity to the small amount of water that is entrained in the fuel cell. The water content is obtained by a neutron transmission measurement coupled with a prior calibration measurement. The ability to spatially resolve the water content in the components – land vs. channels and anode vs. cathode – enables comparing the measurements with model predictions of the water content to advance the understanding of the heat and mass transport. The present state of the art in spatial resolution is about 10 µm, and is primarily limited by the range of the charged particle that results from the neutron capture reaction in the neutron imaging detector. Another limitation to the spatial resolution is the inability to achieve image magnification in the standard pinhole optics geometry used in standard neutron imaging.

While the neutron image spatial resolution of 10 µm has enabled directly studying water transport in commercial gas diffusion layers, one must employ thick membranes or catalyst layers to study the membrane electrode assembly (MEA). The current work describes two MEA studies that were suitable for current neutron imaging technology: membrane water content under strong hydration gradients and flooding in non-precious metal catalysts. As is widely observed in polymer-electrolyte membranes, there is a jump in the water content when the membrane is exposed to 100 % relative humidity (RH) vs. liquid water (Schroeder's paradox). Schroeder's paradox is included in many water content models as a "jump condition" where there is liquid water on the cathode and less than fully saturated vapor on the anode. Intuitively, the jump condition is not sustainable, as the large pressure difference in the membrane cannot be supported. The water content in thick membranes (~300 µm) under multiple water vapor or liquid water gradients was measured by neutron radiography (Figure 1). Rather than evidencing a "jump" in the water content, there is a clear continuous gradient from one side of the membrane to the other. This data also confirms similar experiments using x-ray microtomography [1].

A potential non-precious metal catalyst (NMPC) layer for the cathode is based on Fe functionalized from a polyaniline precursor [2]. This NMPC is quite thick (~100 µm) and there was evidence from electrical impedance spectroscopy that flooding reduced performance of this catalyst. It was not clear if the flooding was due to the layer thickness or other properties. This was studied by preparing two membrane electrode assemblies of similar thickness, one NPMC (~80 µm) and one Pt/C (50 µm). Looking at the open circuit data (Figure 2) it is clear that the NPMC-membrane interface is hygroscopic compared to the Pt/C. Thus, the flooding was not an effect of layer thickness but the wetting properties of the NPMC.

While standard neutron radiography with 10 µm resolution has yielded useful insight into water transport in thick MEAs, better spatial resolution is required to study commercially competitive materials. There are two paths to improve the resolution: 1) using narrow slits and 2) a novel neutron magnifying lens. The slit technique is akin to structured illumination, and would require ~12 h to acquire one image with 1 µm resolution. With a neutron lens, one no longer requires pinhole collimation to obtain spatial resolution which would increase the usable neutron flux by a factor of ~100. We recently tested a prototype of such a lens [3]. With magnification of 10, one could obtain 1 µm images in the same time as it currently takes to obtain 10 µm resolution images. The lens is based on reflective, axisymmetric optics created from thin foils of nickel. The fabrication of the foils is ongoing to improve the angular resolution and depth of focus.

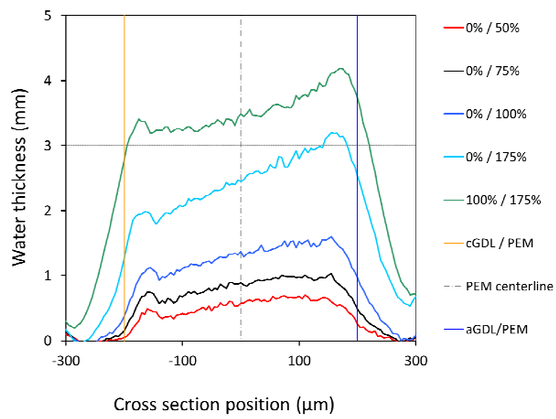

Figure 1 Water content of a membrane under differential relative humidity conditions.

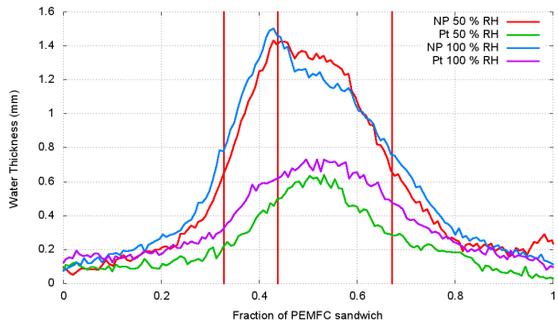

Figure 2 Comparison of water uptake in the non-precious (NP) metal catalyst and Pt/C (Pt) at open circuit voltage for 50 % RH and 100 % RH.

1. Hwang, et al, ACS Macro Lett. **2** pp. 288-291 (2013).
2. G. Wu, et al, Science **332** (6028) (2011), pp. 443–447
3. D. Liu, et al, Appl. Phys. Lett. **102**, 183508 (2013).