ZrO$_2$–SiO$_2$/Nafion® composite membrane for polymer electrolyte membrane fuel cells operation at high temperature and low humidity

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Abstract

Recast Nafion® composite membranes containing ZrO$_2$–SiO$_2$ binary oxides with different Zr/Si ratios are investigated for polymer electrolyte membrane fuel cells (PEMFCs) at temperatures above 100 °C. Fine particles of the ZrO$_2$–SiO$_2$ binary oxides, same as an inorganic filter, are synthesized from a sodium silicate and a carbonate complex of zirconium by a sol–gel technique. The composite membranes are prepared by blending a 10% (w/w) Nafion®-water dispersion with the inorganic compound. All composite membranes show higher water uptake than unmodified membranes, and the proton conductivity increases with increasing zirconia content at 80 °C. By contrast, the proton conductivity decreases with zirconia content for the composite membranes containing binary oxides at 120 °C. The composite membranes are tested in a 9-cm^2 commercial single cell at both 80 °C and 120 °C in humidified H$_2$/air under different relative humidity (RH) conditions. Composite membrane containing the ZrO$_2$–SiO$_2$ binary oxide (Zr/Si = 0.5) give the best performance of 610 mW cm^{-1} under conditions of 0.6 V, 120 °C, 50% RH and 2 atm.

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Keywords: ZrO$_2$–SiO$_2$ binary oxide; Composite membrane; High temperature; Low humidity; Polymer electrolyte membrane fuel cell; Power density

1. Introduction

Most recent research on polymer electrolyte membrane fuel cells (PEMFCs) has been focused on the development of new proton-conducting membranes (CPEMS) for operation at higher temperatures with lower humidification levels [1–6]. Operation of PEMFCs above 100 °C has many advantages such as faster electrode kinetics, higher tolerance to impurities in the fuel gas, the need for smaller heat exchanger, and easier water and thermal management [7]. Common PEMs are based on a hydrated perfluorosulfonic acid (PFSA) polymer such as Nafion®. This type of polymer requires water for proton conductivity, and the proton conductivity decreases considerably at temperatures above the boiling point of water due to dehydration. In addition, dehydration also causes shrinkage of the membrane and increases the contact resistance at the membrane and electrode interface [8]. Therefore, conventional membranes cannot be used in PEMFC operation at temperatures above 100 °C. Hence, the develop-

ment of novel membranes that are thermomechanically stable at higher temperature is vital for further commercialization of PEMFCs in a wide range of applications.

Many approaches have been adopted in the search for improved membranes and include the modification of conventional PFSA membranes to improve their water retention properties at higher temperatures through the incorporation of various hygroscopic inorganic particles. Such species improve the mechanical properties of the membranes because specific interactions between the inorganic and organic components help to improve membrane water management [9]. Moreover, the inorganic particles form a new membrane structure that inhibits the direct permeation of reaction gases [1].

The PFSA polymers-based organic/inorganic composite membranes have been investigated using hydrophilic and/or proton-conducting compounds such as SiO$_2$, TiO$_2$, and ZrO$_2$ as inorganic fillers [1,3,5]. Saccá et al. [1] developed composite membranes containing different percentages of commercial ZrO$_2$ that were tested in a commercial single cell in the temperature range of 80–130 °C [1]. The composite membranes showed a higher water retention capacity and better single-cell performance than a Nafion® 112 membrane. A membrane

containing a 10% (w/w) ZrO_2 gave the highest power density of $387\,mW\,cm^{-2}$ at 130 °C and 85% RH. Zeng at al. [5] modified PFSA membranes by incorporating a silica sol. The perfluorosulfonic acid ionomer (PFSI)/silica composite membrane exhibited better water uptake, proton conductivity and cell performance [5].

In this study, a ZrO_2–SiO_2 binary oxide is synthesized as an inorganic filler to modify a PFSA membrane. ZrO_2–SiO_2 binary oxide is known to be a catalyst for oxidizing cyclohexane [10] and the isomerization of *n*-hexane [11], because ZrO_2–SiO_2 is a solid-state acid and has been widely examined in the catalytic field [12,13]. The acidity of the ZrO_2–SiO_2 binary oxide can be improved further by post-treatment with a strong acid [14]. Therefore, the ZrO_2–SiO_2 binary oxide can effectively improve the proton conductivity of the membranes. The binary oxide contains ZrO_2 and SiO_2 in a single particle and has bonding structures of Zr–O–Zr, Si–O–Si, and some Zr–O–Si [15].

Fine particles of the binary oxide are synthesized at different Zr:Si mole ratios, and ZrO_2 and SiO_2 are synthesized individually using a sol–gel technique. Composite membranes of SiO_2/Nafion®, ZrO_2/Nafion® and ZrO_2–SiO_2/Nafion® are also prepared by means of the doctor-blade casting method. The prepared membranes are characterized both physically and chemically and tested in a commercial single cell to determine the influence of the binary oxide as an inorganic filler on the properties of PEMs in PEMFCs for higher temperature operation.

2. Experimental

2.1. Synthesis of ZrO_2–SiO_2 binary oxide

The ZrO_2–SiO_2 binary oxide was synthesized using the following procedure [14]: $ZrOCl_2·8H_2O$ was dissolved in a distilled water and a solution of $(NH_4)_2CO_3$ was added until a white precipitate of $ZrOCO_3$ was formed. The precipitate was washed several times with distilled water to remove the chloride ions. The $(NH_4)_2CO_3$ solution was added to the precipitate with constant stirring until the pH 8. Subsequently, anionic surfactant sodium dodecyl sulfate was added to the solution. The mixture was stirred well for 30 min, which was followed by the addition of a sodium metasilicate solution to the mixture to form a semi-transparent gel. The gel was kept overnight at room temperature and then aged at 80 °C for 2 days followed by 100 °C for 1 day. The product was washed several times with distilled water to remove the surfactant. The surfactant-free ZrO_2–SiO_2 binary oxide was dried at 90 °C for 6 h, and heated at 600 °C for 6 h to remove any organic contaminants and nitrides.

ZrO_2 was synthesized using the method reported by Parera [16]. An ammonium hydroxide solution was added dropwise to a 0.2 M $ZrOCl_2·8H_2O$ solution until the pH 10. The obtained $ZrO_2·nH_2O$ sol was washed with distilled water and dried at 110 °C for 10 h and treated at 600 °C for 3 h.

SiO_2 was also synthesized using the sol–gel process [17]. The SiO_2 particles were prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) in an ethanol medium in the presence of ammonium hydroxide. First, ethanol was taken and kept in a

sonication bath. After 10 min, a known volume of TEOS was added, and after 20 min, a 28% ammonium hydroxide solution was introduced as a catalyst to promote the condensation reaction.

2.2. Preparation of composite membrane

Composite membranes were prepared using the following procedure from 10% (w/w) Nafion® solution (DuPont) with an equivalent weight (EW) of 1100. The Nafion® solution was concentrated to 15% (w/w) using a vacuum evaporator. The prepared inorganic particles were dispersed in isopropyl alcohol (IPA) in an ultrasonic bath for 30 min, and mixed with the concentrated Nafion® solution. The suspensions were stirred vigorously for 1 h, and treated in an ultrasonic bath for 30 min to eliminate bubbles. The suspensions were then cast on a glass plate using the doctor-blade casting method and kept at 40 °C for 12 h. The cast membranes were then heated to 160 °C for 1 h. Finally, the composite membranes were detached from the glass plate and chemical treatment was carried out in a 5% (w/w) hydrogen peroxide (H_2O_2) solution for 30 min, then in 1 M sulfuric acid (H_2SO_4) for 30 min, and finally in de-ionized water for 1 h at 80 °C. Composite membranes with 10% (w/w) of the various inorganic fillers were prepared and the recast Nafion® membrane was prepared using the same procedure without an inorganic filler. Table 1 describes the types and inorganic contents of the membranes.

The morphology of the composite membrane containing 10% (w/w) ZrO_2–SiO_2 binary oxide (Zr/Si = 1) was examined with a field-emission scanning electron microscope (Hithch) at 15 kV. Fig. 1 shows the cross-section morphologies of composite membrane containing 10% (w/w) ZrO_2–SiO_2 binary oxide (Zr/Si = 1). It is seen that the binary oxide particles are dispersed uniformly in the membrane and the binary oxide particles exhibit good compatibility with the polymer matrix.

2.3. Physical and chemical characterization

The prepared binary oxides were characterized by Fourier transform-infrared (FT-IR) spectroscopy (DA-8, Bomen). The FT-IR spectra were recorded in the wave number range from $400\,cm^{-1}$ to $4000\,cm^{-1}$.

The ion-exchange capacity (IEC) of the membranes was measured by means of a titration method, as follows. The dry

Table 1
Type and inorganic content of tested membranes

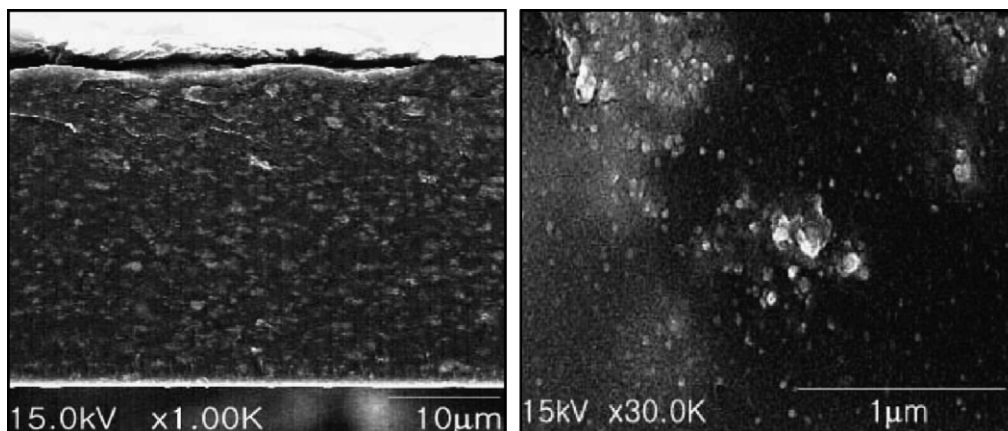| Membrane	Inorganic filler	Inorganic content (%, w/w)	Thickness (μm)
Nafion® 112	–	0	51
Recast Nafion®	–	0	51
MZ10	ZrO_2	10	52
MZS21-10	ZrO_2–SiO_2 (Zr:Si = 2)	10	51
MZS11-10	ZrO_2–SiO_2 (Zr:Si = 1)	10	51
MZS11-10P	ZrO_2–SiO_2 (Zr:Si = 1)	10	51
MZS12-10	ZrO_2–SiO_2 (Zr:Si = 0.5)	10	52
MS10	SiO_2	10	51

Fig. 1. Scanning electron micrographs of a cross-section of a composite membrane containing 10% (w/w) ZrO_2–SiO_2 binary oxide (Zr/Si = 1).

membranes were soaked in a 1-M NaCl solution for 12 h at ambient temperature. This solution was titrated against a 0.01-M NaOH solution to neutralize the exchanged proton (H^+) using an automatic titrator (Metrohm). The IEC was calculated using the following equation:

$$IEC = \frac{V \times M}{m} \qquad (1)$$

where IEC is the ion exchange capacity (mequiv. g^{-1}); V is the added titrant volume at the equivalent point (mL); M is the molar concentration of the titrant; m is the dry sample weight (g).

The water uptake of each membrane was calculated by the difference between the wet and dry weight of the membrane. The wet weight was measured after immersing the membrane in distilled water for 24 h at room temperature. For the dry weight (m_{dry}), the measurement was made after drying the membrane at 100 °C for 2 h. The water uptake ($W_{up}\%$) was calculated using the following equation:

$$W_{up}\% = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \qquad (2)$$

where m_{wet} and m_{dry} are the weights of the wet and dry samples (g), respectively.

Thermogravimetric analysis of the membranes was conducted with a thermal analysis system (TGA 2050, TA, instruments) at temperatures that ranged from room temperature to 700 °C at a heating rate of 10 °C min^{-1} in a N_2 atmosphere.

2.4. Ex situ conductivity measurements

The proton conductivity of the membranes was determined by electrochemical impedance measurements (IM 6ex, Zahner) using the following equation:

$$\sigma = \frac{l}{RS} \qquad (3)$$

where σ, l, and S are the proton conductivity, thickness, and area of the membrane, respectively. The value of R was derived from the low intersect of the real part axis.

2.5. Preparation of membrane electrode assembly (MEA)

The MEAs were prepared by direct spraying of the catalyst slurries on the membranes and then pressing the latter between gas-diffusion layers (GDLs). The catalyst slurries were obtained by mixing a 40% (w/w) Pt/C catalyst (Johnson Matthey) with IPA (HPLC grade) and 5% (w/w) Nafion® solution (DuPont), followed by ultrasonication for 15 min. The platinum (Pt) loading on both electrodes was 0.4 mg Pt cm^{-2}. SGL carbon papers of 400 μm in thickness were used as the GDLs.

2.6. Single cell performance

The electrochemical measurements were carried out using a 9-cm^2 single cell in humidified H_2/air gases. The single cell was operated at 80 °C and 120 °C under various RH conditions. In the case of operation at 120 °C, the inlet gases were at a pressure of 2 atm. in order to prevent dehydration of the membranes. The flow rates of the gases were fixed at 1.5 times the stoichiometry of the fuel and twice the stoichiometric value of the oxidant. The polarization curves were measured
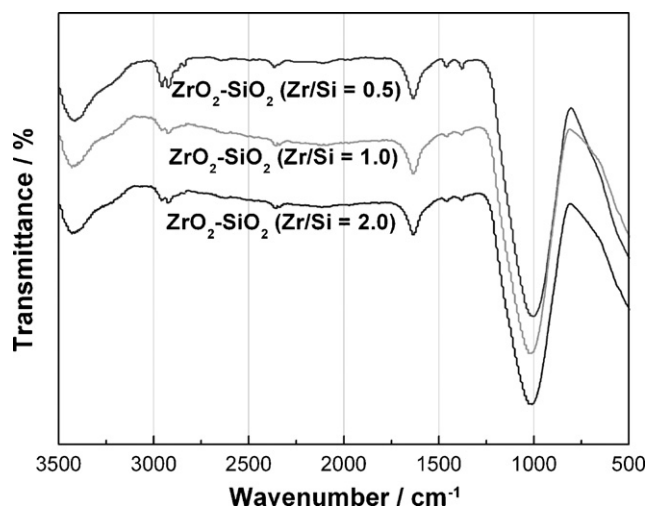

Fig. 2. FT-IR spectra of ZrO_2–SiO_2 particles with different Zr:Si mole ratios.
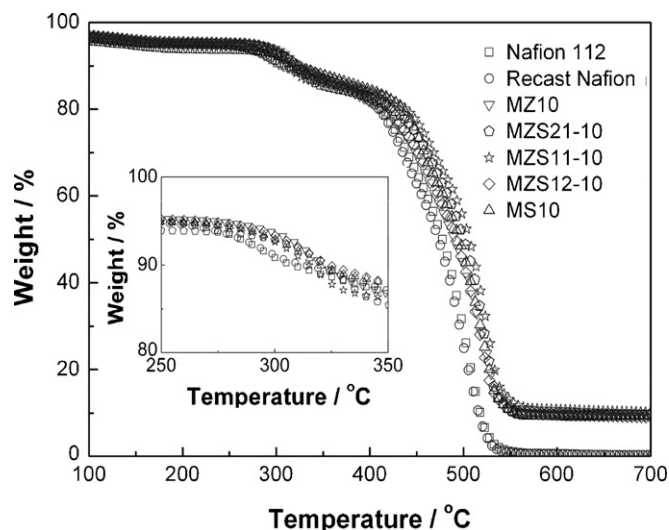
Fig. 3. Thermograms of composite membranes compared with the Nafion® 112 and recast Nafion® membranes.

by applying a constant current for 3 min at each point using an electronic loader (EP-1000, Deagil Electronics). The power densities were calculated from the steady-state voltages and applied currents.

3. Results and discussion

3.1. FT-IR spectroscopic analysis of ZrO_2–SiO_2 binary oxides

The FT-IR spectra of the ZrO_2–SiO_2 particles with different Zr:Si mole ratios are presented in Fig. 2. The spectra show a sharp peak at $1020\,cm^{-1}$ and this suggests the formation of a Zr–O–Si bond. By comparison, asymmetric stretching vibration of the Si–O–Si bond is observed at $1100\,cm^{-1}$ for pure silica. The shift in stretching frequency is due to deterioration of the silica framework after insertion of zirconium atoms [14]. The absorption peak at $1630\,cm^{-1}$ is attributed to coordinated and absorbed water, and the peak at $1400\,cm^{-1}$ to the bridging OH
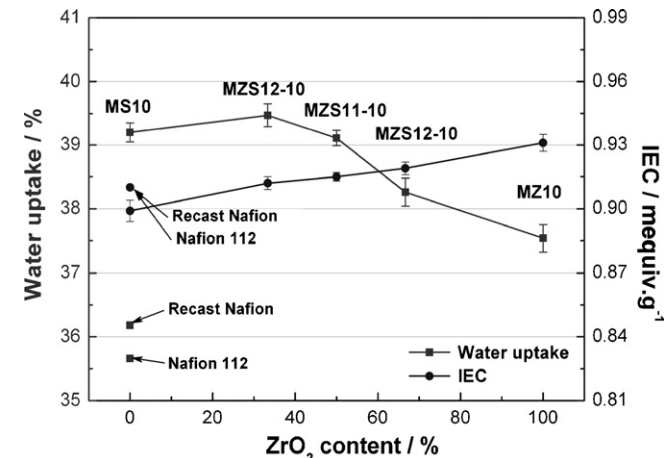
group in $Zr(OH)_4$ [15]. These results show that the binary oxides are successfully synthesized and have Zr–O–Si bonds.

3.2. Thermogravimetric analysis (TGA)

Fig. 3 shows TGA thermograms of the composite membranes together with those of Nafion® 112 and recast Nafion® membranes. There is no significant difference between the Nafion® 112 and recast Nafion® membranes. This means that the procedure for preparing the recast Nafion® membrane does not produce any substantial variation in the original polymer. The loss of mass at approximately $100\,°C$ corresponds to water desorption. The de-sulfonation process begins at approximately $280\,°C$, and the CF_2 backbone chains start to decompose after $400\,°C$. The temperature at which these decompositions occur shift in the composite membranes. For example, the inset in Fig. 3 shows that the unmodified membranes are de-sulfonated
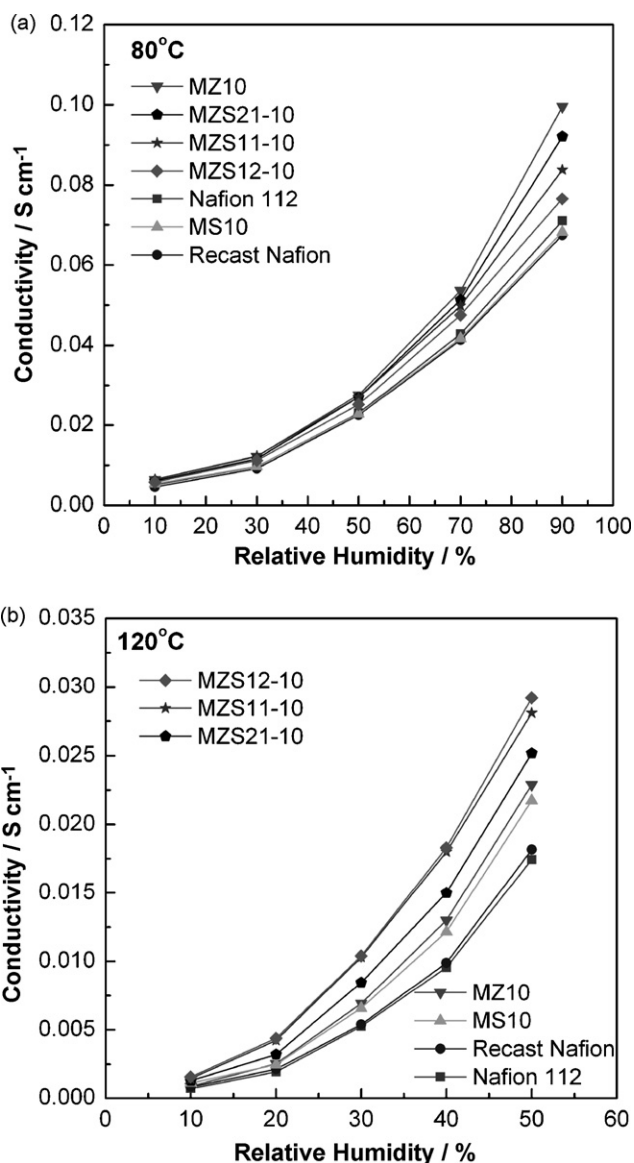

Fig. 4. Water uptake and IEC measurements for all membranes as a function of zirconia content.

Fig. 5. Proton conductivity of membranes as a function of RH: (a) $80\,°C$, 30–100% RH and (b) $120\,°C$, 10–50% RH.

at approximately 280 °C. By contrasts, de-sulfonation of the composite membranes begins at approximately 300 °C. Thermal degradation of the backbone chain of the unmodified membranes occurs at approximately 400 °C, whereas the temperature shifts to about 410 °C for the composite membranes. Above 600 °C, the unmodified membranes are completely decomposed whereas the composite membranes are decomposed to approximately 10% (w/w) due to the remaining inorganic compounds.

3.3. Ion-exchange capacity and water uptake of membranes

Fig. 4 shows the water uptake and IEC measurements for all the tested membranes as a function of the zirconia content. All the composite membranes display better water uptake than the unmodified membranes. A different water uptake is observed for recast Nafion® and Nafion® 112. The recast Nafion® shows a slightly higher water uptake of about 0.5% (w/w) than Nafion® 112 due to the crystallinity of membrane. The recast Nafion® treated at 160 °C has lower crystallinity than Nafion® 112 and the water uptake increases with decreasing crystallinity [18]. Water uptake is also enhanced with increasing silica content, except for the MS10 sample, particularly in the case of compos-

ite membranes containing binary oxides. On the other hand, the IEC of the composite membranes increases with increasing zirconia content. These results demonstrate the relative effects of the zirconia and silica contents on the enhancement of the IEC and water uptake, respectively. Tarafdar et al. [14] reported that ZrO_2–SiO_2 binary oxides contain both Lewis and Brönsted acid sites. The number of Lewis acid sites increases with increasing silica content, while the number of Brönsted acid sites decreases. The Brönsted acid sites provide extra proton-exchanging sites and the Lewis acid sites attract water molecules in the composite membrane. Therefore, the zirconia and silica in the binary oxide can enhance the proton conductivity and the water uptake of the composite membrane, respectively.

3.4. Proton conductivity measurements

The effects of the binary oxide were also examined by proton conductivity measurements. Fig. 5(a) shows the proton conductivity of the membranes at 80 °C and different RH conditions. As expected, the proton conductivity increases with increasing zirconia content. The MZ10 containing only ZrO_2 has the highest proton conductivity. The order of proton conductivity is
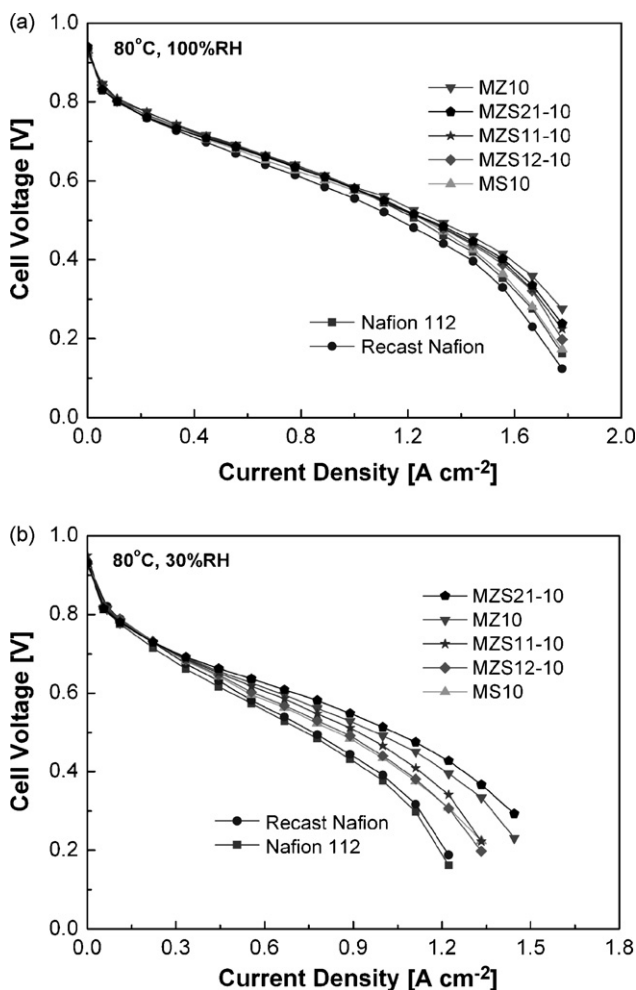

Fig. 6. Polarization curves for membranes at 80 °C: (a) 100% RH and (b) 30% RH.
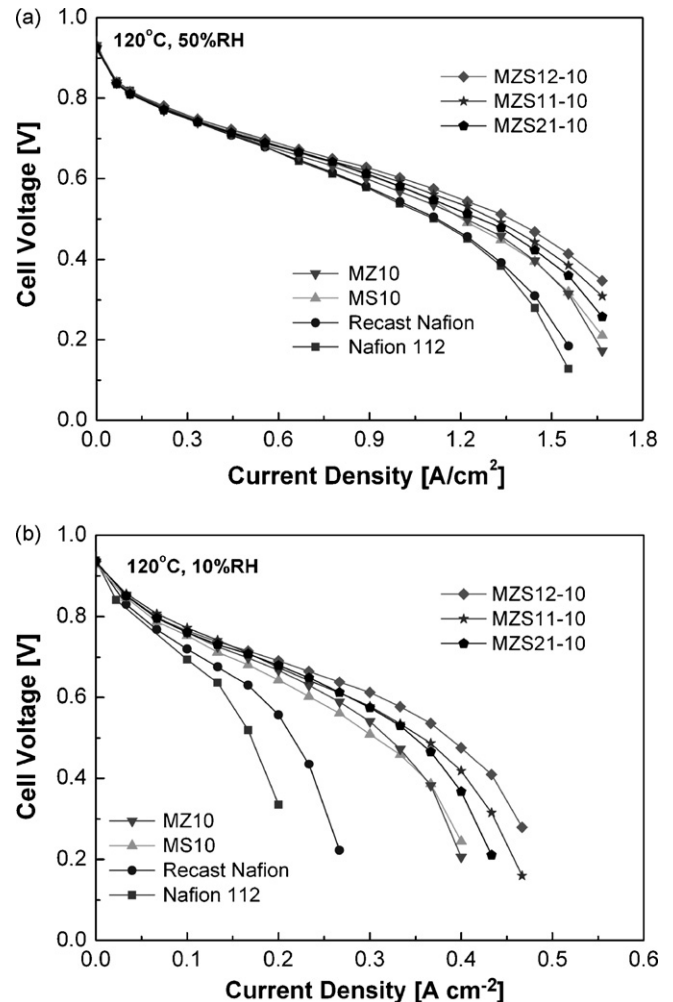

Fig. 7. Polarization curves for membranes at 120 °C: (a) 50% RH and (b) 10% RH.

reversed at 120 °C, as shown in Fig. 5(b). This can be explained by the synergistic effects of both oxides. At temperatures below 100 °C, water molecules can exist in the liquid state and are used to conduct protons. Above 100 °C, however, almost all water molecules exist in the vapour phase. Under this severe condition, the effect of zirconia cannot be determined due to the insufficient water content in the membrane. The silica content in the binary oxide provides extra water to the membrane because it provides Lewis acid sites. Consequently, the binary oxide is effective in improving the proton conductivity at 120 °C, and MZS12-10 shows the highest proton conductivity.

3.5. Single cell performance

Figs. 6 and 7 give the polarization curves of the single cells with Nafion® 112, recast Nafion®, and composite membranes at 80 °C and 120 °C, respectively. Comparison of Fig. 6(a) and (b) shows that the composite membranes are more effective at low RH conditions, and membranes containing a high-zirconia content display good performance with MZS21-10 providing the best performance. By contrast, the cell performances increase

with increasing silica content in the composite membrane containing the binary oxide at 120 °C, as illustrated in Fig. 7. These results are in accordance with those for water uptake and proton conductivity.

The polarization curves for recast Nafion® and Nafion® 112 are similar for 100% and 30% RH at 80 °C and 50% RH at 120 °C, but are different for 10% RH at 120 °C, see Fig. 7(b). The recast Nafion® yields a better cell voltage than Nafion® 112 because the water uptakes of recast Nafion® is high compared with Nafion® 112 as shown in Fig. 4. This difference is not seen at low temperature or moderate RH conditions.

A comparison of the polarization curves for the binary oxide with the physically mixed oxide is given in Fig. 8. The MZS11-10 and MZS11-10P contain a binary oxide and physically mixed oxides at the same composition, respectively. MZS11-10 gives higher performance than MZS11-10P. Therefore, the binary oxide is more effective as inorganic filler for electrolyte membranes than a mixture of each oxide. It is believed that the synergistic effects are more effective when the both oxides co-exist in a single particle.

4. Conclusions

Fine particles of a ZrO_2–SiO_2 binary oxide are synthesized with different Zr:Si ratios, and composite membranes are prepared using the recasting procedure. The bonding structure of the binary oxide and the Si–O–Zr linkage are verified by FT-IR spectroscopy. Scanning electron micrographs confirm good distribution of inorganic fillers in the polymer matrix, and thermogravimetric analysis shows the presence and amount of inorganic fillers.

Water uptake increases with increasing silica content, and the proton conductivity is enhanced with increasing zirconia content at 80 °C. The order of proton conductivity is reversed at 120 °C, particularly for the composite membranes containing binary oxides; the MZS12-10 sample provides the highest conductivity. These results are confirmed by cell performance measurements. The highest power density of 657 mW cm^{-1} at 80 °C with 100% RH is obtained for MZ10, while MZS12-10 gives the best performance of 683 mW cm^{-1} at 120 °C with 50% RH. A comparison of the binary oxide with physically mixed oxide shows MZS11-10 to have a higher performance than MZS11-10P. Consequently, the binary oxide is found to be effective in improving proton conductivity and water uptake at high temperatures and low humidity.
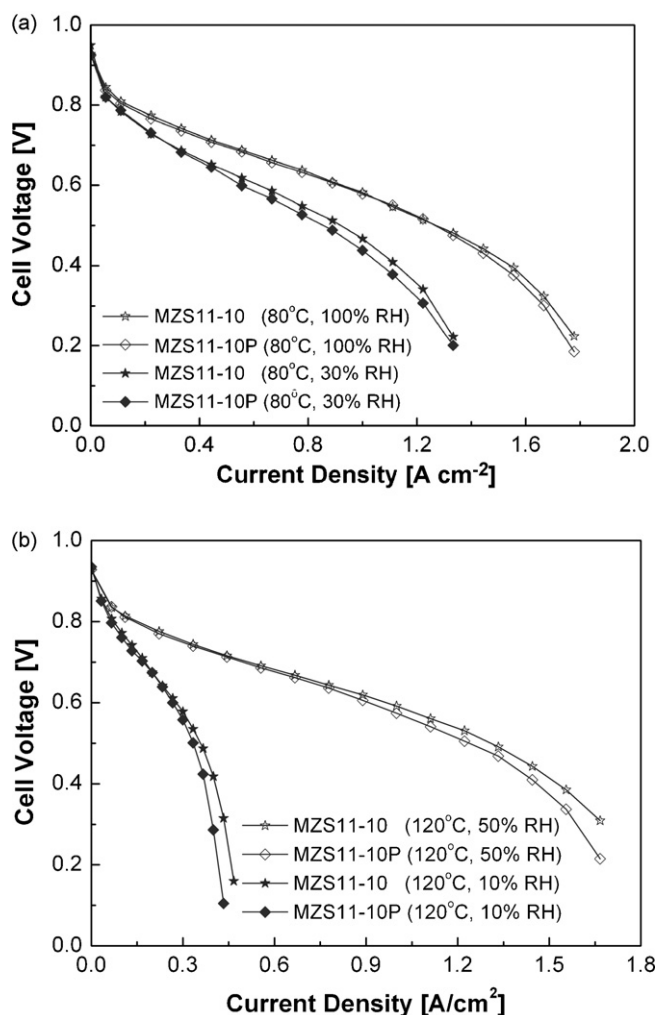
Fig. 8. Polarization curves for binary oxide (MZS11-10) and physically mixed oxide (MZS11-10P) at (a) 80 °C and (b) 120 °C different RH conditions.

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