Proton Exchange Membranes for Hydrogen Generation - A Tutorial on Research Needs and Challenges for PEM Electrolysis vs. Fuel Cells

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Hydrogen generation via electrolysis is rapidly gaining international interest for energy storage applications due to the carbon-free chemical cycle and response characteristics of this technology. Proton exchange membrane (PEM) electrolysis offers advantages vs. liquid hydroxide systems in footprint, turndown capability, lack of corrosive electrolyte, and system simplicity. Many companies including Proton OnSite have therefore chosen PEM technology as the platform for development of megawatt-scale hydrogen generation for applications such as capturing peak wind energy, grid frequency regulation, vehicle fueling, and improving biogas conversion efficiency. PEM electrolysis is already cost competitive on an equal output capacity basis vs. other sources of hydrogen for industrial applications, but overall lifecycle cost needs to be reduced for these energy markets. The membrane is a key limitation in both cost and efficiency, impacting capital and operating cost. Figure 1 shows the contribution of membrane ionic resistance to the total cell overpotential for current commercial electrolyzers operating at 50°C.

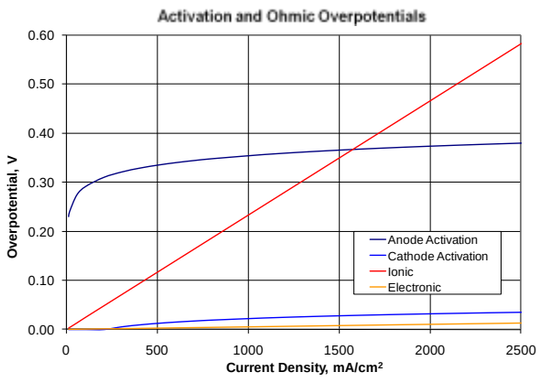

Figure 1. Contributions to activation and ohmic overpotential in an operating PEM electrolysis cell.

While PEM electrolyzers use similar materials to PEM fuel cells, there are unique challenges in electrolysis which have slowed adaption of advancements made in fuel cell materials, in the absence of direct research focus on these challenges. Commercial electrolysis cells have continued to use thick PFSA-based membranes due to the high differential pressures and sealing loads used in the electrolyzer, as well as the very long lifetimes required for industrial applications. Still, much of the progress in PEM technology for fuel cells to enable more robust and efficient performance, such as higher mechanical strength, tolerance to higher temperature, and higher chemical stability, should be able to be translated to membranes suitable for electrolysis. Electrolysis, electrochemical compression, and hydrogen-based flow batteries are thus rich areas for high impact research and development.

Specific differences between electrolysis and fuel cell membranes include the membrane hydration state and mechanical loads on the membrane. Electrolysis membranes are fully hydrated at all times, which eliminates the stresses caused by hydration and dehydration of the membrane which can happen in fuel cells, but also results in swelling and can reduce mechanical strength and integrity of the membrane, especially at high IEC values. Thinner membranes can crack under the high sealing loads or in transition areas, especially hydrocarbon membranes which tend to have short elongation to break, but even traditional PFSA materials have tended to limit the practical operating thickness to 7-10 mils. Long term creep characteristics have also limited operating temperature to 40-60°C.

In addition, electrolyzer and electrochemical compressor cells tend to operate at differential pressures of at least 200-400 psi and as high as thousands of psi. At the highest operational pressures, untreated membranes allow too much hydrogen crossover to the oxygen side of the cell, resulting in a potentially unsafe condition. In addition, the load-following characteristics of PEM electrolysis cells are a key advantage for their application in energy storage, and even at lower pressures crossover can become an issue at lower current density since not enough oxygen is produced to dilute the hydrogen diffusing through the membrane. Current processes to mitigate this hydrogen buildup add cost and system complexity, or require custom treatments to the membrane electrode assembly which preclude standardization with fuel cells.

In this tutorial, recent advancements and understanding in electrolysis-specific membrane characteristics will be presented. For example, membrane reinforcements and alternate polymer chemistries have been developed which have shown dramatically improved durability in the electrolyzer cell vs. standard PFSA membranes. Figure 2 shows the decrease in membrane lifetime as the thickness is decreased from 175 to 125 to 90 microns (blue bars). In contrast, stable performance can be achieved at 90 and even 60 micron thicknesses with reinforced membranes (red bars). The inherent hydrogen diffusion rates of the reinforced membranes were also reduced vs. base membranes of equivalent thickness. Continuing research needs and collaborations between research institutions and industry will also be discussed.

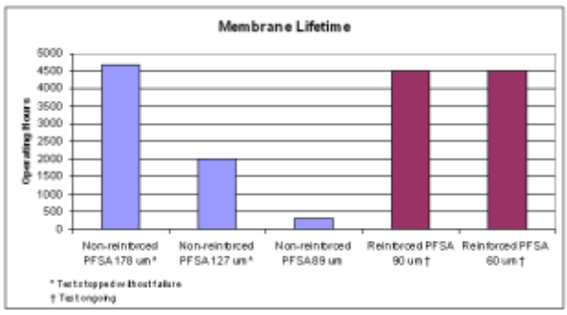

Figure 2. Membrane durability comparison for reinforced and non-reinforced proton exchange membranes of various thicknesses in an operating PEM electrolysis cell.

Acknowledgements:
Authors gratefully acknowledge financial support from the Department of Energy, the Office of Naval Research and the National Science Foundation for the work described in this paper.