

The development of membranes for high temperature PEMFC

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Introduction

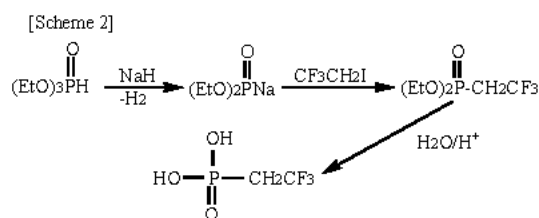
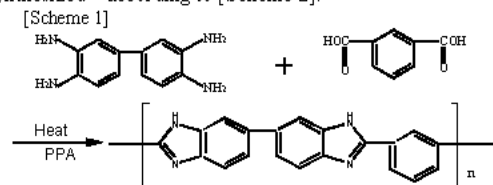
Polymer electrolyte membrane fuel cells (PEFC or PEMFC) are of interest as power sources in vehicles, portable electronic appliances and residential applications because of their high energy efficiency and environmentally friendly qualities [1]. These fuel cells have typically used perfluorinated, modified perfluorinated and partially perfluorinated polymer electrolytes as the hydrogen (or methanol) gas streams [2]. The perfluorinated acid polymer Nafion® is one of the most extensively studied proton exchange membrane for PEFC applications. However, it has a number of drawbacks that need to be overcome, which are the high cost, due to its complicated manufacturing procedure, the high methanol permeability and the poor performance at temperature above 80°C due to the loss of the water. One of the arguments of the development of the new polymer electrolytes is the necessity to operate the cell under high temperature conditions. The operation of the cell at temperature more than 100°C is very interesting because anode catalyst poisoning by carbon monoxide is less important and the kinetics of the fuel oxidation will be improved and the efficiency of the cell should be significantly enhanced. Therefore, there has been a great demand for new electrolyte membranes for the high temperature PEMFCs. Sulfonated aromatic polymers, organic-inorganic composite electrolyte membranes, and blend of different polymers with phosphoric acid (PA) have been explored. In the first two types of electrolytes, the ionic conductivity depends upon the presence of water. Among the blends with phosphoric acid, polybenzimidazole (PBI) has been successfully tested in the fuel cells which were operated at temperature up to 200°C though long-term durability of these electrolytes have not been published yet [3]. In the PA doped polymer matrix system, the proton source and carrier is phosphoric acid. The proton conductivity is determined by PA doping level. The roles of polymer matrix are confined to holding PA, spatial separation between cathode and anode, and blocking gas cross-over. The excess doping of PA which increases the proton conductivity generates polyphosphoric acid (PPA), which can dissolve PBI. These dissolving phenomena are accelerated, partially at high temperatures, generally above 130°C. The dissolution of PBI in PPA causes gas cross-over, followed by the decrease in open circuit potential. Therefore the solutions to increase the PA doping level without sacrificing chemical and mechanical stability of the membrane are strongly needed. However at high PA doping levels above 150°C, the mechanical properties of the membrane became poor and not suitable for membrane electrode assembly (MEA) fabrication. Therefore further progress is still necessary for mechanical properties and long term durability of PA doped PBI membranes at high temperature and low or non humidification. Even though several ways to improve the shortcomings of PA doped PBI membranes have already been proposed [4]. In our research, we intend to find out the influence of other substitution groups instead of *m*-phenylene for membrane performances for example introducing diphenylether, or cross-linking. Also, we modified PA into fluoroalkyl-phosphonic acids (F-PA). The main reasons are as follows, first of all F-PAs are stronger acids than PA and alkylphosphonic acids which should promote proton hopping and transport. In addition, F-PA has weaker adsorption onto Pt which help to prevent electrocatalyst poisoning and promote higher oxygen reduction activity. Finally F-PA-based electrolytes can provide higher oxygen solubility than other phosphoric acid based electrolytes which should also promote higher oxygen reduction activity.

Experimental

Preparation of polybenzimidazole and Fluoroalkyl phosphate

We have succeeded in the preparation of high molecular weight polyphenylenebenzimidazoles by solution polycondensation of 3,3'-diaminobenzidine tetrahydrochloride with isophthalic acid,

terephthalic acid, or with their derivatives using polyphosphoric acid both as solvent and as condensing agent according to [Scheme 1]. 3,3'-diaminobenzidine tetrahydrochloride is dissolved in polyphosphoric acid at 140°C in a flask equipped with a stirrer under a thin stream of nitrogen. The aromatic carboxylic acid component is added to this solution and heating is continued with stirring. The reaction mixture develops a blue or violet fluorescence and gradually becomes viscous. After several hours, polyphenylenebenzimidazole is isolated as a yellowish to dark brown resinous mass by pouring the solution into water. The polymer mass is washed with alkaline water, and afterwards thoroughly with water and methanol, and dried. The yield is almost quantitative. Also, mono(trifluoroethyl) phosphate was synthesized according to [Scheme 2].



Fuel cell test

The membrane electrode assemblies (MEA) were prepared by stacking of a couple of catalyst/gas diffusion layer electrodes and PA doped PBI. The Current-Voltage (I-V) profile was measured using a fuel cell test station (Chino Co.) under flowing H₂ (100 ml/min)/Air (200 ml/min) gases for supplying to anode/cathode without humidifier at 150°C.

Results and discussion

The ionic conductivity of 85% H₃PO₄ doped membranes show 10⁻² Scm⁻¹ to 3x10⁻² Scm⁻¹ at 150°C. It is near to that from literature already published [3]. The polarization curves of the test cells using highly doped membranes at 150°C are shown in Figure 1. The membranes are doped with pure 85% H₃PO₄, mono(trifluoroethyl) phosphate 2%-added one and 5%-added one, respectively. From the graph, 2%-added electrolyte shows slightly higher cell voltage than others. It is quite likely that as mono(trifluoroethyl)phosphate is stronger acid than PA, so it promotes proton hopping, weaker adsorption onto Pt catalyst and higher oxygen solubility. However electrolytes more than 2% addition make cell voltage lower than without or 2%-added membranes also the exact reason is not known yet.

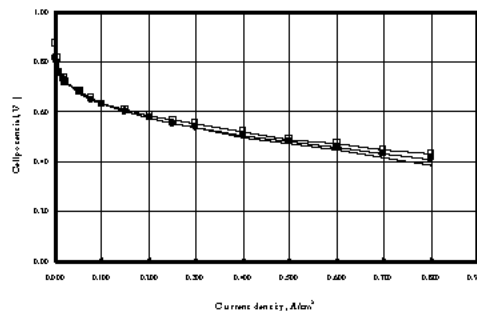


Figure 1. Polarization curves for test cells at 150°C in non-humidification. Gas utilizations were not considered

References

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