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ORIGINAL PAPER

Nanocomposite hybrid membranes containing polyvinyl alcohol or poly(tetramethylene oxide) for fuel cell applications

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Abstract New hybrid membranes containing polyvinyl alcohol (PVA) and poly(tetramethylene oxide) (PTMO) with heteropolyacid (HPA) as a hydrophilic inorganic modifier in an organic/inorganic matrix were developed for low-temperature proton exchange membrane fuel cells (PEMFCs). A maximum conductivity of 4.8×10^{-3} S cm^{-1} was obtained at 80 °C and 75% RH for PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%), whereas the PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) membrane demonstrated a maximum conductivity of 8.5×10^{-3} S cm^{-1} under identical conditions. These hybrid composite membranes were subsequently tested in a fuel cell. A maximum current density of 240 mA cm^{-2} was produced at 70 °C for the PVA/PWA/PTMO/H_3PO_4 membrane, and the corresponding value for the PVA/SiWA/MPTS/H_3PO_4 membrane under identical conditions was 230 mA cm^{-2}. The small deviations in cell performance can be explained in terms of the variations in thickness of the membranes as well as differences in their conductivities. The fuel cell performances of these membranes decreased drastically when the temperature was increased to 100 °C.

Keywords Heteropolyacid · Poly(vinylalcohol) · Ionic conductivity · Current density · PEMFCs

1 Introduction

Fuel cells are expected to become one of the key technologies of the twenty-first century, both for stationary applications, such as block power stations, and in stationary and portable devices including personal vehicles, trucks, buses, and locomotives. The reason for the expected success is that fuel efficiency in fuel cell engines is markedly higher than in their combustion counterparts. The proton exchange membrane fuel cell (PEMFC) is a low-temperature fuel cell expected to be commercialized for stationary power and transportation applications [1, 2]. PEMFCs, including direct methanol fuel cells (DMFCs), rely on the reduction of oxygen at the cathode and the oxidation of hydrogen or organic fuels at the anode. Direct methanol fuel cells (DMFCs) can be used as power sources not only for vehicles (i.e. large scale) but also for portable electronic devices (i.e. small scale) [3, 4]. For the above applications, numerous kinds of proton exchange membranes have been developed. Hence, the development of novel electrolytes plays an important role for future PEMFCs. Requirements include new polymer electrolyte membranes with a high proton conductivity, a low reactant permeability, and a reduced water uptake [5, 6].

The incorporation of other inorganic species in the hybrid materials can be used to control the chemical and physical properties, and makes it possible to expand the application field. In hybrid organic–inorganic membranes, one associates an inorganic part, usually offering good mechanical and thermal stability, with an organic functional group or compound presenting a specific chemical reactivity [7]. The present study has been devoted to the proton-conducting properties of such organic–inorganic nano-composite materials for application in PEMFCs.

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Heteropolyacids (HPAs) are strong Brønstic acids as well as solid electrolytes [8]. However, HPAs are generally water soluble and may leach out of the membrane, which would give declining cell performances. Li and Wang [9, 10] have prepared proton-conducting membranes based on PVA with embedded phosphotungstic acid (PWA) and found that the water uptake, proton conductivity, and methanol permeability increased with the PWA content. In order to improve the reagent endurance and thermal stability of PVA/PWA membranes, SiO_2 was added [11]. Most of the previous studies on PVA/PWA composite membranes have mainly been dedicated to the aspects related to preparation and transport properties but none of them have focused on the fabrication of membrane-electrode-assemblies (MEA) or on fuel cell tests. PVA has very good mechanical properties and chemical stability, which render it suitable for preparing PEMFCs [12]. However, PVA membranes are poor proton conductors, and several methods have, therefore, been proposed to prepare PVA-based proton-conducting membranes with high proton conductivities for fuel cell applications [13–15]. Recently, some researchers [16, 17] have used poly(vinyl pyrrolidone)/PVA polymer blends, and have stated that the PVP polymer employed in the membrane can efficiently improve the oxidative stability and mechanical properties. Moreover, PVA membranes doped with H_3PO_2 or H_3PO_4 have been prepared [18–20]. Li et al. [10] also fabricated PVA membranes doped with phosphotungstic acid (PWA) with a dimethylsulfonoxide (DMSO) reagent; however, these membranes swelled too much to be used. Furthermore, Deng et al. [21] found that the incorporation of silica in PVA membranes could improve their thermal stability.

Honma et al. [22] have studied organic/inorganic nanocomposite membranes consisting of SiO_2/polymer: polyethylene oxides (PEO); polypropylene oxide (PPO); and polytetramethylene oxide (PTMO). They reported that the hybrid membrane was more stable than its Nafion counterpart at temperatures higher than 100 °C. Moreover, protonic conductivities of 10^{-4}–10^{-3} S cm^{-1} at 160 °C were achieved at 100% relative humidity. Also Honma et al. demonstrated that the maximum proton conductivities for a zirconium phosphate–PTMO membrane and a titania–PTMO–40 wt% PWA hybrid were 2×10^{-3} and 8×10^{-2} S cm^{-1}, respectively, under saturated humidity conditions up to 150 °C [23]. The maximum power densities for zirconium phosphate–PTMO and titania–PTMO–PWA composite membranes were 13 and 30 mW/cm^2, respectively.

Nevertheless, to the best of our knowledge, no previous studies have been devoted to the properties of PVA blended with PTMO and the performances of single cells made from such membranes. PTMO is one of the most interesting chain molecules to explore with regard to its spatial configurations in the random-coil state. Additionally, PTMO is a hydrophobic molecule, and consequently hydrated protons have only weak interactions with the PTMO polymer, resulting in a strengthening of the polymer. In the present investigation, two membrane-electrode-assemblies were prepared in order to be evaluated in fuel cell tests and the observed performances were reported.

2 Experimental section

2.1 Materials

The following chemicals were used: poly(vinyl alcohol), with an average molecular weight of 80,000 g mol^{-1} and a degree of alcoholysis of 99%; polytetramethylene oxide with a molecular weight of 1,000 g mol^{-1}; phosphotungstic acid ($H_3PW_{12}O_{40}29H_2O$, PWA); silicotungstic acid (SiWA, Chameleon Reagent); H_3PO_4 (Wako, reagent grade); and 3-mercaptopropyltrimethoxysilane (MPTS, ICT Trade Mark). All the reagents were of analytical grade and used as received without further purification.

2.2 Fabrication of membrane-electrode-assembly (MEA)

Catalyzed membranes were prepared by painting both sides with an airbrush using a catalyst ink. The ink consisted of 0.2 g of platinum nominally 40% on carbon black (Alfa Aesar) to which 6 g of isopropanol and 1.7 g of 5 wt% of a Nafion® solution were added. This ink slurry was stirred overnight to break up the catalyst powder and obtain a homogenous ink. During painting, the membrane was kept near a lamp to dry the ink. The Pt loading on each electrode was measured by the difference in weight before and after painting. It was kept in the range 0.50 ± 0.05 mg cm^{-2} on both sides.

MEAs with an active area of 5 cm^2 were prepared by incorporating two gas diffusion layers (GDL Sigracet GDL 10BB, 420 µm, SGL Carbon Group) on both sides of the catalyzed membrane. The MEA was assembled in a single-cell (5 cm^2) PEMFC with single serpentine flow fields (Fuel Cell Technologies, Inc.). The pinch, defined as the difference between the thickness of the MEA and the gaskets, was 40 µm. The performance of the MEAs was evaluated after conditioning at 0.5 V, 80 °C and 75% RH during 24 h to reach steady state conditions.

2.3 Characterization

The conductivity was calculated from the impedance data with the relation $r = d/RS$, where d and S are the thickness and area of the membrane, respectively. 'R' was derived from the low intersection of the high frequency semicircle on a complex impedance plane with the Re (*z*)-axis. AC impedance spectra were recorded using a Princeton Applied Research Potentiostat/Galvanostat model 273 A and a Frequency Response Detector 1025, with a constant reactant flow rate of 0.2 L min^{-1}. The cathode and anode were the working and counter electrodes, respectively. An AC signal with a 15 mV amplitude superimposed to a DC signal of 0 V versus OCV was applied in the frequency range 10 kHz to 0.1 Hz (potentiostatic mode).

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were used to verify the amount of active catalyst, the crossover of reactants, the absence of short-circuits, and the movement of membrane electro-active constituents toward the electrodes in the MEAs. The tests were performed using 0.2 L min^{-1} of dry hydrogen at the anode side (reference and counter-electrode) and 0.2 L min^{-1} of dry nitrogen at the cathode side (working electrode). CV traces were recorded in the potential range of 0.05 to 0.8 V at a scan rate of 40 mV s^{-1} and the LSV was performed in the potential range of 0.15 to 0.5 V at a scan rate of 2 mV s^{-1}. Only cells demonstrating low hydrogen crossover and no shorting were chosen for further testing.

The evaluation of fuel cell performances at varying temperature and humidity of the gases was made by using a Compact Fuel Cell Test System model 850e (Scribner Associates, Inc.) controlled with a Fuel Cell® 3.9c software. The polarization curves were recorded at atmospheric pressure using humidified oxygen (0.2 L min^{-1}) and hydrogen (0.2 L min^{-1}) at temperatures ranging from 60 to 100 °C. The cell resistance was measured with the current-interrupt technique.

3 Results and discussion

3.1 Ionic conductivity of the membranes

A series of measurements were carried out on the PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%) and PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) hybrid composite membranes which displayed high ionic conductivities from 60 to 100 °C. The results obtained at 50 and 75% RH are shown in Figs. 1 and 2, respectively. The ionic conductivities were in the range of 10^{-4}–10^{-3} S cm^{-1} and there was little difference in the conductivity between the two systems. However, the values were found to be larger when the MEA was operated with gases humidified to 75% RH. It was proposed that the ionic conductivity, occurring due to proton transport via Grotthus hopping, increased with an increasing water content. The Grotthus mechanism involves stationary vehicle molecules (i.e., without translational motion), with the proton itself moving from molecule to molecule: a process known as "hopping". The proton conductivities in the composite polymers were thus based on the migration of hydronium H_3O^+ cations interacting with the oxygen of the PVA chains and/or the oxygen of the Keggin anions. Moreover, the fact that the heteropolyacids enhanced proton transport under increasingly dry conditions would imply that the HPAs could enhance Grotthus proton hopping [24].

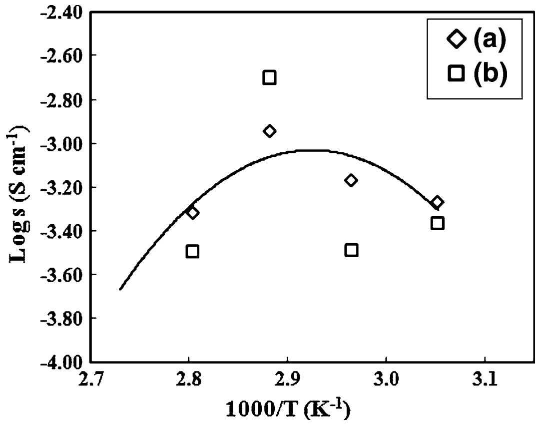

Fig. 1 Arrhenius plots for (*a*) the PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%) and (*b*) the PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) hybrid membranes at 50% RH

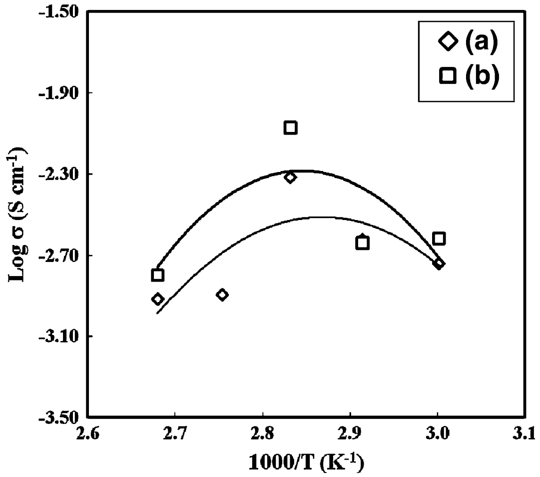

Fig. 2 Arrhenius plots for (*a*) the PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%), and (*b*) the PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) hybrid membranes at 75% RH

3.2 Cyclic voltammetric study

Figure 3 presents cyclic voltammetry curves of the membranes, and as can be seen, the peak around 0.5 V was not present at the beginning but developed after running the fuel cells for 24 h. Consequently, it was believed to be due to material moving from the membrane. Moreover, this material should be electrochemically active (which was the

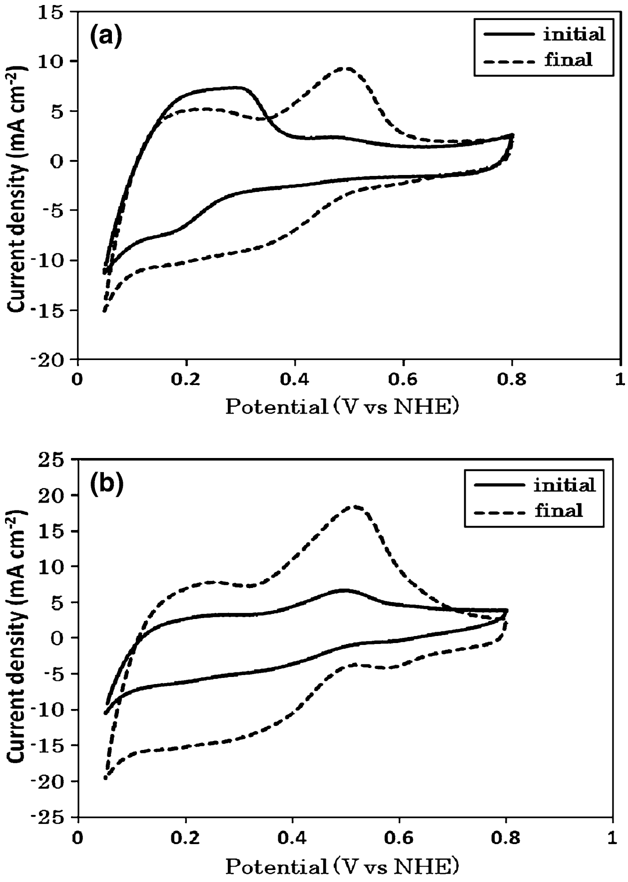

Fig. 3 Cyclic votammetry curves for **a** the PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%), and **b** the PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) membranes, displaying a comparison of the results before and after recording the polarization curves

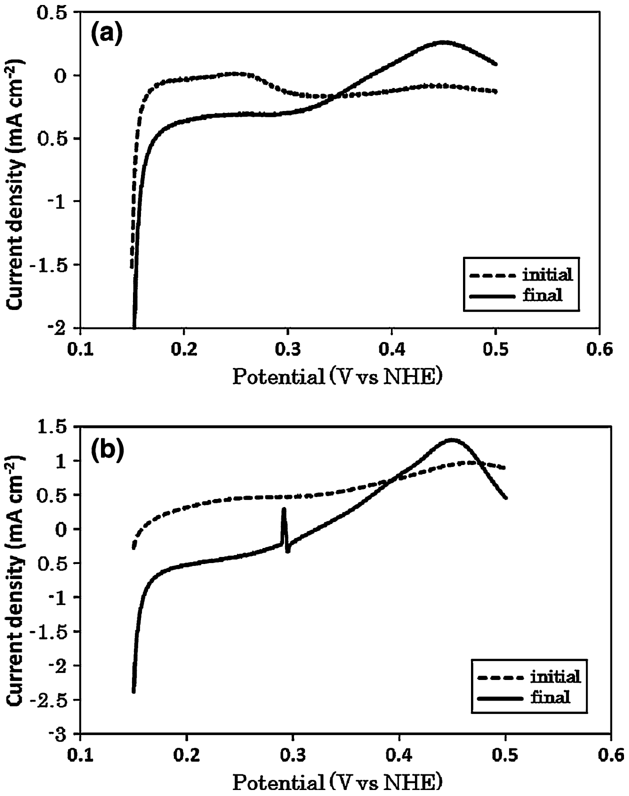

Fig. 4 Linear sweep voltammetry curves for **a** the PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%) and **b** the PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) hybrid membranes

reason it could be detected by the presence of a reduction peak in the CV), probably PWA. The peak height was comparable to the hydrogen absorption peak (0.1–0.3 V), signifying that an important amount of material had moved from the membrane to the cathode. This fact has important implications on the stability of the membrane and its potential use in fuel cell applications. The proton conduction material should be stabilized in the membrane to avoid any decrease of ionic conductivity during its lifetime. An equivalent behavior was observed in the case of PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) membranes, as illustrated in Fig. 4. The electrochemical active area (ECA) calculated from CV measurements performed prior to running the fuel cell (to avoid any changes in the electrodes) was 26 $m^2\ g^{-1}$ Pt.

3.3 Linear sweep voltammetry

As can also be seen in Fig. 4, the crossover current was below 1 mA cm^2 which corresponds to a hydrogen crossover flux of 5×10^{-9} mol S^{-1} cm^{-2}. This low gas permeability led to an OCV close to 1 V. The linear sweep voltammetry did not reveal the presence of any short-circuit in the MEAs, as ascertained by the absence of any positive slope in the region beyond 0.4 V.

3.4 Electrochemical study

The next step involved testing the hybrid composite membranes in a fuel cell. Identical fuel cell test conditions were employed for both systems. Figures 5 and 6 show the relationship between the current (*I*) and the voltage (*V*): a maximum current density of 240 mA cm^{-2} was produced at 70 °C for the PVA/PWA/PTMO/H_3PO_4 hybrid composite membrane. The PVA/SiWA/MPTS/H_3PO_4 membranes were also tested at the same temperatures and a maximum current density of 230 mA cm^{-2} was in this case found at 70 °C. This result was comparatively higher than other reported results [23]. This was due to the membrane consisting of heteropolyacids and H_3PO_4, as heteropolyacids are the highest protonconducting inorganic solid electrolytes at near ambient conditions [25]. The small deviations in the cell performance could consequently be explained in terms of varying thicknesses of the membranes as well as differences in the membrane

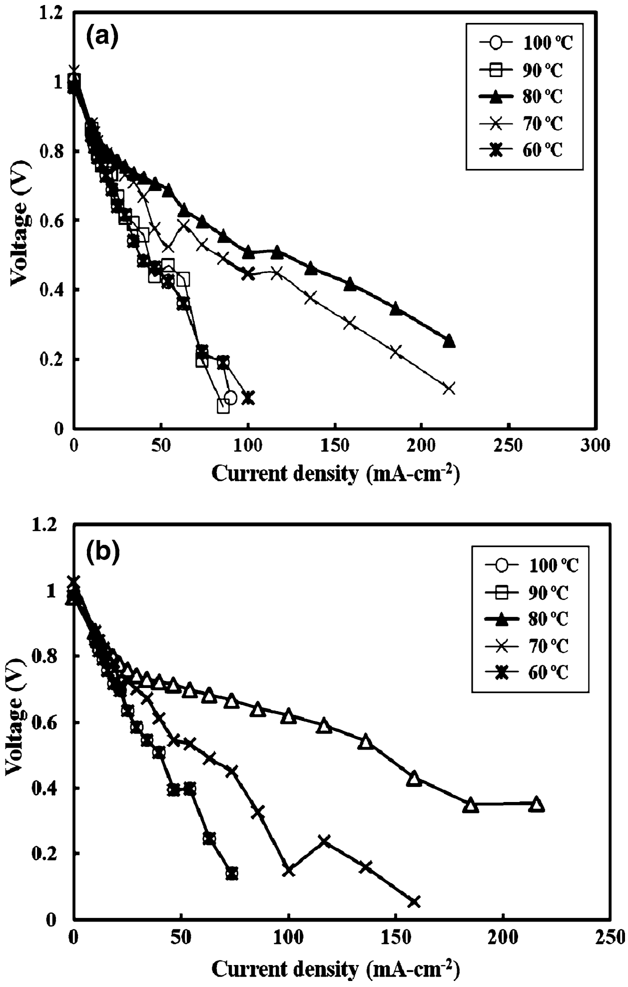

Fig. 5 The *I*–*V* relationship for **a** the PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%) and **b** the PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) hybrid membranes

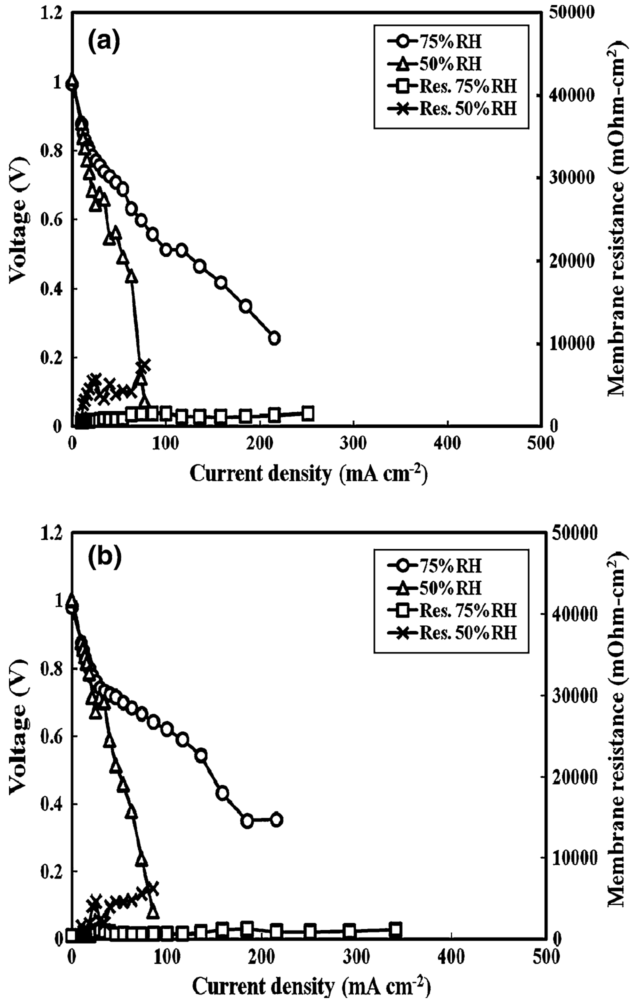

Fig. 6 *I*–*V* curves and resistance values for **a** the PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%), and **b** the PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) membranes at various percentage of relative humidity

conductivities. The best performance was achieved at 70 °C, and when the temperature was increased gradually up to 100 °C, the fuel cell performance decreased drastically. The membrane-electrode-assembly was stable during the entire experiment and at the end of the test, no cracks were noticed. Additionally, the open circuit voltage (OCV) was in the vicinity of 0.95 V, indicating a very low gas permeability through the membrane due to the good mechanical properties of the PVA composite membrane.

In general, the cell voltage should either increase or decrease with respect to the flow rate of gas at the anode and cathode sides. Figure 7 presents a comparison of the two composite membranes at 80 °C and 75% RH. The performance was similar for both types of hybrid composite membranes despite that the compositions were different. Consequently, based on these limited cell performances, it was concluded that advanced methods are required in order to prepare MEAs that will enhance the cell performances in PEM fuel cells at low and high temperatures.

4 Conclusions

This article, reports on a new class of proton-conducting hybrid composite membranes for fuel cell applications. Maximum proton conductivities of 4.8×10^{-3} and 8.5×10^{-3} S cm^{-1} were obtained at 80 °C and 75% RH for the PVA/PWA/PTMO/H_3PO_4 and PVA/SiWA/MPTS/H_3PO_4 composite membranes, respectively. Moreover, maximum current densities of 240 and 230 mA cm^{-2} were found at 70 °C for, respectively, the PVA/PWA/PTMO/H_3PO_4 and PVA/SiWA/MPTS/H_3PO_4 composite membranes. We have concluded from this study, that the conductivity and current densities were low, thus showing a poor perspective for application. On-going work, thus

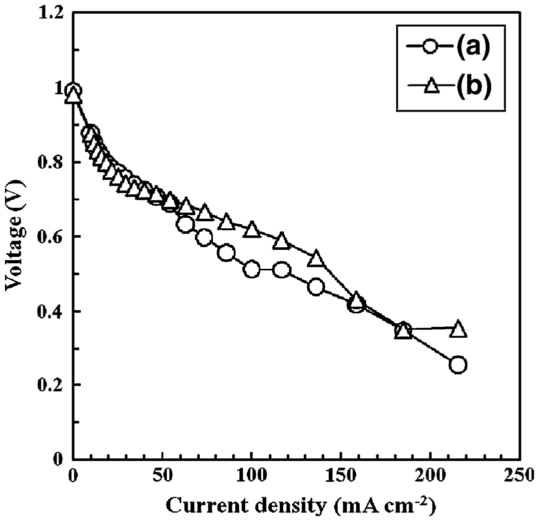

Fig. 7 A comparison of the PEMFC performance at 80 °C and 75% RH for (*a*) the PVA/PWA/PTMO/H_3PO_4 (10/15/70/5 wt%), and (*b*) the PVA/SiWA/MPTS/H_3PO_4 (50/10/10/30 wt%) membranes

involves improving the cell performances by fabrication of MEAs under various operating conditions through novel techniques.

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