

# Oxygen Permittivity Studies on Alternative Proton Exchange Membranes Designed for Elevated Temperature Operation

L. Zhang, C. Ma and S. Mukerjee

Department of Chemistry, Northeastern University  
360 Huntington Avenue, Boston, MA 02115

Proton exchange membranes operating at elevated temperatures (<100-130°C) are expected to diminish problems of system integration and water management in the current state of the art PEMFCs stacks. Since the current state of the art low temperature proton conductor (Nafion, from Dupont) requires greater than 80 percent relative humidity for maintaining proton conductivity, alternative approaches for elevated temperature are required. One approach under active consideration is the use of Nafion membrane composites containing inorganic oxide gels. This approach relies on the ability of the composite on maintaining higher levels of hydration within the membrane structure at lower relative humidities. The other approach is to use alternative membrane chemistry to enable sufficient proton conductivity at lower relative humidity such as at 50% level. These alternative polymer membranes under active consideration include (a).poly(arylene-ether-sulfone), (b).Poly(sulfide sulfone). Ongoing studies at our laboratory have shown promising results with conductivity at low relative humidity.

In order to enable the use of these proton exchange membranes in a fuel cell it is essential to understand their gas permittivity characteristics (solubility and diffusion coefficients), especially with respect to oxygen. Understanding these characteristics is important for designing the appropriate interface in the membrane electrode assembly (MEA). Since the chemistry of the polymer backbone, side chains and sulfonation in these membranes is very different from Nafion, there is a strong motivation to understand these mass transport issues.

The objective of this investigation therefore is to determine the oxygen permittivity as a function of ion exchange capacity, relative humidity of the inlet gas, temperature and presence of microcomposite additives such as hetero-poly acids. For measurement of oxygen permittivity, a solid state microelectrode assembly has been built in-house. Use of microelectrode for determination of oxygen permittivity was first reported by Parthasarathy *et. al.*,(1). Later Holdcroft *et. al.* (2, 3) has shown that the O<sub>2</sub> transport parameters are very sensitive to parameters such water uptake, ion exchange capacity etc.,

## Experimental

The alternative proton transport membranes under investigation were (a) sulfonated poly(arylene-ether-sulfone), (b) sulfonated poly phenyl sulfone and (c) sulfonated Poly(sulfide sulfone). These membranes were procured as a part of a collaborative effort from Virginia Polytechnic Institute (Professor Mcgrath's research group, for poly (arylene ether sulfone) and from Foster Miller Inc., (Waltham, MA, for sulfonated poly sulfide sulfone and poly phenyl sulfone).

A microelectrode set up was designed and built at Northeastern University. Design principles were the same as those described before (1). Further improvements were however made which included a calibrated micrometer stage that greatly eliminated issues related to contact pressure. An impedance analyzer (Autolab PGSTAT 30) was used to ensure that the contact impedance was same

between runs and different samples. The microelectrode was a 100 μm Pt wire encased in a glass electrode. The reference was a dynamic hydrogen electrode, while the counter electrode was a Pt disk, all electrodes being on the same side of the membrane. The gas inlet was designed to be opposite to the working microelectrode and the set up had arrangements for humidity control using an in-house humidity control setup. This setup incorporated a constant temperature oven, which housed the microelectrode setup. The humidity was controlled by a feed back loop setup using mass flow meters and proportioning valves, mixing wet and dry oxygen gas. This arrangement was controlled via a computer using Labview software. The gas in this experimental setup was directly fed to the microelectrode setup at the membrane electrode interface. This in our view is more akin to fuel cell conditions and hence provided an accurate picture of the interfacial mass transport characteristics.

## Results and Discussions

The solubility C and diffusion coefficient D of O<sub>2</sub> in alternative membranes were measured as a function of temperature and relative humidity. Chronoamperometry method was used to estimate these parameters. According to Cottrell Equation, C and D can be determined from the slope and intercept of the *I* versus *t*<sup>-1/2</sup> plot (Figure 1). This investigation will present a full picture of O<sub>2</sub> transport characterizations within these alternative membranes.

## Acknowledgements

The authors wish to acknowledge financial

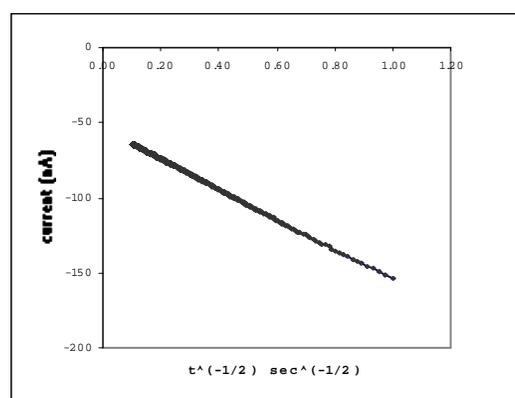


Figure 1. Chronoamperometric plot for O<sub>2</sub> reduction at the Pt/ Nafion 117 interface.

support from the Department of Energy (Office of Transportation Technologies) as well as from Foster Miller Inc., (Waltham, MA).

## References

1. A. Parthasarathy, C. J. Brumlik, C. R. Martin, *Polym. Mater. Sci. Eng.* **68**, 117-18 (1993).
2. S. Holdcroft, M. S. Abdou, P. Beattie, V. Basura, *New Mater. Fuel Cell Mod. Battery Syst. II, Proc. Int. Symp.*, **2nd**, 861-863 (1997).
3. S. Holdcroft, V. I. Basura, P. D. Beattie, *Book of Abstracts, 217th ACS National Meeting, Anaheim, Calif., March 21-25*, MSE-374 (1999).