ELECTRO-OSMOTIC DRAG EFFECT ON THE METHANOL PERMEATION FOR sPEEK AND NAFION MEMBRANES

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Keywords: SAXS, sPEEK, proton conductivity, and electro-osmotic drag.

Abstract

Electro-osmotic drag effect on the methanol permeation was investigated for sPEEK membrane, and its result was compared to that of Nafion. The electro-osmotic drag coefficient was determined from the limiting current density which is a function of applied potential and temperature. The methanol permeability of sPEEK membrane increased with temperature but its temperature dependence was not as strong as Nafion. The methanol permeability or the total methanol flux of Nafion was at least twice higher than that of sPEEK 75, as it was highly associated with the electro-osmotic drag. This higher electro-osmotic drag of Nafion is attributed to the bigger ion cluster size and thus more free water absorption than sPEEK.

1. Introduction

DMFC is an electrochemical device that generates the electric energy through the oxidation/reduction reaction associated with the fuel, methanol. It is considered to be very ideal as it has the following advantages: i) fuel is methanol (liquid state) so that it is easily distributed, stored, and regenerated; ii) its structure is quite simple with low weight and volume; and iii) relatively low cost because of its uncomplicated structure and cheap fuel. In DMFC, the water existing in the nano channels and ion clusters of the electrolyte membrane plays an important role in proton conduction. If there is too much water, the excess amount of water called free water can attach to the proton in the forms of \( \text{H}_2\text{O}^+ \), \( \text{H}_3\text{O}^+ \) and \( \text{H}_4\text{O}^+ \) due to the strong polar interaction between water and proton.

Nafion is well-known to have wider water channel and bigger ion cluster size than sPEEK [1]. Because of this, Nafion is supposed to accommodate more free water than sPEEK. At present, the biggest problem of Nafion beside its high cost as the electrolyte in fuel cell is the methanol crossover, which is closely related to the channel and cluster structure of membrane [2-4]. Methanol crossover is the phenomenon that the methanol penetrates through a polymer electrolyte membrane from the anode to cathode side. This phenomenon causes low energy efficiency by mixed potential, loss of fuel, and poisoning of the cathode catalyst by carbon monoxide produced from the methanol oxidation at the cathode. There are two major mechanisms of the methanol crossover: diffusion and electro-osmotic drag [5]. The former is caused by the concentration difference between the anode and cathode sides (the diffusional flow). The latter is because the methanol molecules are transported along with the proton bound water (the convective flow). If there is more amount of free water in ion clusters, more methanol molecules can travel to the cathode in a convective way. As mentioned earlier, Nafion possesses larger amount of free water than sPEEK, and thus it’s expected to have higher methanol flux associated with electro-osmotic drag. As estimation of electro-osmotic drag is important as such, in this research, a method was developed to determine the electro-osmotic drag fluxes and the results were compared for sPEEK and Nafion membranes at different temperature.

2. Experimental

Material

PEEK (Vitrex ® 450PF, Mn = 100,000g/mol) was purchased from ICI Company (Rotherham, UK). Nafion 117 was purchased from Dupont. Its thickness was 189 µm and the basic weight 360 g/m². Sulfuric acid (Duksan, Korea) was used as a sulfonation reagent. Methylsulfonic acid (MSA, Acros Organics, New Jersey, USA) was used as the solvent for PEEK. N,N-dimethyl acetamine (DMAc, Fluka Chemie AG, CH-9470 Buchs, Switzerland) was used as a cast solvent in membrane fabrication. All the chemicals were used as received without further purification.

Sulfonation of PEEK

Poly(etheretherketone) PEEK Vitrex ® 450PF was sulfonated according to the procedure described elsewhere [6-8]. PEEK, 20 g, was dissolved completely in 100 mL MSA. The amount of 800 mL of 97% sulfuric acid was added to sulfonated PEEK under nitrogen atmosphere at 30 °C. The reaction mixture was stirred for the desired time with respect to the sulfonation degree. The sulfonated polymer was precipitated in 2 L of deionized water, followed by filtration and washing with deionized water until pH 7. The polymer was dried in a vacuum oven at 100 °C for 1 day before use.

Preparation of membrane

The casting method was applied to prepare membrane. The dry sPEEK with different degrees of sulfonation of 65%, 70%, and 75% were dissolved in N,N-dimethyl acetamine (DMAc) to form a solution of 3–5 wt% concentration and cast on glass plates, followed by drying in a vacuum oven at 100 °C until completion. After
all solvents were removed, the glass plates with sPEEK membrane were cooled to room temperature and immersed in the water bath so that the membranes can be detached from the glass plates. The sPEEK membranes were stored in deionized water at ambient temperature.

Measurement of limit current density

Methanol solution was brought into the anode compartment, while nitrogen gas was continuously fed to the cathode. In the circumstance of open circuit, the methanol permeation through the electrolyte membrane is caused by the concentration difference between anode and cathode compartments. Methanol permeates from the anode are accumulated in cathode during this operation. When the DC potential is applied to the cathode site, methanol can be electrochemically oxidized to produce protons and electrons, which subsequently transfer to the anode site through the membrane and external circuit, respectively where they are combined to produce hydrogen. In this proton transport process, the methanol accompanied to water is transferring to the anode by electro-osmotic drag effect. The current is generated during this process by application of the external potential. The current density will increase with the applied potential and eventually meet the plateau called the limiting current density where the diffusional methanol flux is constant. Figure 1 shows the schematic of the limiting current density measurement.

In the cell configuration to measure limit current density, the working electrode was connected to the cathode of membrane electrode assembly (MEA) under humidified nitrogen purge, and the counter electrode and reference electrode were to the anode under methanol solution feed fed, respectively [9-10].

Figure 1. Schematic diagrams for \( J \) measurement in DMFC configuration; (a) carbon cloth backing; (b) Pt-Ru thin film catalyst layer; (c) electrolyte membrane; (d) Pt black thin film catalyst layer.

Measurement of methanol permeability

Methanol permeability of sPEEK and Nafion electrolyte membranes was measured using the glass diffusion cell with two compartments. The left-side compartment contained 50 ml of 2M methanol aqueous solution and the other 50 ml of pure water. Magnetic stirrer in each compartment was continuously stirring the solution to maintain the uniform concentration. The change in the methanol concentration in the permeated compartment was detected continuously by the refractive index detector (RI750F, Young Lin Instrument, Korea). Figure 2 shows the schematic of the method for the methanol permeability measurement cell [11-12].

3. Results and discussion

In Fig. 1, the net flux of methanol from the anode to the cathode, \( F_{net} \), can be obtained as follows:

\[
F_{net} = F_{diff} - F_{drag} \tag{1}
\]

Here, \( F_{diff} \) and \( F_{drag} \) are the diffusional (total) methanol flux from cathode to anode caused by the concentration gradient between the two electrode and the convective methanol flux from the cathode to anode driven by the electro-osmotic drag, respectively.

Equation (1) is turned into the equation (2) by introducing the drag correction coefficient, \( k_d \), which is the ratio of \( F_{drag} \) to \( F_{diff} \), and replacing the \( F_{net} \) by \( J_{lim} \) and the \( F_{diff} \) by \( DC_m \) and the \( F_{net} \) by \( J_{lim} \) and the \( F_{diff} \) by \( DC_m \) and

\[
\frac{J_{lim}}{6F} = (1 - k_d) \frac{DC_m}{l} \tag{2}
\]

Here, \( D \) is the diffusion coefficient, \( C_m \) methanol concentration of membrane in anode side, and \( F \) Faraday’s constant, respectively.

The drag correction coefficient, \( k_d \) is always less than one because the net methanol flux from the anode to the cathode is affected by the electro-osmotic drag flux from the cathode to the anode in the reversed DMFC scheme. If the electro-osmotic drag flux is high, the net
flux will be low so the drag correction coefficient may be also high.

The methanol permeability can be obtained by multiplying a diffusion coefficient \( D \) by a partition coefficient \( K \) [13].

\[
P = DK = D \frac{C_s}{C_o}
\]  

(3)

where \( C_s \) is methanol concentration in bulk solution.

From equations (2) and (3), we can obtain equation (4).

\[
\frac{J_{\text{lim}}}{6F} = (1 - k_d) \frac{PC_o}{l}
\]  

(4)

In order to investigate the effect of the electro-osmotic drag in equation (4), the limiting current density, \( J_{\text{lim}} \), and the methanol permeability, \( P \) are required to be measured from the reversed DMFC and methanol permeable cell operation as illustrated in Fig. 1 and Fig. 2, respectively.

**Figure 3** shows the methanol permeability of Nafion and sPEEK with 70% sulfonation at different temperature. As the temperature increases, the methanol permeability increases due to more water absorption. It is also clear that the methanol permeability of sPEEK membrane is lower than that of the Nafion® 117.

**Figure 3.** Temperature dependence of methanol permeability of Nafion and sPEEK membranes with different degrees of sulfonation. Methanol feed concentration is 2M.

As shown in **Fig. 4**, when the applied potential increases, the current density also increases and finally reaches the plateau where the entire methanol accumulated in the cathode side was electrochemically oxidized. The maximum current density is called the limiting current density. At higher temperature, current density increases faster with the applied potential, and reaches higher limiting current density. It is because at high temperature the methanol transfer from the anode to the cathode by diffusion is so fast that there is much more methanol in cathode side to be electrochemically oxidized to generate the electric current. Although Nafion has higher methanol crossover, it has lower limit current density as shown in **Fig. 4**.

![Figure 4. Limiting current density of Nafion and sPEEK70 membrane at different temperatures.](image)

**Table 1.** Water uptake, limiting current density \( J_{\text{lim}} \), and electro-osmotic correction coefficient \( k_d \) of Nafion and sPEEK at different temperatures.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Temperature (°C)</th>
<th>Water uptake (% w.t)</th>
<th>( J_{\text{lim}} ) (mA/cm²)</th>
<th>( \frac{F_{\text{osm}}}{F_{\text{diff}}} = k_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>25</td>
<td>15.3</td>
<td>35.84</td>
<td>0.631</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>15.8</td>
<td>51.52</td>
<td>0.684</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>16.4</td>
<td>63.84</td>
<td>0.702</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>19.3</td>
<td>80.64</td>
<td>0.652</td>
</tr>
<tr>
<td>sPEEK 70</td>
<td>25</td>
<td>23.6</td>
<td>24.16</td>
<td>0.551</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>26.5</td>
<td>57.28</td>
<td>0.322</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>28.6</td>
<td>65.76</td>
<td>0.321</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>32.1</td>
<td>78.40</td>
<td>0.423</td>
</tr>
</tbody>
</table>

Once the methanol permeability \( P \) and the limiting current density \( J_{\text{lim}} \) were measured, the electro-osmotic correction coefficient \( k_d \), \( \frac{F_{\text{osm}}}{F_{\text{diff}}} \) of Nafion and sPEEK at different temperatures could be calculated by equation (4). The resulting data are illustrated in **Table 1**. From **Fig. 3, 4** and **Table 1** it is assured that the methanol permeability is significantly affected by the electro-osmotic drag. Even though the water uptake of sPEEK 70
is higher than Nafion, methanol permeability of the first is less than the latter. One of the important reasons for this behavior is attributed to the electro-osmotic drag effect associated with theionic cluster size. As the ionic cluster size of sPEEK is smaller that of the Nafion® 117 as shown in SAXS patterns (see Fig. 5). The lower methanol permeability for sPEEK than Nafion is due to less electro-osmotic drag associated with smaller cluster size containing less free water.

![Figure 5. SAXS patterns of Nafion and sPEEK 70 membranes.](image)

**Conclusion**

The methanol permeability of sPEEK increased with temperature but not as much as that of Nafion in the present experimental temperature range. The limiting current density was affected by the temperature and degree of sulfonation of PEEK membranes. When one of these factors increased, the limiting current density also increased. The electro-osmotic correction coefficient of Nafion and sPEEK could be calculated so that the electroosmotic drag effect could be investigated. Higher methanol crossover for Nafion membrane than sPEEK membrane is caused by higher electroosmotic drag effect associated with larger ion clusters accommodating more amount of free water.

**Acknowledgements**

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant (R0A-2007-000-10029-0) and the National Research Foundation (NRF-2009-0093033) of the Korean Government (MEST).

**References**


