

Alternative proton-conducting electrolytes and their electrochemical performances

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Received: 31 October 2011 / Revised: 17 December 2011 / Accepted: 2 January 2012 / Published online: 12 January 2012
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Abstract This study was focused on the performances of membrane electrode assemblies (MEAs) consisting of the proton-conducting 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and 80PVA/10PWA/6GPTMS/2P₂O₅/2GI hybrid membranes as electrolytes together with a Pt/C electrode for proton exchange membrane fuel cells. The MEAs were fabricated and tested as a function of temperature and humidity, and yielded a current density value of about 350 mA cm⁻² at 60 °C and 100% relative humidity (RH) for the membrane electrolyte 80PVA/10PWA/6GPTMS/2P₂O₅/2GI. These values were compared with Nafion[®] membranes, and the single-cell performances based on proton-conducting organic/inorganic hybrid electrolytes were discussed. The test conditions employed were equivalent for each MEA that had an active area of 5 cm². These hybrid membranes showed a high proton conductivity in the range of 10⁻³–10⁻² S cm⁻¹ at low temperatures, i.e., 60, 80, and 90 °C, and 50%, 75%, and 100% RH.

Keywords PEMFC · Pt/C electrode · Temperature · Humidity · Conductivity

Introduction

The proton exchange membrane fuel cell (PEMFC) is an attractive power source for a variety of applications [1] due to its high efficiency and environmental-friendly characteristics. There are a number of potential advantages of fuel cell systems compared to other energy conversion or storage devices. Since the efficiency of fuel cells is much higher than that of internal combustion engines, fuel cells are of interest for automobile, stationary, and portable applications. The low operating temperature of PEMFCs allows for a fast start-up at low temperatures and a quick response to power demands. The PEM fuel cell technology has advanced significantly in the last 20 years. In general, proton exchange membranes need the following properties: (1) be able to be easily synthesized from low-cost starting materials, (2) a high protonic conductivity (at least 0.01 S cm⁻¹ or greater than 0.1 S cm⁻¹) [2], (3) a minimized permeation to reactant gases (H₂ and O₂), and (4) high chemical, thermal, and mechanical stabilities.

Proton conductivity is one of the membrane requirements for PEMFC applications, especially at low operating temperature. A majority of commercially available fuel cell systems today use Nafion[®], produced by DuPont[®]. Nafion[®] is a perfluorinated sulfonic acid polymer. Nafion[®] has long been known to produce high power densities at low-temperature operation (<100 °C). In recent years, there has been an intensive effort to develop a low-cost membrane to replace Nafion[®] and significant progress has been made [3–6].

In recent years, organic–inorganic hybrid membranes have attracted considerable attention due to their extraordinary properties with improved physical, mechanical, and thermal properties as compared with pure polymeric membranes or inorganic membranes [7, 8]. Peng et al. [9, 10]

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attempted to introduce γ -glycidylpropyltrimethoxysilane (GPTMS) into a matrix of either chitosan or polyvinyl alcohol (PVA). GPTMS is an organofunctional alkoxy silane monomer that can undergo both sol–gel polymerization with regard to methoxysilane groups and curing of the epoxy functionality to form a hybrid network with covalent bonds between the organic and inorganic phases.

Recently, a new class of hybrid membranes has been reported. It consists of SiO_2 /polymer (poly(ethylene oxide), poly(propylene oxide), poly(tetramethylene oxide) (PTMO)) with a urethane-linking structure obtained through sol–gel reactions when doped with acidic moieties such as monododecylphosphate or 12-phosphotungstic acid (PWA) [11, 12]. Several researchers have carried out systematic investigations on the pervaporative dehydration of EG aqueous solutions. In most cases, polymeric materials including PVA [13], chitosan [14], sulfonated polyethylene [15], polyvinylpyridine-*N*-oxide [16], and sulfonated poly(ether ether ketone) [17] were used. Our group has also presented results on the development of a novel proton-conducting membrane, which consists of heteropoly acids (PWA and silicotungstic acid (SiWA)), polymers (PVA and PTMO), and aqueous acid, as well as on a PEMFC based on this membrane [18].

Presently, it has become necessary to find less expensive alternative proton exchange membranes in order to construct a class of membrane electrode assemblies (MEAs) operating at low temperatures. With the aim of developing a low-cost, low-temperature fuel cell, we thus synthesized and characterized a new class of composite proton exchange membranes. These were based on a proton-conducting hybrid membrane in which the electrolyte contained polymer, heteropoly acid, and ionic liquid. The membranes were then investigated with respect to proton conductivity and current density in a fuel cell test station.

Experimental section

Hybrid membranes were prepared through a sol–gel process using PVA, PWA, 3-glycidylpropyltrimethoxysilane, glutaraldehyde, and trimethylphosphate. PVA was dissolved in distilled water at 90 °C for 4 h. Different quantities of PVA (80 and 90 wt.%), PWA (3 and 10 wt.%), and GPTMS (4 and 6 wt.%) were mixed and this was followed by cross-linking with glutaraldehyde. This mixture was then stirred for 12 h at room temperature. The thus obtained matrix was doped with 12-phosphotungstic acid to provide the resultant hybrid membrane with a proton-conducting character. The solution was then cast on Petri dishes and, after drying, the films were heated at 120 °C for 6 h to form free-standing, transparent, and flexible membranes.

A catalyst ink was prepared by a conventional method at room temperature. A mixture of 0.2 g platinum nominally 40% on carbon black (Alfa Aesar), 6 g of isopropanol, and 1.7 g of 5 wt.% Nafion[®] solution was constituted in an ink slurry that was stirred in an ultrasonic bath overnight to break up the catalyst powder and obtain a homogenous ink. Catalyzed membranes were prepared by painting this catalyst ink on both sides of the membrane with an airbrush. During the painting, the membrane was kept near a lamp to dry the ink between applications. The Pt loading on each electrode was measured by the difference in weight before and after painting and was kept in the range $0.50 \pm 0.05 \text{ mg cm}^{-2}$ on both sides. Before weighing the membranes, they were kept at room temperature.

The preparation of MEAs was followed by the thin-film technique [19]. 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 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, 60 °C, and 75% relative humidity (RH) within 24 h to reach steady-state conditions. OCV was applied in the frequency range 10 kHz–0.1 Hz (potentiostatic mode). A constant gas pressure was given as an absolute pressure throughout the measurement. Cell temperatures of the fuel cell, gas pipes, gas flow rates, humidification of the gases, and gas pressure were controlled by the fuel cell test stations. The evaluation of fuel cell performances at varying temperatures and humidities 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. Pure oxygen and hydrogen gases were used; the gases' flow was humidified to 100% relative humidity.

The AC impedance spectra were recorded in H_2/O_2 (using a Princeton Applied Research potentiostat/galvanostat model 273A and a frequency response detector 1025). An AC signal with a 15-mV amplitude was superimposed to a DC signal of 0 V. 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, and R was derived from the low intersection of the high-frequency semicircle on a complex impedance plane with the Re (z)-axis. The thickness of each membrane was measured at room temperature before equilibrating the samples for the conductivity measurements. The proton conductivity (σ) is one of the most important properties for proton-conducting membranes used in fuel cells. Conductivity measurements were based on a two-electrode configuration along the long

axis of membrane samples that were cut into strips of approximately 0.5 cm wide and 3 cm long. The conductivity was measured while the sample was in the equilibration chamber using AC impedance between 1 Hz and 10 kHz. The measurements were performed with a Solartron 1260 frequency response analyzer with an interconnected Solartron 1287 potentiostat. The resistance value associated with the membrane conductance was determined from the high-frequency intercept of the impedance with the real axis. Following the conductivity measurements, the samples were removed from the equilibrium bottle and weighed quickly, then dried at 100 °C under vacuum, and weighed again. The water content of the membrane samples was calculated from the weight loss on drying the sample, normalized to the dry weight.

Results and discussion

The proton conductivity measurements were performed on hybrid membranes with different concentrations of PVA, PWA, and GPTMS in the composites. The values of the proton conductivity as a function of the relative humidity (50%, 75%, and 100% RH) at 60, 80, and 90 °C are reported in Fig. 1. The conductivity of the samples increased with an increasing humidity level as well as with their content of PWA and GPTMS. The 80PVA/10PWA/6GPTMS/2P₂O₅/2GI hybrid composite, with 10% PWA, demonstrated the highest conductivity of 4.2×10^{-3} at 90 °C and 100% RH. At 60 °C (Fig. 7b), the fuel cell with the 10% PWA composite membrane showed the best performance. Overall, the performance of the fuel cells with the different membranes followed the trend found in the conductivity data. Figure 2 presents the cell temperature versus the conductivity of the two hybrid composite membranes. The temperature varied from 60 to 90 °C, and the relative humidity was either 50%, 75%, or 100%. The humidity was controlled using the humidity control of the test station (Scribner 850c). The gas (air, oxygen, and/or hydrogen) was bubbled in a bottle through a humidifier containing water at a controlled temperature. The gas became saturated at a temperature that was different from the fuel cell operating temperature. The relative humidity of the gas that entered the fuel cell corresponded to the ratio of the water vapor pressure at the humidifier temperature/water vapor pressure at the fuel cell temperature. As can be seen, the proton conductivity values remained high for fuel cells operating at low temperatures (high relative humidity).

The conductivity values under the varying temperature and humidity conditions were compared with a standard membrane Nafion® as well as with similar studies based on heteropoly acids. Staiti et al. [20] successfully prepared composite polybenzimidazole (PBI) membranes with silica

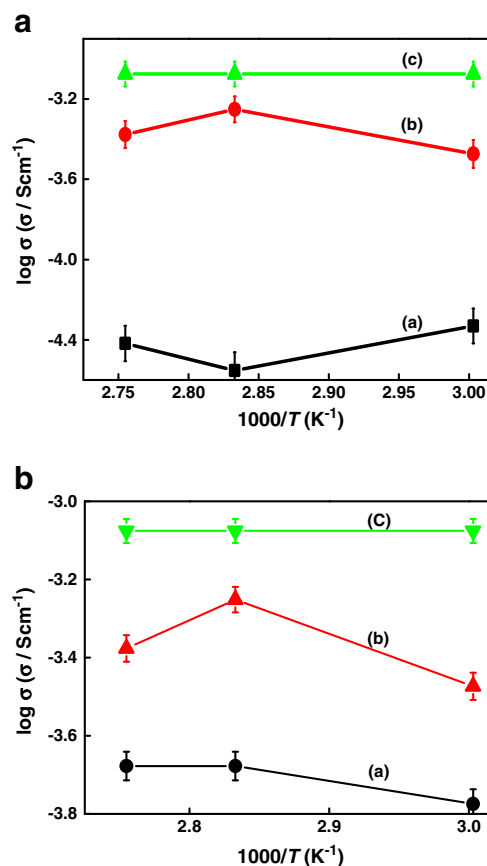


Fig. 1 The proton conductivity of the composite membrane electrolytes: **a** 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and **b** 80PVA/10PWA/6GPTMS/2P₂O₅/2GI measured at various temperatures (a) 60, (b) 80, and (c) 90 °C with 75% and 100% RH

supported by PWA and SiWA. The reported conductivity at the operating condition was, however, low, i.e., around $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at 150 °C for PWA/SiO₂/PBI and $2.23 \times 10^{-3} \text{ S cm}^{-1}$ at 160 °C for SiWA/SiO₂/PBI. He et al. [21] presented a conductivity of 0.058 S cm^{-1} for 30% PWA/PBI doped with phosphoric acid.

PWA is a heteropoly acid with high proton conductivity. The basic structural unit of the PWA is the Keggin anion (PW₁₂O₄₀)₃, which consists of the central PO₄ tetrahedron surrounded by four W₃O₁₃ sets linked together through oxygen atoms. Each W₃O₁₃ set is formed by three edge-sharing WO₆ octahedra. They form channels that can contain up to 29 water molecules in different hydrate phases. This variety leads to different protonic species and hydrogen bonds of varying strengths [22, 23], resulting in a high proton conductivity at room temperature. Hydrated PWA has been known to present values around 0.18 S cm^{-1} [24].

These hybrid membranes were then employed as electrolytes in MEAs for which the single-cell performances were determined during operation at 60, 80, and 90 °C, and the obtained results are presented in the following section. The

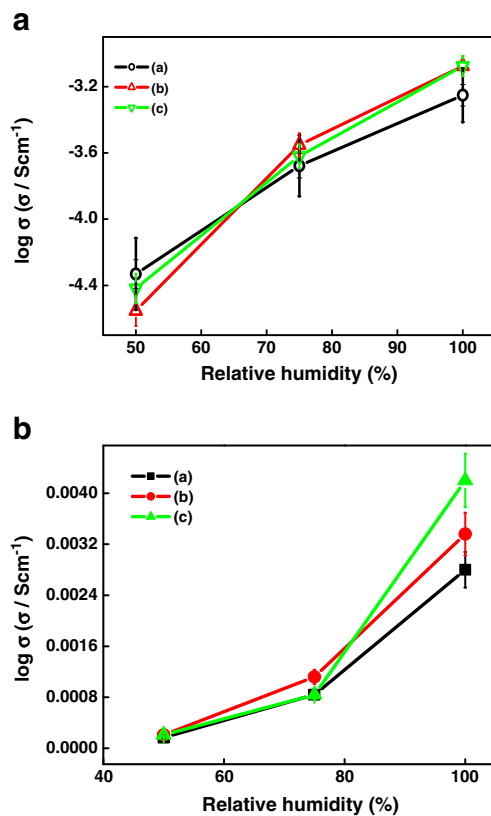


Fig. 2 The proton conductivity of the composite membrane electrolytes: **a** 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and **b** 80PVA/10PWA/6GPTMS/2P₂O₅/2GI measured at various humidity conditions (a) 50%, (b) 75%, and (c) 100% RH at 60, 80 and 90 °C

single-cell performances were evaluated with pure hydrogen and oxygen in unhumidified air as the fuel and oxidant under atmospheric pressure. The single cells were operated at various temperature and humidity conditions for different structures of MEAs. The polarization curves (Fig. 3) show the relationship between the cell voltage and current density of the single cell for an MEA investigated at 60 °C under various conditions of relative humidity (75% and 100% RH). Figure 3a shows that the cell voltage was 0.95 V and the current density values of 65 and 100 mA cm⁻² for MEAs consisting of the 90PVA/3PWA/4GPTMS/1P₂O₅/2GI electrolyte. Figure 3b displays current density values of 250 and 320 mA cm⁻² for the MEA consisting of the 80PVA/10PWA/6GPTMS/2P₂O₅/2GI electrolyte membrane. As can be seen in Fig. 3b, the cell voltage was 1 V. According to this result, the MEA with the higher amount of PWA (10%) in the membrane electrolyte demonstrated the higher current density at otherwise equivalent operating conditions.

Figure 4 shows results for the relationship between cell voltage and current density, when the temperature of the cell was maintained at 80 °C throughout the measurement and the humidification was either 75% or 100% RH. The two MEAs presented differing results at the operating temperature

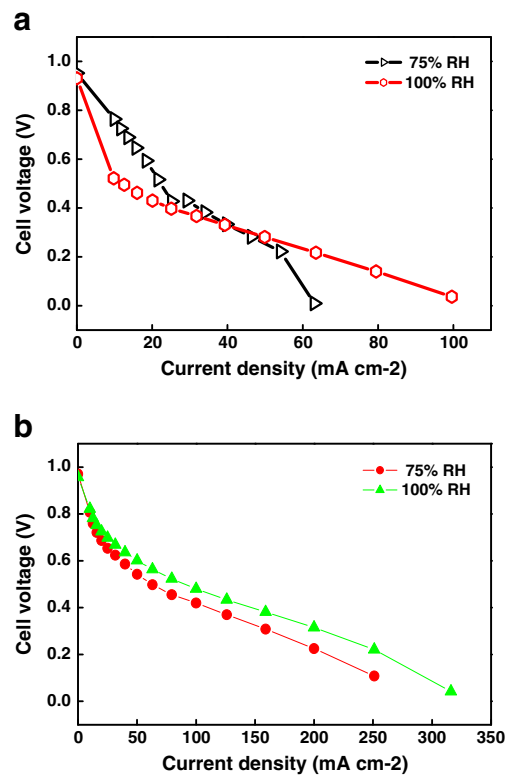


Fig. 3 The *I*–*V* curves of the single cell incorporating Pt/C electrodes with the **a** 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and **b** 80PVA/10PWA/6GPTMS/2P₂O₅/2GI hybrid composite membrane electrolytes. The temperature of the cell was maintained at 60 °C throughout the measurement and the humidification was either 75% or 100% RH

of 80 °C: the current density was 65 and 100 mA cm⁻² for the 90PVA/3PWA/4GPTMS/1P₂O₅/2GI MEA (Fig. 4a), whereas higher current density values, i.e., 200–250 mA cm⁻², were obtained for the MEA comprising the 80PVA/10PWA/6GPTMS/2P₂O₅/2GI membrane (Fig. 4b). From these results, it was confirmed that the cell performances depended on the chemical composition of PWA and GPTMS in the membrane composite.

Figure 5 shows the single-cell performances at 90 °C with a humidification of either 75% or 100% RH. The results were higher for the MEA with the higher amount of PWA (10 wt.%). In this case, the cell performances did not increase as a function of temperature. In total, the cell performances depended on the quality of the high proton-conducting membrane in the MEA. The curves displayed current density values of 40 and 100 mA cm⁻² as well as 150–250 mA cm⁻² obtained for the two MEAs. Since these results had been obtained at low temperatures, the cell was determined to show a good stability during the electrochemical measurements, with a cell voltage of about 0.95 and 1 V. When comparing Figs. 3a, 4a, and 5a, it can be seen that the performances of the three MEAs were not significantly different in the low current density region. Similarly,

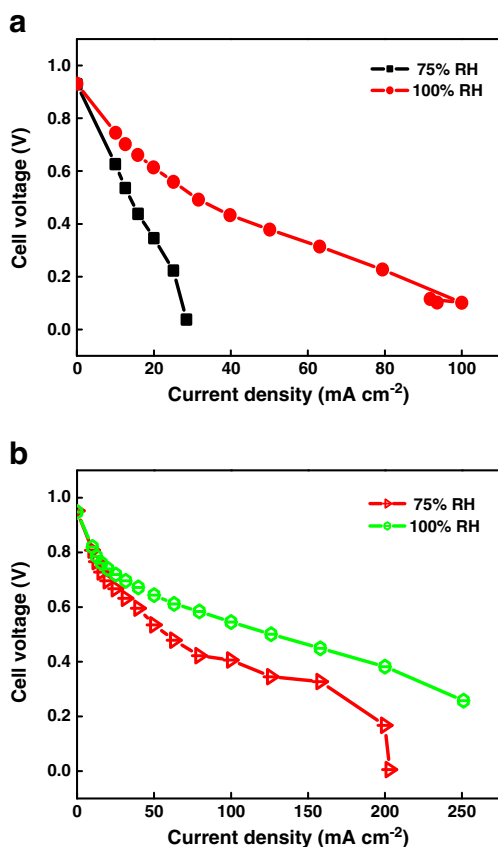


Fig. 4 The *I*–*V* curves of the single cell incorporating Pt/C electrodes with the **a** 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and **b** 80PVA/10PWA/6GPTMS/2P₂O₅/2GI hybrid composite membrane electrolytes. The temperature of the cell was maintained at 80 °C throughout the measurement and the humidification was either 75% or 100% RH

Fig. 3a, b showed the highest performances in the high current regions. It was, thus, suggested that the performances of the novel MEAs were improved due to the chemical composition in the composite electrolyte.

The single fuel cell was assembled with the Pt/C electrode and proton composite membrane electrolyte so as to perform a study at the various temperatures. The corresponding polarization curves are presented in Figs. 6, 7, and 8. The MEAs of this fuel cell contained a Pt/C loading of 0.5 mg cm⁻². The single-cell performances of the MEAs consisting of either the 90PVA/3PWA/4GPTMS/1P₂O₅/2GI or 80PVA/10PWA/6GPTMS/2P₂O₅/2GI electrolytes together with the Pt/C electrode were obtained during operation at various temperatures with three conditions of relative humidity. In Fig. 6, the MEA with the 90PVA/3PWA/4GPTMS/1P₂O₅/2GI electrolyte presented current density results of 30, 40, and 65 mA cm⁻² at 75% RH, when operated at temperatures of 60, 80, and 90 °C. The current density values thus increased as the temperature was raised. Figure 6b displayed the current density results for the second electrolyte, and they were found to be 150, 200, and

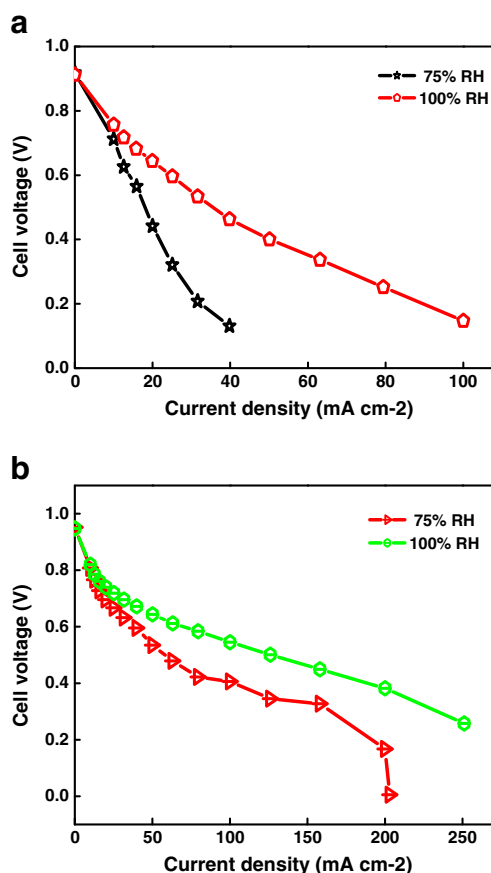


Fig. 5 The *I*–*V* curves of the single cell incorporating Pt/C electrodes with the **a** 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and **b** 80PVA/10PWA/6GPTMS/2P₂O₅/2GI hybrid composite membrane electrolytes. The temperature of the cell was maintained at 90 °C throughout the measurement and the humidification was either 75% or 100% RH

250 mA cm⁻² obtained under identical operating conditions. These results confirmed that the current density values increased for higher cell temperatures and, also, that the MEA comprising the composite electrolyte containing the higher content of PWA showed superior results.

Figure 7 illustrates the performance of the cell utilizing a proton membrane electrolyte, with cell temperatures of 60–90 °C and the anode and cathode side humidified to 100% RH. These results followed a similar trend to those above: a current density value of 100 mA cm⁻² was obtained for the various temperatures, but no improvement was found when the temperature was increased from 60 to 90 °C (Fig. 7a). However, the results seen in Fig. 7b were higher compared with those from Fig. 7a. The maximum current density was 320 mA cm⁻² at 60 °C and 100% RH using the MEA comprising the 80PVA/10PWA/6GPTMS/2P₂O₅/2GI electrolyte. At 60 °C (Fig. 7b), the fuel cell with the 10 wt.% PWA composite membrane showed the best performance.

From the two sets of MEA results, the best MEA performances in each category (variation of temperature and

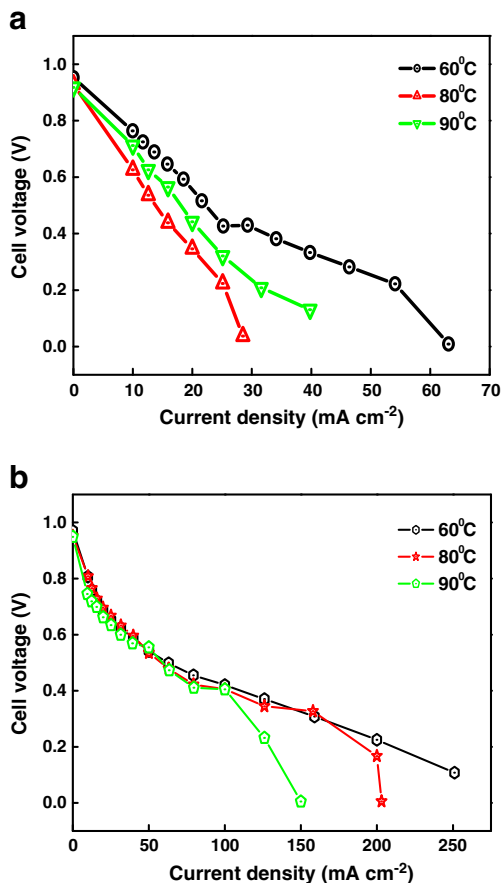


Fig. 6 The I - V curves of the single cell incorporating Pt/C electrodes with the **a** 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and **b** 80PVA/10PWA/6GPTMS/2P₂O₅/2GI hybrid composite membrane electrolytes. The humidification of the cell was maintained at 75% RH throughout the measurement and the temperature was either 60, 80, or 90 °C

humidity) were compared with regard to the polarization curves (Fig. 8). Figure 8a, b displays plots of the main effect at various current densities. Based on the chemical composition factor, the cell performances clearly showed a variation in the current density for MEA1 (Fig. 8a) and MEA2 (Fig. 8b). Overall, the experiment concluded that the single-cell performances were affected by two factors: the chemical composition and the environmental condition, including the temperature and humidity. The performance of MEAs in Figs. 3b and 7b was similar, displaying a current density up to 320 mA cm⁻². The overall observation was that the single-cell performances depended more on the characteristics of the proton membrane than on the operating temperature. The curve fitting of the polarization curves revealed no difference with regard to the exchange current or the Tafel slope within the experimental error. The polarization curves confirmed that the novel MEAs promoted ohmic, activation, and mass transport of the PEMFC. Moreover, the electrochemical analysis indicated that the concentration of the PWA in the composite membrane was responsible for

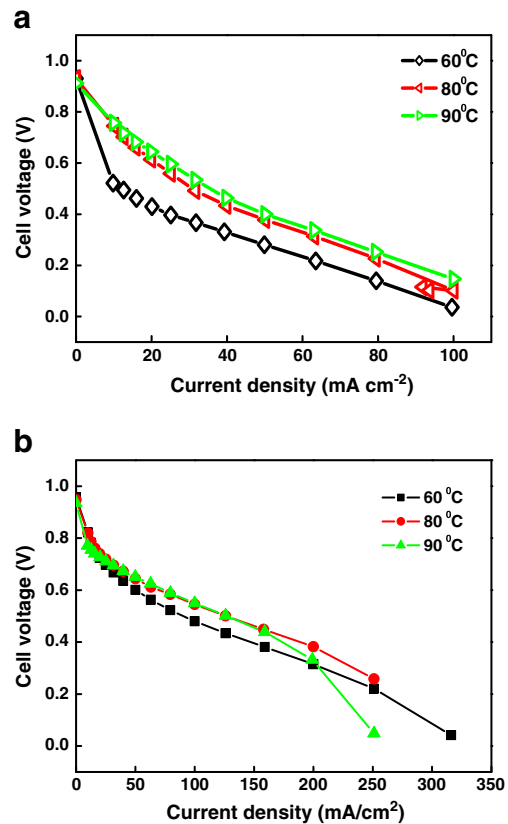


Fig. 7 The I - V curves of the single cell incorporating Pt/C electrodes with the **a** 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and **b** 80PVA/10PWA/6GPTMS/2P₂O₅/2GI hybrid composite membrane electrolytes. The humidification of the cell was maintained at 100% RH throughout the measurement and the temperature was either 60, 80, or 90 °C

the performance at the studied operating temperatures and relative humidities.

The performances were compared with a standard Nafion 115 membrane under similar experimental conditions. The open circuit potential of the hybrid membrane was about 900 mV and, thus, approximately 50 mV lower than that of Nafion 115. A similar observation was also made for some of the newly synthesized hybrid membranes [25, 26]. In a following step, a comparison was made with similar hybrid membranes. For this, the I - V data, from [27] corresponding to a PWA-doped poly(tetramethylene oxide)-based hybrid membrane (PTMO/PWA) at 80 °C, were used. Staiti and Minutoli [28] tested the electrolyte in a PEMFC and achieved a power density of around 700 mW cm⁻² at atmospheric pressure and room temperature.

According to Fig. 9, the proton conductivity of the hybrid electrolyte membranes was found to depend on the water content in the membrane. In particular, the hybrid membrane with 10 wt.% PWA showed a higher performance than its counterpart with less PWA. This result indicated that the rate of proton conduction through the hybrid membrane containing 10 wt.% PWA exceeded that with 3 wt.%

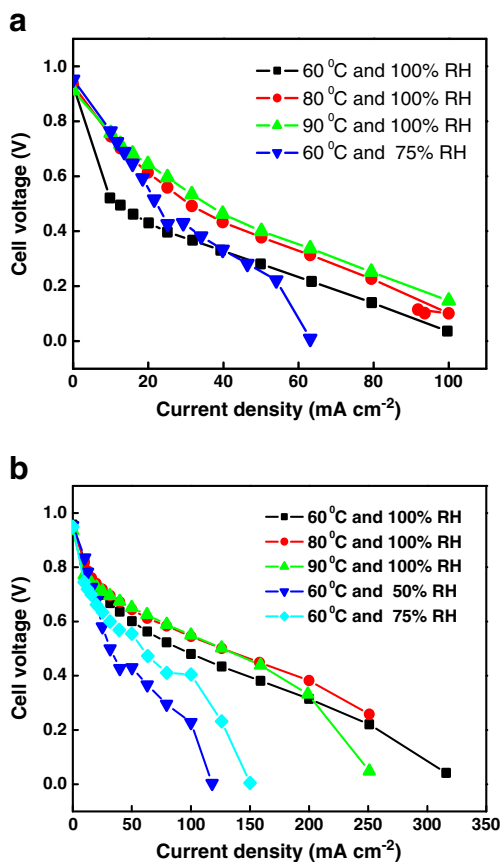


Fig. 8 A comparison of the best current density values of the membrane electrode assemblies: **a** MEA1 and **b** MEA2

PWA. Thus, the water content in the hybrid membrane with 10 wt.% PWA seemed to be higher. It was due to higher water uptake, a significant conductivity contribution of PWA. Consequently, the heteropoly acids embedded in the membrane played an important role in maintaining the humidity in the PEMFC.

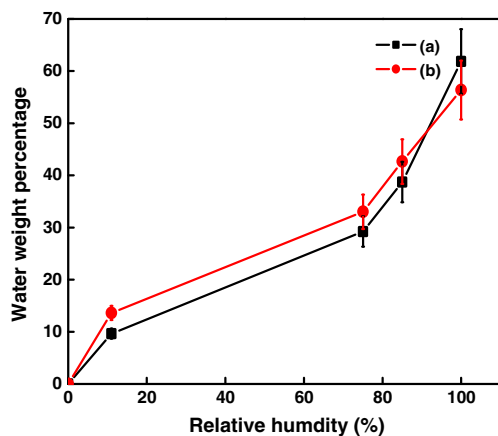


Fig. 9 The water weight percentage of the hybrid composite membrane electrolytes: **a** 90PVA/3PWA/4GPTMS/1P₂O₅/2GI and **b** 80PVA/10PWA/6GPTMS/2P₂O₅/2GI calculated at various relative humidities

Moreover, the calculated water weight percentage of the MEA under humid conditions could be increased by increasing the humidity level. At a high level of humidity, the membrane demonstrated a high conductivity and good cell performances. In future experiments, the same proton-conducting membranes will be put through long-term cell measurements under otherwise similar conditions in order to calculate the cell lifetime operation at low temperatures. Further, in order to reduce the cost of fuel cell materials, MEAs with non-platinum catalysts will be investigated. The performance of the PEMFC was directly affected by the proton conductivity, which is highly dependent on the water content in the membrane [29]. At low humidity conditions, the performance of the PEMFC was more sensitive to the amount of water molecules in the membrane. Generally, the performance of the PEMFC is strongly dependent on the cell's operating temperature. Without reliable methods of water management, the MEA structure may start to dry out, resulting in a lower ionic conductivity and a higher charge transfer resistance across the electrode–electrolyte interface [30, 31].

Therefore, this study investigated the performance of a PEMFC with respect to cell temperature and humidity. The water content in the PEMFC can be varied by the production of water from chemical reactions and external humidification of gases entering the cathode and anode. Since the amount of water production is directly associated with current generation, the control of the external humidification level is an effective way to manage the water content in the PEMFC. The hydration of the membrane is a very important determinant of the performance and durability of a PEMFC. If not properly hydrated, the membrane exhibits higher ionic resistance, and in extreme cases, it can be physically damaged [32]. Membrane hydration is affected by the water transport phenomena in the membrane itself, which in turn are affected by the condition of the inlet gases and the operating parameters of the fuel cell.

Summary

A highly conductive hybrid composite membrane was prepared using PVA/PWA/GPTMS/P₂O₅/GI, and the aim was for it to be used in low-temperature PEMFCs. The composite membrane showed a decent conductivity that was similar to that of a standard Nafion® membrane at low temperatures. At 90 °C, the conductivity of the 80PVA/10PWA/6GPTMS/2P₂O₅/2GI composite membrane was 4.2×10^{-3} at 90 °C and 100% RH. However, under the prevailing experimental conditions, it was confirmed that these composite membranes were suitable only for temperatures below 100 °C. MEAs were fabricated using high proton-conducting membranes, and single-cell tests were performed at low temperatures. High current density values

could be obtained. It was believed that these novel MEAs will be beneficial for long-term PEMFC operation. Although the performance of the MEAs using Pt/C electrodes was not high enough, a maximum current density of 320 mA cm^{-2} was nevertheless obtained at $60 \text{ }^\circ\text{C}$ and 100% RH. This result was reasonably good but not as high as that of Nafion[®] membranes.

Acknowledgments This work was financially supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the Special Coordination Funds for Promoting Science and Technology of Japan. Professor B. Rambabu and Dr. J. Parrondo express their gratitude to Dr. Robert Mantz (Electrochemistry and Advanced Energy Conversion at the ARO-Chemical Sciences) and to Dr. Thomas L. Reitz (Electrochemistry and Thermal Sciences at the AFRL Wright Patterson Airbase, OH) for supporting the fuel cell research at the SUBR (U.S-DOD grant # W911NF-08-C-0415).

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