Materials Chemistry and Physics 164 (2015) 188–197

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Formation of semi-IPN membrane composed of crosslinked SPS-[PVdF-co-HFP/Nafion] for application in DMFC: A fine tuning between crosslinker and initiator

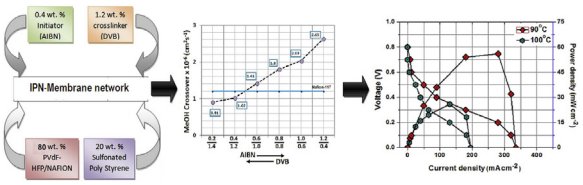
Piyush Kumar, Patit Paban Kundu*

Advanced Polymer Laboratory, Department of Polymer Science & Technology, University of Calcutta, 92, A. P. C. Road, Kolkata, 700 009, India

HIGHLIGHTS

- PEM composed of 0.4/1.2 wt% of AIBN/DVB produced best result.
- Lower methanol crossover (1.02×10^{-6} cm^2 s^{-1}) compare to Nafion-117.
- Higher membrane selectivity i.e 3.05×10^4 Ss cm^{-3} was obtained.
- A maximum power density of 56 mW cm^{-2} was obtained at 90 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 May 2015
Received in revised form
9 August 2015
Accepted 15 August 2015
Available online 29 August 2015

Keywords:
Polymers
Thin films
Chemical techniques
Electrochemical techniques
Electrochemical properties

ABSTRACT

The semi-interpenetrating (semi-IPN) membrane composed of crosslinked sulfonated polystyrene (SPS) within the host blend of PVdF-co-HFP (Polyvinylidenefluoride-co-hexafluoropropylene) and Nafion has already been tested as a promising polymer electrolyte membrane (PEM) in terms of improved water uptake, proton conductivity and electrical efficiency for application in the direct methanol fuel cell (DMFC). These desired results have generated further curiosity about a fine tuning between the contents of divinyl benzene (DVB) as a crosslinker and azobisisobutyronitrile (AIBN) as an initiator for the optimization of PEM characteristics. It has been observed that an increase in AIBN content leads to an acceptable degree of water uptake, swelling ratio and proton conductivity in PEM, while higher DVB content causes declined methanol crossover, leading to higher membrane selectivity. These two opposing effects are optimized in terms of proton conductivity, tensile strength and membrane selectivity for the membrane consisting of 0.4 wt% of AIBN and 1.2 wt% of DVB. Moreover, the maximum power density obtained for the membrane having optimum selectivity is 56 mW cm^{-2}, when analyzed at 90 °C. These results indicate that one can achieve a high power density in comparison to Nafion by fine tuning the contents of initiator and cross-linker during the synthesis of the semi-IPN membrane.

1. Introduction

Current research in the field of DMFC is focused on low-cost PEM fabrication with high membrane selectivity (i.e. higher proton conductivity and lower methanol permeability) as compared to Nafion-117 [1–10]. However, a bulk of these materials has to compromise either with high methanol crossover or low proton conductivity [11–15]. Therefore, attaining a balance between these two interrelated phenomena becomes quite crucial in order to optimize the productive performance of a DMFC.

The earlier investigation shows that the IPNs are capable of obtaining high proton/membrane selectivity by cautiously adjusting the structure and molar ratio of the two polymers [16–20]. For example, the semi-IPN membrane proposed by Prakash et al. [16]

* Corresponding author.
E-mail address: ppk923@yahoo.com (P.P. Kundu).

http://dx.doi.org/10.1016/j.matchemphys.2015.08.042
0254-0584/

composed of poly(styrene sulfonic acid) (PSSA) and poly(vinylidene fluoride) (PVDF) has shown about 50% reductions in methanol permeability as compared with Nafion-117. Li et al. [17] proposed a novel semi-interpenetrating polymer network (semi-IPN) membrane composed of Nafion-117 and cross-linked poly(vinyl pyrrolidone) (PVP). Under the optimal conditions, the semi-IPN membrane exhibited 53% lower methanol permeability as compared to Nafion117. Semi-IPN membranes based on Nafion® and cross-linked divinylbenzene (DVB) when prepared by coating, casting and dipping, exhibited reduced swelling properties and methanol permeability [18]. However, compared with Nafion, these IPNs had a better selectivity for water over methanol, but its proton conductivity decreased about an order of magnitude. Recently, the semi-IPN membrane prepared by incorporation of cross-linked sulfonated styrene (SS) within the blend of PVdF-co-HFP (Polyvinylidenefluoride-co-hexafluoropropylene)/Nafion, has shown acceptable results in terms of higher water uptake/swelling, proton conductivity and power density over pristine Nafion-117 membrane [19,20]. While possessing several advantages over Nafion-117, the semi-IPN membrane was found poor to serve solely as a highly selective PEM because of higher extent of methanol crossover.

In semi-IPN membrane, the methanol permeability can be controlled either by adjusting the ratio of the two polymers and or by the extent of crosslink density [16–23]. Since, the crosslink density directly affects the physiochemical properties of the semi-IPN membrane [21–23], an increase in cross-linker (DVB) content within the membrane can raise the crosslink density, while increment in initiator (AIBN) content results in the opposite [24–27]. These two opposing effects are investigated in this study for optimization of PEM performance in terms of lower methanol crossover and higher proton conductivity, leading to higher membrane selectivity. A number of tests have been executed such as water uptake, swelling ratio, XRD, crystallinity, proton conductivity and methanol crossover to accomplish the aim of fine tuning the content of crosslinker and initiator in the semi-IPN membrane. This fine tuning will help in achieving higher electrical efficiency (in terms of power density) of a single cell DMFC.

2. Experimental

2.1. Chemicals and instruments used

Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-*co*-HFP) (M_w = 455,000), sodium salt of sulfonated styrene (SS), Nafion® (5 wt% solution in a mixture of lower aliphatic alcohols and water, density: 0.924 kg m^{-3}) and azobisisobutyronitrile (AIBN) was obtained from Sigma Aldrich (USA). Dimethyl formamide (DMF) and divinyl benzene (DVB) were purchased from Merck Millipore, India. Nafion-117 membrane was obtained from M/S Anabond synergy India Pvt. Ltd. All chemicals were used as received.

2.2. Preparation of PEM

The membranes were prepared by following the two step procedure as explained in details in the previous articles [19,20]. Briefly, in the first step, PVdF-*co*-HFP pellets were dissolved in DMF with the subsequent drop wise addition of Nafion resin solution. The whole blend mixture was kept under continuous stirring at 80 °C for 2 h until a desired viscous solution was obtained. Finally, the resulting viscous solution was casted on a flat glass plate and kept in an oven at 80 °C overnight. In the second step, the obtained blend membrane was again re-dissolved in DMF and transferred into a three-necked round bottom flask, containing sodium salt of SS. After the addition of initiator (AIBN) and cross-linker (DVB), the resultant mixture was kept under continuous stirring to allow the *in situ* polymerization of SS in the blend of PVdF-co-HFP and Nafion. Finally, the obtained viscous solution was again casted and dried. A detail of chemical composition of different semi-IPN membranes are reported in Table 1. In addition, the chemical structure of the materials used for preparation of membrane along with a schematic of proposed structure for semi-IPN membrane is illustrated in Fig. 1(a) and (b), respectively.

2.3. Protonation and pretreatment of membrane

The protonation of a prepared membrane is an important step before serving it as a proton exchange membrane for the application in DMFC. All the prepared membranes were treated in a mixture of water and H_2SO_4 (50:50) for 24 h under continuous stirring. Furthermore, all the membranes were washed repeatedly until a neutral pH was obtained. Finally, they were dried in the oven. The pretreatment of Nafion-117 membrane was conducted by following the method as explained in the previous literature [28].

2.4. X-ray diffraction (XRD)

The XRD spectra of the membranes were measured by using Goniometer. The entire sample was tested at 2θ angle within the range of 10–40°. The scan rate of 1° min^{-1} was fixed for the entire test. The percentage of crystallinity and the inter-chain separation as R-value (present within the amorphous regions of the samples), was calculated by using Eqs. (1) and (2), respectively.

$$\text{Crystallinity} = \frac{A_{Crystalline}}{A_{Total}} \times 100 \quad (1)$$

where $A_{crystalline}$ represents the area of the crystalline regions and A_{Total} represents the total area under the peak.

$$R = 5\lambda/(8\ sin\theta) \quad (2)$$

where λ is the wavelength and θ is the Bragg angle.

2.5. DSC

Differential scanning calorimetry (DSC, Mettler Star SW 9.01) was used to analyze the effect of variation of the contents of crosslinker and initiator on the thermal behaviour of prepared membranes. Prior to the DSC measurements, the membranes were dried at 80 °C in a vacuum oven for 1 day. The entire test was conducted by putting the sample in a crimpled aluminium pan and under nitrogen atmosphere. For proper analysis, the specimen weight was kept constant (i.e. 5.0 ± 0.1 mg) for the entire test. A constant heating rate of 10 °C min^{-1} was employed in a temperature range of 30–250 °C.

Table 1
Variation in the ratio of AIBN/DVB in semi-IPN membrane[a].

SL. No.	Samples	AIBN (wt% of SS)	DVB (wt% of SS)
1.	A-20	0.2	1.4
2.	B-20	0.4	1.2
3.	C-20	0.6	1.0
4.	D-20	0.8	0.8
5.	E-20	1.0	0.6
6.	F-20	1.2	0.4

[a] Membrane composed of 64 wt% of PVdF-HFP, 16 wt% of Nafion and 20 wt% of SS.