Thin Film Tri-layer Proton Exchange Membranes for Direct Methanol Fuel Cell (DMFC) Applications

Ruichun Jiang, H. Russell Kunz, James M. Fenton

Department of Chemical Engineering,
University of Connecticut
Storrs, CT 06269, USA

Direct methanol fuel cells (DMFCs) have many advantages over internal combustion engines and batteries and have become a subject of considerable interest. Methanol as a liquid fuel at room temperature has a higher energy density and simplifies the fuel cell system. However, two main factors still hinder wide spread use of DMFCs for commercial applications: poor kinetics of methanol oxidation and large methanol crossover through the membrane. Both factors significantly reduce cell performance. Crossover is the undesirable transport of anode fuel through the membrane to the cathode side where it is oxidized by chemical reaction with the cathode reactant without any contribution to power generation. Methanol crossover also deactivates the cathode electrocatalyst resulting in further efficiency losses.

Nafion® membranes from DuPont are the most widely studied polymer electrolyte for application in hydrogen fuel cells. Nafion® membranes are not satisfied for DMFC applications, since the methanol crossover rate through Nafion® is high. To reduce methanol crossover, thick Nafion® membranes, such as Nafion®117 (175 µm thickness) are usually used, which leads to a high cell resistance. In recent years, a relatively cheap material, poly(ether ether ketone) (PEEK) was sulfonated and evaluated as a polymer electrolyte for fuel cell applications. The sulfonation of PEEK is performed by directly dissolving and modifying the polymer using concentrated sulfuric acid. The degree of sulfonation is controlled by reaction temperature and time. This sulfonation method is called direct sulfonation

In this work, besides the direct sulfonation method, an indirect sulfonation method was studied and applied for forming SPEEK. According to the indirect sulfonation procedure, PEEK was first dissolved in a non-reactive solvent to form a homogenous solution, then sulfuric acid was added to perform the sulfonation reaction. SPEEK samples obtained by indirect sulfonation were more homogeneous than that by direct sulfonation, especially for the samples with a lower degree of sulfonation.

The sulfonated PEEK (SPEEK) membranes have good thermal stability and appropriate mechanical properties for fuel cell applications. Figure 1 shows the thermogravimetric analysis (TGA) results. For SPEEKs with different degree of sulfonation, no degradation happened until the temperature is higher than 260°C. With the increasing of sulfonation degree, the conductivity of SPEEK increases as well as the methanol permeability. To achieve lower methanol crossover while maintaining lower cell resistance. Thin SPEEK membranes (~ 25 µm) with tri-layer structure were developed and applied for DMFC study. The structure of the tri-layer membranes is shown in Figure 2.[1, 2] An ultra thin SPEEK layer with low sulfonation degree was used in the middle as the methanol barrier layer, while high sulfonation degree SPEEK (or Nafion®) were applied on the outer surfaces as conductive layers. Our previous work[2] showed that MEAs using tri-layer membranes with Nafion® outer layers demonstrate better DMFC performance than that with the same thickness pure Nafion® membranes. In this study, a series of tri-layer membranes with various sulfonation degree and thickness of SPEEK as the outer layer and barrier layer were produced for DMFC study. The high sulfonation SPEEK conductive layers provided proton-rich membrane/electrode interfaces that ensured less contact resistance. The low sulfonation SPEEK barrier layer effectively enhanced the stability of the MEAs and reduced methanol crossover without much resistance loss.

Reference:
1. Yongchao Si, Jung-chou Lin, H. Russell Kunz, James M. Fenton, J. Electrochem. Soc. 151, A463 (2004).
2. Ruichun Jiang, H. Russell Kunz, James M. Fenton, Electrochemical Society 204th Meeting at Orlando, FL, Oct. 2003, Abstract #1024.

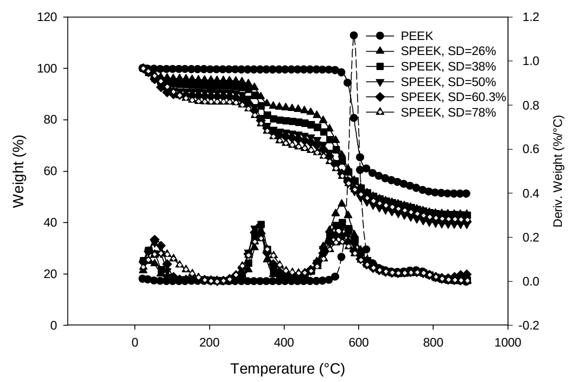

Figure 5. Thermo-gravimetric Analysis (TGA) of PEEK, SPEEK in Nitrogen.

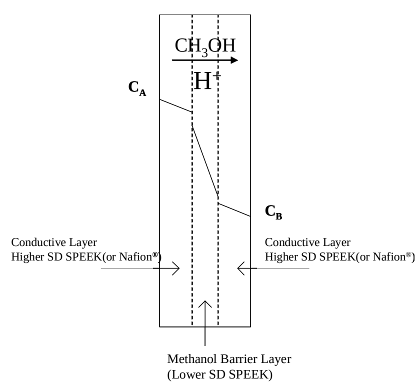

Figure 2. Schematic of tri-layer structure membrane.