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Thin film electrodes and PVDF-g-PSSA membrane for direct methanol fuel cell

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Introduction

It has been previously shown that the properties of poly(vinylidene fluoride) membrane grafted with polystyrene sulfonic acid (PVDF-g-PSSA) are suitable for use in direct methanol fuel cell (DMFC) [1]. It has also been shown that painting the fuel cell electrode on Nafion® membrane can enhance the performance of DMFC [2]. In this work, the applicability of painting the electrode on PVDF-g-PSSA with Nafion® as the electrode matrix has been investigated.

Experimental

The experimental PVDF-g-PSSA membrane was made in the Laboratory of Polymer Chemistry at the University of Helsinki [3]. The membrane-electrode assemblies (MEA) were made by the thin film method developed by Wilson and Gottesfeld [4]. The electrode ink consisted of carbon supported catalyst, Nafion solution and methanol and was mixed in an ultrasonic bath. After spraying both sides of the membrane with the electrode ink the assembly was hot-pressed. The Nafion content and hot-press temperature were varied for fuel cell tests. The amount of catalyst was 2.0 mg cm⁻² (Pt-Ru) on the anode and 1.0 mg cm⁻² (Pt) on the cathode. Fuel cell experiments were conducted with 2 M MeOH feed (2 ml min⁻¹) at the anode and dry oxygen feed (270 ml min⁻¹) at the cathode. Fuel cell temperature was varied.

Results

Comparison between the performance of MEAs made on Nafion-115 (solid curves) and PVDF-g-PSSA (dashed curves) is presented here at different temperatures. It can be seen that PVDF-g-PSSA performs slightly better than Nafion-115 especially in the high current density region. Maximum performance is approximately 5% higher than with Nafion.

Conclusions

It can be concluded that PVDF-g-PSSA membrane can performance better than Nafion in DMFC when temperature is between 30°C and 60°C. However, with Nafion matrix the MEAs will not be stable enough for use in DMFC. According to the measurements it can be concluded that the decline of performance has two stages: first a quick and steep decrease over a couple of days and after that a slow decay. The former can be attributed to the failing of the electrode structure. This causes proton and electron conductive channels and diffusion routes to be cut off or blocked. The active amount of catalyst decreases strongly. The latter can be attributed to the solvent action of methanol that slowly removes both Nafion and catalyst from the electrodes. The cause of decomposition is probably the mechanical incompatibility between the membrane (PVDF-g-PSSA) and the matrix material of the electrode (Nafion). The membrane also curls up when wetted so that it may have strong tension when it is spread out and put in the fuel cell. Further research with different matrix materials and manufacturing techniques is required if thin film electrodes are to be used with PVDF-g-PSSA.

Table 1. Properties of Nafion-115 and PVDF-g-PSSA.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ionic exchange capacity (meq g⁻¹)</th>
<th>Thickness dry (μm)</th>
<th>Thickness wet (μm)</th>
<th>Conductivity (mS cm⁻¹)</th>
<th>Methanol permability (10⁻⁶ cm² s⁻¹ atm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion-115</td>
<td>8.00</td>
<td>110</td>
<td>125</td>
<td>60</td>
<td>2.6</td>
</tr>
<tr>
<td>PVDF-g-PSSA</td>
<td>2.50</td>
<td>80</td>
<td>85</td>
<td>47</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Hot-press temperature has a large effect on the performance of the PVDF-g-PSSA MEA. The blue curve corresponds to 80°C and red curve to 120°C. Higher hot-press temperatures destroyed the membrane.

Nafion content of the electrode affects performance. With the blue curve the mass ratio of Nafion to metal catalyst is 0.30, with the black curve the ratio is 0.60 and with the red curve 1.00. The optimum is clearly the mass ratio of 0.60. When the mass ratio was less than 0.30, the electrode did not stick to the membrane.

The problem with MEA made on PVDF-g-PSSA is illustrated here. The performance declines very fast after startup. Neither changing the hot-press temperature or the Nafion content of the electrode had significant effect on this. With lower temperatures the decline can be slowed down. At 60°C the degradation of maximum power is 90% in 5 days but in 30°C its 10%.

References