Methanol crossover of Nafion-clay-heteropolyacid nanocomposite membranes for direct methanol fuel cell applications

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Abstract

Nafion-cesium salt of heteropolyacid- proton exchange membrane containing clay was prepared via solution casting method for direct methanol fuel cell applications. The XRD analysis was conducted to characterize the nanocomposite membrane structure. Methanol crossover through polymer electrolyte membranes is a critical issue and causes an important reduction of performance in direct methanol fuel cells. In this work cesium hydrogen salt of heteropolyacid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) are incorporated into K10 type of montmorillonite in an effort to improve the selectivity of Nafion membrane**.** Methanol permeability of casted membranes was measured by refractive index method. Results show all composite membranes have lower methanol permeability than the recast Nafion membrane. The lowest methanol permeability of the developed membranes in this study was 16.51×10^{-7} cm^2S^{-1} which was lower than recast Nafion membrane.

Keywords: Nafion-nanocomposite-heteropolyacid-direct methanol fuel cell-permeability.

Introduction

Direct methanol fuel cells (DMFCs) are promising candidates to replace existing batteries as power generators in portable devices. Easy refueling and high energy storage capacity are their main advantages [1]. It is known that perfluorosulfonic polymers, such as Nafion®, are the most commonly used proton conductors in membranes for fuel cells due to their good mechanical and chemical properties, thermal stability, and high protonic conductivity [2]. However, Nafion faces several drawbacks which limit its industrial applications. The key problem for Nafion use in DMFC is the high methanol crossover which allows methanol diffusivity of 1.0×10^{-6} cm^2 s^{-1} even at room temperature [3]. Several attempts have been made to reduce methanol permeability without sacrificing too much proton conductivity by using silane agent [4]. In this work cesium hydrogen salt of heteropolyacid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) are incorporated into K10 type of montmorillonite in an effort to improve the selectivity of Nafion membrane.

Experimental

Nafion resins (DuPont), N,N-Dimethylformamide, (Merck), montmorillonite K10 fillers (Aldrich), tungstophosphoric acid hydrate (Merck) and cesium carbonate (Merck) were used. Cesium hydrogen salt of heteropolyacid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) hereafter CsHPs, was prepared by precipitation titration [10]. Membranes were prepared by recast procedure. The Nafion resins were solved in DMF under 90°C to reach 5% wt. nafion solution. CsHP and MMT was dispersed in DMF with stirring then added to Nafion 5 % wt. solution and sonicated for 30 minute and then cast on the petridish to obtain the membrane films. The X-ray diffraction (XRD) analysis was performed for investigation of nanocomposite membrane structure. Methanol permeability measurements were conducted by using a diffusion cell. In this diffusion cell the concentration of alcohol diffused from compartment A to B across the different membranes was examined with time by Refractive Index method using (ATAGO's Abbe Refractometer). The sample formulations prepared are shown in Table 1.

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Table 1. Sample formulation of different type of membranes

Membrane Sample	MMT (% wt.)	CsHP (% wt.)
Membrane 1	0	8
Membrane 2	2.5	0
Membrane 3	2.5	8
Membrane 4	1.25	12
Membrane 5	3.75	4
Membrane 6	5	0
Membrane 7	0	16
Membrane 8	0	0

Results and Discussion

XRD patterns in Fig. 1 show that the original MMT K10 reveals the presence of a peak at 2θ=6.86° from Bragg's law, which its interlayer distance is estimated to be 1.29 nm. In the most of nanocomposite membranes this characterization peak shifted to lower 2θ angles. It means that intercalated nanocomposite structure was formed and introduction of ionomer into the interlayer of CsHP-MMT layers and destroyed the stack of layers. The methanol permeability of the membranes was calculated using following Equation:

$$C_B(t) = \frac{A}{V}\frac{DK}{L}C_A(t - t_0)$$

where C is the alcohol concentration, A and L are the polymer membrane area and thickness; D and K are the alcohol diffusivity and partition coefficient between the membrane and the solution. The product DK is the membrane permeability (P), to, also termed time lag, is related to the diffusivity: to=L2/6D. The methanol permeability of different membranes is presented in Table 2.

Table 2. The methanol permeability of different membranes

Membrane Sample	Methanol Permeability ($\times 10^{-7}$ cm^2/s)
Membrane 1	17.75
Membrane 2	16.09
Membrane 3	16.51
Membrane 4	19.25
Membrane 5	15.83
Membrane 6	13.52
Membrane 7	20.45
Membrane 8	20.78

High methanol permeability in Nafion is attributed to its larger hydrophilic channels formed by sulfonic acid groups in the hydrated phase [13]. All the composite membranes have lower methanol permeability than the Nafion membrane. The Nafion/MMT and Nafion/CsHP/MMT nanocomposite membranes have lower methanol permeability than Nafion membrane because of the presence of MMT which affects the microstructure of hydrophilic domain and obstructs the connected hydrophilic channels, resulting in lower methanol crossover through a longer diffusive pathway [7].

Conclusions

Cesium hydrogen salt of heteropolyacid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) is incorporated into K10 type of montmorillonite and the nanocomposite Nafion membranes were prepared for DMFC applications. XRD patterns of different types of prepared nanocomposites membranes showed the intercalated structure was formed and introduction of ionomer into the interlayer of CsHP-MMT layers and destroyed the stack of layers. The developed intercalated Nafion membranes have successfully improved the membrane barrier properties due to the unique feature of MMT which contributed to the formation of a longer pathway towards methanol across the membrane. The methanol permeability was significantly reduced by the incorporation of MMT and CsHP in the Nafion membrane.

References

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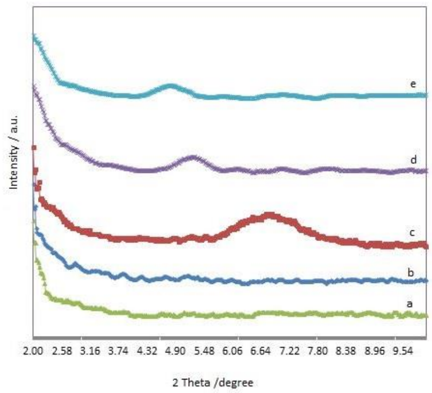

Fig.1. XRD patterns of OMMT and PS nanocomposites