Design and Modeling of High Temperature Water Free Proton Exchange Membranes in DEA PEMFC Operations

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Polymer electrolyte membrane fuel cell (PEMFC) is a great alternative in transportation application however there are still some issues on the commercialization, such as complexity in balance-of-plant design that is leading low power density. A new approach, dead ended anode (DEA) design might be a solution to reduce the complexity of PEMFC by eliminating its expensive hardware, such as mass flow controllers and hydrogen recovery components.

On the other hand, the operation of the DEA PEMFC causes voltage transients due to accumulation of nitrogen, liquid and vapor water in anode channels and gas diffusion media in the presence of Nafion® membrane. The one issue regarding Nafion® membrane in DEA operation is membrane dry-outs, may occur especially at anode inlet due to electro-osmotic drag of water from the anode to the cathode. On the other hand, too much water will cause accumulation on anode electrode and gas channels, which prevents reactant gasses from the catalyst layers and raises the mass transport loss. Even the PEMFC has been simplified with DEA operation, it might still has above shortcomings related with most accepted PEMFC membranes, (i.e., Nafion®) and operating temperature which is limited to be below 100°C, is typically 60-80°C.

In this study, high temperature (100-120 °C) DEA PEMFC operation is targeted with synthesized water free radiation grafted proton exchange membranes. ETFE, poly(ethylene-alt-tetrafluoroethylene) has been used as the base polymer and irradiated with ^{60}Co source. 4-vinyl pyridine (4VP), 2-vinyl pyridine (2VP), *N*-vinyl-2-pyrrolidone (NVP) have been used as alternating nitrogen containing monomers. Graft copolymerization is followed by phosphoric acid (H_3PO_4) doping. The nitrogen containing monomers in this study enhanced the ionic conductivity while H_3PO_4 maintaining water independent ionic conductivity at temperatures above 100 °C. In **Figure 1** SEM-EDX micrographs of the synthesized ETFE-*g*-P4VP membranes is demonstrated. The pinhole free, smooth surface of membrane is observe. Ex-situ characterizations of the resultant membranes have been completed. [1-2] It was observed that resultant membranes exhibit reasonable mechanical properties and ionic conductivity for preparation of membrane electrode assembly (MEA).

Fuel cell testing according to both DEA and flow through anode (FTA) conditions have been studying. FTA fuel cell testing of the water free ETFE-*g*-P4VP membranes have been completed for the first time as a novelty in literature and shown in **Figure 2**. Since the membranes and high temperature DEA operation are new in literature, a comprehensive degradation study at temperatures 100-120 °C will be performed to examine what kind of mechanisms will dominate the degradation while there will be no water inside the PEM fuel cell.

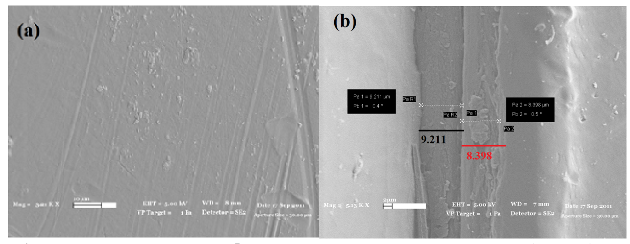

Figure 1: Scanning electron microscopy energy (SEM) micrographs of P mapping on cross section of ETFE-g-4VP phosphoric acid doped membranes a) Surface b) Cross-section (graft level of 32%)

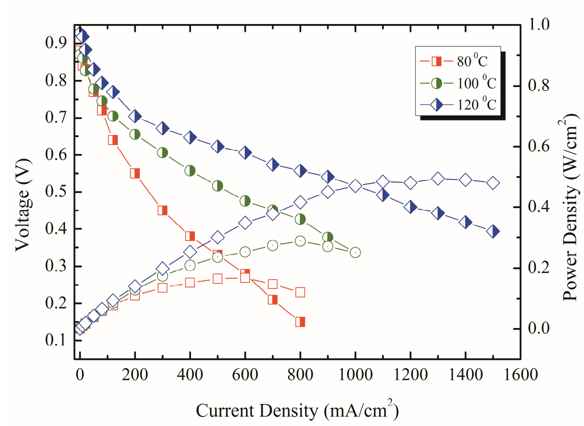

Figure 2: H_2/O_2 FTA single cell performance of ETFE-g-P4VP membranes

Moreover, a transient, one dimensional along the channel numerical model is evolved in COMSOL® for our synthesized ETFE-*g*-P4VP membranes in DEA PEMFC operation to improve the understanding of related local mechanisms.

As conclusion, our study targets two main cost factors in PEMFC commercialization. The first one is replacement of the commercial Nafion® membrane with synthesized ETFE-*g*-P4VP water free proton exchange membranes that operates in the range 80-120 °C in dry conditions. This membrane is cost competitive and suitable to be adopted by large scale production. The second aim is simplified system design by DEA operation to reduce the use of expensive hardware and increase power density in PEMFC for transportation applications.

References

[1] Şanlı I., L., Gürsel A., S., 'Synthesis and characterization of novel graft copolymers by radiation induced grafting', Journal of Applied Polymer Science, 120 (4), 2313-2323, 2011

[2]. Şanlı I., L., and Taş, S., and Yürüm, Y., and Gürsel A., S., 'Novel phosphoric acid doped radiation-grafted proton conducting membranes for high temperature polymer electrolyte membrane fuel cells' (2013) (Submitted)