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Proton-conducting PVA/PMA Hybrid Membranes for Fuel Cell Applications

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***Abstract*—**The hybrid membranes containing inorganic materials in polymer matrix are identified as a remarkable family of proton conducting hybrid electrolytes. In this work, the proton conducting inorganic/organic hybrid membranes for proton exchange membrane fuel cells (PEMFCs) were prepared using polyvinyl alcohol (PVA), tetraethoxyorthosilane (TEOS) and heteropolyacid (HPA). The synthesized hybrid membranes were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD), Scanning electron microscopy (SEM) and Thermogravimetry analysis (TGA). The effects of heteropolyacid incorporation on membrane properties, including morphology and thermal stability were extensively investigated.

***Keywords*—**PEMFC; Hybrid membrane; FTIR; TGA; Phosphomolybdic acid

I. INTRODUCTION

HYBRID composite membranes incorporating an inorganic/organic component are receiving much attention as promising proton conducting electrolytes for fl cells. In recent years, proton conducting inorganic/organic hybrid materials of high performance has attracted much attention of scientists, and many works have been carried out [1]. Proton exchange membrane (PEM) is one of the critical components in PEMFCs. The preparation of hybrid organic/inorganic composites has attracted much attention because such hybrids may show controllable physical properties, such as optical, electrical, and mechanical behaviors, by combining the properties of both organic polymers and inorganic compounds [2], [3]. In these organic/inorganic hybrids, the inorganic minerals precipitate in situ in a regular manner in the organic polymer matrix, and a strong interaction between the organic polymer and inorganic mineral is expected to result in a hybrid with markedly improved mechanical properties [4]. The starting materials for the sol-gel process are the corresponding metal alkoxides, along with a small concentration of acid or base as a catalyst. Hybrids are usually prepared using the sol-gel process by incorporating organic polymers containing alkoxysilanes (usually tetramethoxysilane, TMOS or tetraethoxysilane, TEOS) [5].

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In recent years, attention has been focused on the preparation of organic/inorganic composite membranes through sol-gel processes [6] and [7] for PEMFC due to their promising opportunity in enhanced mechanical and thermal properties and reduced methanol permeability with appreciable conductivity. The thermal stability is provided by the inorganic backbone, while the organic chains confer the required specific properties such as flexibility, processibility, and so on.

In the recent literature, a new class of hybrid composites consisting of SiO_2/polymer [polyethylene oxide (PEO); polypropylene oxide (PPO); polytetramethylene oxide (PTMO)] with urethane linking structure through sol-gel reactions has been reported [8]-[10]. The hybrid membranes become proton conducting by doping with acidic moieties such as monododecylphosphate (MDP) or 12-phodphotungstic acid (PWA).

Polyvinyl alcohol (PVA) seems to be very attractive material for preparing PEM because this polymer can function as an excellent methanol barrier [11]. As well known, PVA also has both excellent mechanical property and chemical stability which are adequate for preparing PEMs [12]. Recently, Rhim et al. reported the preparation of PEMs employing PVA as a base material [13]. In addition, Kim et al. demonstrated that the PVA/SSA/silica hybrid membranes prepared via a sol-gel process possess low methanol permeability (i.e. 10^{-8} to 10^{-7} cm^2 s^{-1}) as well as excellent proton conductivity [14]. Moreover, the degree of crosslinking of the PVA-based membranes was shown to be very easy to control via successive thermal and chemical treatments [15]-[18].

HPAs with the Keggin structure constitute the most extensively studied and important class of polyoxometalates. Certain proton conductors, such as HPAs and protonic acids, become dehydrated or thermally decomposed at medium-ranged temperatures and relatively low humidity, whereas the thermal stability of an HPA can be improved by incorporating it into a modified silica matrix under high humidity [8]. The PMA riches phases in the hybrid membrane form continuous ionic conducting pathways and subsequently give high ionic conductivity. Many heteropoly compounds have very high solubility in polar solvents and fairly high thermal stability in the solid state. The results suggest that the obtained membrane shows good thermal stability, excellent mechanical property and high ionic conductivity, and the low-cost hybrid membrane can be a promising candidate for low/intermediate temperature fuel cell systems.

The aim of this study was to prepare membranes for possible use in a PEMFC. To do this, PVA/SiO_2 hybrid membranes

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containing heteropoly acid groups were synthesized using the sol-gel process. In this case, a new inorganic/organic hybrid proton conducting membrane based on PMA and PVA-SiO_2 particles was prepared. PVA is a basic polymer which has good film-forming capacity, thermal stability, and mechanical property [19], [20]. The use of PVA as proton-conducting membrane is well known [21]; however, PVA is a poor proton conductor [22]. In addition, silica particles were dispersed into the polymer matrix via the sol-gel reaction under acidic conditions, which were expected to provide a barrier to methanol transport. The PVA-SiO_2 particles were synthesized through acid catalyzed hydrolysis and condensation reactions. The membranes were characterized for their mechanical, structural, morphological, and thermal properties by employing X-ray diffraction, Fourier transform infrared (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA), respectively. In these membranes, PVA acts as the proton source and PMA act as the proton solvent.

II. EXPERIMENTAL

Inorganic/organic hybrids using the PVA and sol-gel derived silica were prepared by dissolving PVA in water followed by the addition of a TEOS mixture to the solution. The TEOS mixture was prepared by mixing H_2O, 1M.HCl, and TEOS in the molar ratio, which was stirred at room temperature for 1 h. 5 wt.% PVA solutions were prepared by dissolving dry PVA in water and then stirring at 80 °C for 2 h. PMA was dissolved in distilled water. Then, the PVA/TEOS solutions were mixed together along with PMA solution for each composition, and the mixture was stirred at room temperature for 6 h. The solutions were then poured onto a glass plate, and allowed to dry in air at room temperature. The fully dried membranes were peeled away from the glass plate, and then heated at 100 °C for 2 h to induce the crosslinking reaction.

X-ray diffraction (XRD) patterns were recorded by collecting the reflected scans of nickel-filtered Cu Kα radiation using a Rigaku multiflex (Rigaku, Japan). X-ray diffraction-generated at 2 KW and 20 mA at a scan rate of 5°/min; the range of the diffraction angle 2θ was 10-60°. FTIR measurements of the polymer membranes were performed on pellets using a JASCO FTIR-460 spectrometer (spectral range 4000-400 cm^{-1}, 50 scans, and a resolution of 2 cm^{-1}). The degradation process and the thermal stability of the membranes were investigated using thermogravimetry TGA instrument. Thermogravimetric analysis (TGA) of the hybrid membrane was carried out with a DTG-50, Shimadzu instrument, simultaneous DTA-TG was conducted in the range from room temperature to 800 °C in air at a heating rate of 10 °C/min. To investigate the morphology of the membranes, Scanning electron microscopy (SEM) images were collected with a variable pressure Scanning Electron Microscope Hitachi S-3500N using an accelerating voltage of 20 kV.

III. RESULTS AND DISCUSSION

In general, when a polymer contains a crystalline region, then the X-ray diffraction peaks are sharp, and their intensities are high, whereas for an amorphous polymer they are broad [23]. According to the X-ray diffraction measurements shown in Fig. 1, the peak occurring at 2θ = 24°. However, for the PVA/SiO_2/PMA membranes, the hydroxyl groups of the PVA molecules had reacted with the silica and PMA, and the number of hydroxyl groups, therefore, decreased, resulting in a decrease in crystallinity [24].

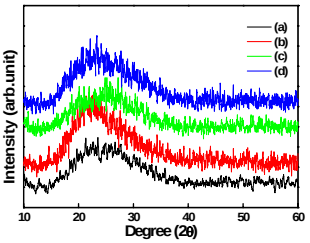


Fig. 1 XRD curves for the PVA/SiO_2-PMA hybrid composites: (a) 5/50-45, (b) 5/55-40, (c) 5/60-35 and (d) 5/65-30.

The FT-IR spectra of the hybrid membranes with various PMA concentrations were prepared by sol-gel method. They hybrid membranes show several characteristic peaks in the wave number range from 400 to 1200 cm^{-1} as shown in Fig. 2. They can be assigned to the Si-O-Si and Si-O- stretching vibrations. The peaks at 450, 548, 566, 667, 804, 969, 1073, 11190, 1208, 1231, 1426, 1441, 1631, 1660, 2931, 3428 and 3456 cm^{-1} indicate the incorporation of HPAs into the nanocomposites. The broad bands occur at around 1050-1231 cm^{-1} (characteristic of Si-O-Si asymmetric stretching) were observed in the spectra of the PVA-SiO_2-PMA hybrid membrane. This indicates that the desertification reaction was complete between the PVA chains and the PMA, and that the hybridization was successfully achieved by the sol-gel reaction. We suppose that these -OH groups provide the sites for hydrogen bonding between the polymer and water, because the silica nanoparticles were observed to retain water, even at high temperatures [25]. In addition there are several strong bands below 1070 cm^{-1} due to polyoxometalates. IR studies have been mostly concerned with Keggin acids and their salts and have been used for elucidating structural relationships between heteropolyanions. IR absorption peaks at 1073 cm^{-1} (Si-O-C) and (Si-O-Si), 1631 and 801 cm^{-1} indicates the development of an organic/inorganic hybrid network during the gel formation.

Thermogravimetric analysis (TGA) curves of different hybrid membranes were recorded in air at a heating rate 10 °C/min, and representing curves are displayed in Fig. 3. All the composite membranes exhibited nearly the similar type of TGA profiles. The TGA curve of the membranes was fitted using two main degradation stages arising from the processes of thermooxidation of the polymer/silica matrix. The first weight loss occurred at temperatures about 150 °C, and was associated with the loss of absorbed water molecules, or from water molecules formed after the etherification reaction of the membranes.

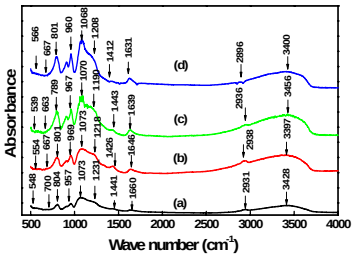


Fig. 2 Infrared absorption spectra of PVA/SiO_2-PMA hybrid composites: (a) 5/50-45, (b) 5/55-40, (c) 5/60-35 and (d) 5/65-30

Most of the absorbed water molecules in the membranes are supposed to exist in a bound state, rather than in the free molecular state [26]. In the second weight loss region (at temperature ~ 200 °C), the polymer residues were degraded at T = ~ 200 °C, which corresponds to the decomposition of the main chains of the PVA. In the case of the hybrid composite membranes, the weight remaining after the polymer decomposition depended on the content of the inorganic component and the degree of crosslinking. These results suggest that the degree of crosslinking and the introduction of silica/heteropolyacid into the PVA chains enhance the thermal stability of the given hybrid materials. This improvement can be attributed to the thermal stability of the inorganic silica networks and the formation of cross-linkages among the hydroxyl groups such as Si–OH, P–OH, and C–OH. It is seen from TG curves that the hybrid membrane begins degradation at 200 °C, which indicates its good thermal stability.

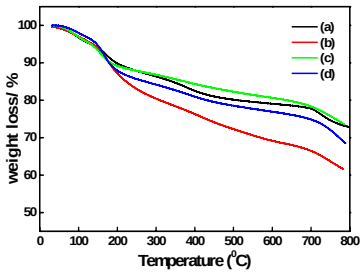


Fig. 3 TGA curves for the PVA/SiO_2-PMA hybrid composites: (a) 5/50-45, (b) 5/55-40, (c) 5/60-35 and (d) 5/65-30

Fig. 4 shows the SEM images of the PVA-SiO_2-PMA hybrid membranes, showing the silica particles that were observed. The presence of the silica particles was confirmed using energy-dispersive X-ray analysis (XRD). We noted that the silica particles were embedded in PVA/PMA matrix, and that this could be expected to reduce the methanol permeability. A uniform distribution of HPA particles into PVA matrix can be seen in the SEM.

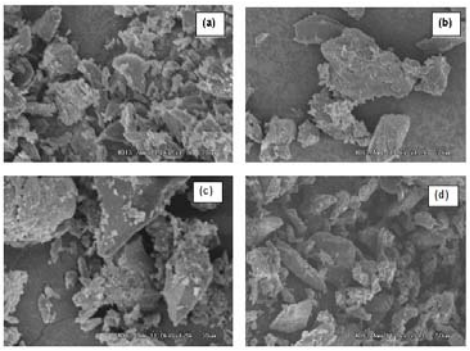


Fig. 4 SEM images of PVA/SiO_2-PMA hybrid composites: (a) 5/50-45, (b) 5/55-40, (c) 5/60-35 and (d) 5/65-30

IV. Conclusion

All results in this work suggest that the low-cost hybrid membrane, quite good mechanical property and high thermal stability can be a promising candidate for low temperature PEMFC applications. From the thermal analysis, it was found that the presence of SiO_2 network was responsible for the higher thermal stability of these hybrid membranes. SEM photograph showed a novel microstructure and it was found that PMA-silica particles were distributed in PVA matrix homogeneously. Further search on fuel cell performance of these hybrid membranes is currently under way and will be reported soon.

Acknowledgment

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