Materials Letters 72 (2012) 81–87

Contents lists available at SciVerse ScienceDirect

Materials Letters

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

Synthesis of organic/inorganic hybrid composite membranes and their structural and conductivity properties

Uma Thanganathan [a,*], Suresh Kumar [a], Akira Kishimoto [b], Kunio Kimura [c]

[a] Research Core for Interdisciplinary Sciences (RCIS), Okayama University, Tsushima-Naka, Kita-Ku, Okayama 700-8530, Japan
[b] Graduate School of Natural Science of Technology, Division of Chemistry and Biochemistry, Okayama University, Tsushima-Naka, Kita-Ku, Okayama 700-8530, Japan
[c] Graduate School of Environmental Science, Okayama University, Tsushima-Naka, Kita-Ku, Okayama 700-8530, Japan

ARTICLE INFO

Article history:
Received 28 October 2011
Accepted 14 December 2011
Available online 21 December 2011

Keywords:
Phosphomolybdic acid
Polyvinyl alcohol
Sol–gel
Hybrid composite
Conductivity

ABSTRACT

The present article describes the use of a less expensive non-perfluorinated polymer (polyvinyl alcohol, PVA), heteropolyacid (HPA), glutaraldehyde and 3-aminopropyltriethoxysilane (APTES) for the formation of high proton-conducting hybrid composite membranes. The conductivity of the PVA/PMA/Gl/APTES hybrid composite membranes was measured under varying conditions of temperature (from −20 °C to 140 °C) and relative humidity (from 30 to 90%). Conductivity values in the range of 10^{-3}–10^{-1} S cm^{-1} were obtained for the hybrid membranes. These free-standing flexible films were mechanically stable and the corresponding composite membranes were thermally stable up to 300 °C. Their swelling ratio was calculated for dry and wet conditions at room temperature.

1. Introduction

Fuel cells are attractive since they provide an innovative alternative to current power sources with higher efficiencies, renewable fuels, and a lower environmental cost. They can operate at relatively low temperatures and offer numerous benefits, such as high efficiency, high power density and low-polluting emissions [1]. The reason that Nafion® is the principal material used as a polymeric electrolyte is because of its excellent chemical and mechanical stabilities, and high proton conductivity. However, Nafion® and similar perfluorinated polymers have relevant drawbacks, including a high methanol permeability, a decrease in conductivity at high temperatures ($T = 80$ °C) and an elevated cost [2,3].

Developing organic–inorganic hybrid membranes may provide a solution that will satisfy the requirements of an unchanged imprinted cavity and good film-forming properties. Hybrid membranes have shown extraordinary properties in pervaporative separation with improved physical and mechanical properties arising from the synergism of the two kinds of building blocks [4,5]. PVA is one of the most important materials for the dehydration of organic mixtures owing to its good chemical stability, film-forming ability, and high hydrophilicity [6,7].

In this study, APTES was mixed with PVA membranes via a sol–gel reaction with the aim to enhance their stability, proton conductivity and electrochemical properties. These new classes of hybrid PVA-based membranes were expected to exhibit a high conductivity and mechanical stability in aqueous medium. Since the ammonium group on the –OH moiety in the PVA chains functioned as an electron acceptor and the amino acid group on the APTES was an electron donor, both groups helped to self-organize the molecules in aqueous solution. This was believed to lead to the formation of a specific self-assembly structure in the hybrid membranes [8].

Moreover, organic/inorganic hybrids have been prepared based on heteropoly compounds [9–13]. The chemical reactions involved in forming PVA membranes using glutaraldehyde have been reported by Purss et al. [14]. The objective of this work was to use a sol–gel reaction to design novel organic–inorganic hybrid composite membranes via the hybridization of PVA/PMA and APTES as a precursor with glutaraldehyde. The current work thus investigated hybrid composite membrane networks with a PVA/PMA/Gl/APTES structure as well as the effect of the crosslinker. Hybrid composite membranes were successfully obtained for use in fuel cell electrolytes at low/intermediate temperatures.

2. Experimental techniques

2.1. Materials

Poly(vinyl alcohol) with a molecular weight of 100,000 g/mol was supplied by Nacalai Tesque, Japan. Phosphomolybdic acid (PMA, Chameleon Reagent, Japan) and glutaraldehyde (Gl, Nacalai tesque) were used as received. 3-aminopropyltriethoxysilane (APTES) was

---

* Corresponding author. Tel.: +81 86 251 8706; fax: +81 86 251 8705.
E-mail address: umthan09@cc.okayama-u.ac.jp (U. Thanganathan).

0167-577X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2011.12.066

obtained from Nacalai tesque, Japan. Nafion® perfluorinated ion-exchange resin (Aldrich, 5 wt.% solution in lower aliphatic alcohols/H_2O mix, 15–20% water), polytetrafluoroethylene (PTFE, Aldrich, 60 wt.% dispersion in water), isoprophyl alcohol (2-propanol, Chameleon reagent), Pt/C powder (EC-40-PTC, 40 wt.% Pt/VXC72, Toyo, Japan), and carbon paper (EC-TP1-060T, Toyo, Electro Chem. Inc.) and other chemicals were all used as received.

2.2. Preparation of membranes

A new class of inorganic/organic hybrid membranes were fabricated by blending of PVA, PMA and APTES followed by crosslinking with glutaraldehyde. The clear PVA solution was prepared by dissolving PVA in deionized water at 90 °C under stirring for 5 h. The hot solution was cooled to room temperature. A particular amount of PMA was dissolved in deionized water rendering a clear yellow solution. The PVA and PMA solutions were mixed together and stirred continuously at room temperature for 6 h. Subsequently, APTES was added to the mixture and vigorously stirred for 5 h. Glutaraldehyde was charged as a crosslinking agent. The mixed solution was stirred for another 24 h. The obtained homogeneous solution was poured onto Petri dishes and left to dry at room temperature for a few days. The dried membranes were removed from the Petri dishes and heated at 120 °C for 6 h. By varying the compositions of PMA, APTES and Gl, three types of composite membranes were obtained (Table 1). The composite membranes were transparent with a bluish and yellowish hue, and the films were mechanically stable and self-standing with thicknesses of 0.5–1.2 mm.

2.3. Characterization

X-ray diffraction measurements were performed on an X-ray diffraction spectroscopy (Rigaku, multiflex, Japan). All the measurements were performed at room temperature at an angular 2θ between 10 and 60° with CuKα radiation generated at 2 kW and 20 mA at a scan rate of 2°/min. The Fourier transform infrared (FTIR) spectroscopic measurements (JASCO FTIR-460 spectrometer) for the hybrid membranes were made in the wave-number range 400–4000 cm^{-1} at room temperature. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermogravimetric analyzer and differential thermal analysis was carried out on a DTG-50 from Shimadzu Instruments as simultaneous DTA–TG instrument from room temperature to 600 °C in nitrogen at a heating rate of 10 °C/min. The surface morphology and the cross-section microstructure was examined by a Hitachi S-2600H scanning electron microscope. The swelling ratio of the membrane was calculated by the mass of the swollen wet membrane divided by its dry counterpart. Impedance measurements were performed using a Solartron SI 1260 impedance/gain phase analyzer which was interfaced to a computer. The experimental setup consisted of a conductivity cell placed in an ESPEC temperature and humidity chamber SH-221, a bench-top type environmental chamber where the temperature, humidity and moisture could be controlled. Impedance spectra were recorded between 1 Hz and 1 MHz with a voltage amplitude of 10 mV.

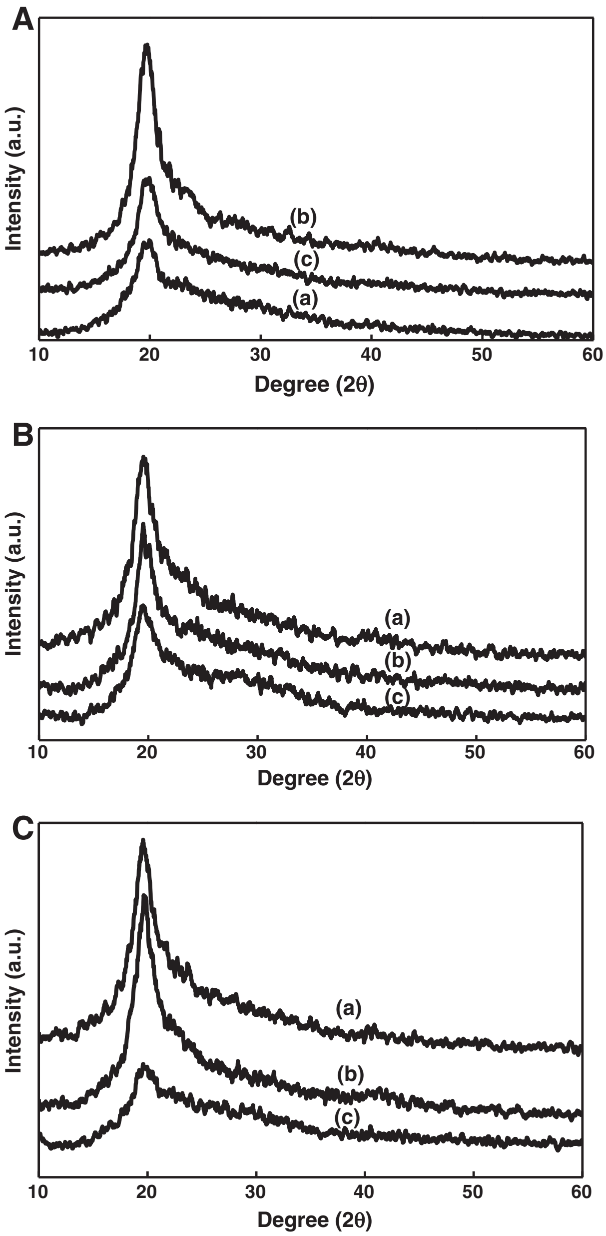

Fig. 1. XRD graphs for the PVA–PMA/Gl/APTES composite membranes (Ref. Table 1).

Table 1
The proton conductivity and swelling properties of the PVA/PMA/Gl/APTES hybrid composite membranes.

No	PVA/PMA/Gl/APTES composite membranes (ratios)	Swelling ratio (%)	Proton conductivity (S cm^{-1})	
			−20–140 °C (A)	30–90% (B)
A	(a) 80 wt.%–2/13/5 (mol%)	98	6.4×10^{-3}–1.1×10^{-2}	6.7×10^{-3}–1.0×10^{-2}
	(b) 80 wt.%–2/8/10 (mol%)	72	4.8×10^{-3}–7.1×10^{-3}	5.3×10^{-3}–1.2×10^{-2}
	(c) 80 wt.%–2/3/15 (mol%)	112	7.1×10^{-3}–1.4×10^{-2}	1.1×10^{-2}–2.1×10^{-2}
B	(a) 80 wt.%–5/13/2 (mol%)	121	7.4×10^{-2}–2.6×10^{-2}	9.3×10^{-3}–1.7×10^{-2}
	(b) 80 wt.%–10/8/2 (mol%)	135	1.9×10^{-2}–5.1×10^{-2}	1.3×10^{-2}–1.9×10^{-2}
	(c) 80 wt.%–15/3/2 (mol%)	156	1.3×10^{-2}–2.3×10^{-2}	1.7×10^{-2}–2.8×10^{-2}
C	(a) 80 wt.%–2/5/13 (mol%)	146	1.2×10^{-2}–1.9×10^{-2}	1.5×10^{-2}–3.7×10^{-2}
	(b) 80 wt.%–2/10/8 (mol%)	179	9.5×10^{-3}–2.3×10^{-2}	4.0×10^{-2}–1.4×10^{-1}
	(c) 80 wt.%–2/15/3 (mol%)	121	5.7×10^{-3}–2.1×10^{-2}	1.6×10^{-2}–3.4×10^{-2}