BLEND MEMBRANES FOR DIRECT METHANOL AND PROTON EXCHANGE MEMBRANE FUEL CELLS*

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Abstract Sulphonated polystyrene ethylene butylene polystyrene (SPSEBS) prepared with 35% sulphonation was found to be highly elastic and enlarged up to 300%−400% of its initial length. It absorbed over 110% of water by weight. A major drawback of this membrane is its poor mechanical properties which are not adequate for use as polymer electrolytes in fuel cells. To overcome this, SPSEBS was blended with poly(vinylidene fluoride) (PVDF), a hydrophobic polymer. The blend membranes showed better mechanical properties than the base polymer. The effect of PVDF content on water uptake, ion exchange capacity and proton conductivity of the blend membranes was investigated. This paper presents the results of recent studies applied to develop an optimized in-house membrane electrode assembly (MEA) preparation technique combining catalyst ink spraying and assembly hot pressing. Easy steps were chosen in this preparation technique in order to simplify the method, aiming at cost reduction. The open circuit voltage for the cell with SPSEBS is 0.980 V which is higher compared to that of the cell with Nafion 117 (0.790 V). From this study, it is concluded that a polymer electrolyte membrane suitable for proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) application can be obtained by blending SPSEBS and PVDF in appropriate proportions. The methanol permeability and selectivity showed a strong influence on DMFC performance.

Keywords: Fuel cell; Impedance; Polymer blend; Proton conductivity.

INTRODUCTION

A fuel cell is an electrochemical energy conversion device that combines a fuel (hydrogen, natural gas, methanol, gasoline etc.) with an oxidant (air or oxygen), and converts a fraction of their chemical energy into electrical energy[1]. Polymer electrolyte membranes (PEMs) are one of the key components for polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). Configuration of DMFC is almost the same as that of PEMFC, except for using different species of feeding fuel and catalyst. The performance of DMFC system is known to be lower than that of PEMFC due to its poor catalyst.

High proton conductivity electrolytes have attracted considerable attention, as they are the main components in polymer electrolyte membrane fuel cells (PEMFCs). They are environment friendly and efficient power sources for different applications. Commercially available Nafion membrane is a perfluorosulphonic acid polymer electrolyte membrane and the most commonly used electrolyte in PEMFC[2]. Though this membrane has high proton conductivity, good mechanical and chemical stabilities, its high methanol permeability and cost are the main obstacles in using it for DMFC applications.

There have been many investigations on the development of novel proton conducting membranes in order to substitute the perflourinated membrane. A reduction in methanol permeability was achieved by modifying the surface of the Nafion membrane with a film of poly(methyl pyrrole) by an electrochemical method[3, 4]. In

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another study, polyelectrolytes were prepared by swelling a ceramic added composite PVDF based membrane in a H₃PO₄ solution[5]. A novel Nafion/silica hybrid membrane suggested that the –OH on the surface of silica nano particles could enhance the hydrophilicity of clusters inside the membranes and improve the proton conductivity at elevated temperature[6]. PVDF grafted polystyrene sulfonic acid proton exchange membranes based on a radiation grafting technique showed higher proton conductivity and higher water uptake ability compared to Nafion membranes[7].

In the present study PSEBS was sulphonated separately to make it proton conducting. It exhibited good conductivity, flexibility and chemical stability but its mechanical properties were not adequate for direct application in fuel cell. Hence it was planned to blend SPSEBS with different proportions of PVDF which was reported to have high mechanical, particularly, tensile properties. As it has fluoro groups, it can get compatibilized, and can confer dimensional stability to other systems carrying hydrogen bonding groups. In this study the support SPSEBS membrane carries sulphonic acid groups, hence it can very well interact with PVDF by hydrogen bonding and can acquire dimensional stability[8].

EXPERIMENTAL

Materials
Polystyrene-block poly(ethylene butylene)-block-polystyrene (PSEBS, $M_w = 89000$) and poly(vinylidene fluoride) (PVDF) were purchased from Aldrich and used as received. Chlorosulphonic acid (CSA), tributylphosphate (TBP), tetrahydrofuran (THF) and chloroform were obtained from Spectrochem India, Lancaster, Merck and SRL, respectively.

Sulphonation of PSEBS
25 g of PSEBS was dissolved in few ml of chloroform with continuous stirring. Tributyl phosphate was added to it and the mixture was allowed to cool to 0°C in an ice bath. Chlorosulphonic acid was then added drop-wise over a period of time. After 3 h the reaction was terminated by adding a lower aliphatic alcohol. The sulphonated PSEBS was recovered after removing all the solvents by evaporation. The product was washed several times with water until neutral pH was obtained and then dried at 75°C for 24 h[9].

Preparation of Blend Membranes
The blend membranes were prepared by a solvent evaporation method. Initially, a desired amount of SPSEBS was dissolved in THF. PVDF was added to it in different proportions and the mixture was kept under vigorous stirring for 8 h to attain homogenization. The polymer solutions were then cast into clean and dry petridishes and the membranes formed by solvent evaporation technique. The weight percentage of blend membranes is given in Table 1. All the prepared membranes were treated with 3% H₂O₂ followed by 10% H₂SO₄ and finally washed with boiling water.

| Membrane code | Weight percentage (%) |
|---------------|-----------------------|
| PVDF-A        | 95:5                  |
| PVDF-B        | 90:10                 |
| PVDF-C        | 85:15                 |

Ion Exchange Capacity, Water and Methanol Uptake
Ion exchange capacity (IEC) depends on the number of sulphonic acid groups that are bonded to the membrane. The SPSEBS blend membrane was immersed in saturated potassium chloride solution over night to allow exchange of protons with K⁺ ions. The protons released from the membrane were neutralized by 0.005 mol/L sodium carbonate solution. Phenolphthalein was used as the indicator. The IEC was calculated using the following formula.