ZrO_2-SiO_2 복합 입자를 이용한 PEMFC용 유기-무기 복합 전해질 막 제조

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Organic-Inorganic composite membrane for PEMFC using ZrO_2-SiO_2 Binary Oxide

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Introduction

The operation of polymer electrolyte membrane fuel cells (PEMFCs) at high temperature above 100℃possesses many advantages such as faster electrode kinetics, higher tolerance to impurities in fuel gases, smaller heat exchanger, and easier water thermal management. For these reasons, the research has been focused on development of membranes for high temperature and low humidification level by modification of conventional perfluorosulfonic acid (PFSA) membrane via incorporation of various inorganic fillers. The inclusion of inorganic species, hydrophilic and/or proton conductive compounds such as inorganic oxides (ZrO_2, SiO_2, TiO_2, etc.) improves thermo-mechanical properties, water retention, and proton conductivity of membrane at high temperature.

This study is to synthesize fine particle of ZrO_2-SiO_2 binary oxide and to prepare recast Nafion® composite membranes containing different ZrO_2-SiO_2 composition. The composite membranes were characterized and the performance of a single cell was compared with commercial Nafion® 112.

Experimental

The fine particles of ZrO_2-SiO_2 binary oxide were synthesized by sol-gel technique using sodium silicate and carbonate complex of zirconium as an inorganic filler. Then the composite membranes were prepared by mixing a 10% (w/w) Nafion®-water dispersion with the inorganic compound and casting on a glass plate by the Doctor-Blade casting method. The cast membranes were dried at 40℃for 12h and heated at 160℃for 1h. Finally, the membranes were purified by H_2O_2 and H_2SO_4 treatments. The prepared composite membranes contain 10% (w/w) inorganic fillers of different Zr/Si ratio as described in Table 1.

The prepared inorganic particles were characterized by Fourier transform-infrared (FT-IR) spectroscopy. The physico-chemical properties of the membranes were investigated by water uptake (Wup%) and proton conductivity (S/cm). The electrochemical measurements were carried out using a 9cm^2 commercial single cell at 80 ^{o}C, 1 atm and 120 ^{o}C, 2 atm in humidified H_2/air of different relative humidity (RH).

Results and discussion

FT-IR spectroscopes of ZrO_2-SiO_2 particles are shown in Fig. 1. The spectroscopes of binary oxides show a sharp peak at 1017 cm^{-1} indicating Si-O-Si asymmetric stretching vibration compared with pure silica at 1100 cm^{-1}. The shift in stretching frequency is due to Si-O-Zr bond in the composite material.

All composite membranes exhibited better water uptake than unmodified Nafion® 112 and recast Nafion®. The water uptake was also enhanced with increasing silica content except for MS10, especially in case of composite membranes containing binary oxides.

A. Tarafdar et al. reported that ZrO_2-SiO_2 binary oxides have both Lewis and Brönsted acid sites. While Lewis acid sites increases with increasing silica content, 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, zirconia and silica of binary oxide can enhance the proton conductivity and the water uptake of composite membrane, respectively.

As we can expect, the proton conductivity is increased with increasing zirconia content. The MZ10 containing only ZrO_2 shows the highest proton conductivity. However, the order of proton conductivity was reversed at 120 ^oC as shown in Fig. 3(b). These results can be explained by the synergy effects of both oxides. At low temperature below 100 ^oC, water molecules can be existed as liquid water and are used to proton conducting by vehicle mechanism, but almost all water molecules are existed in vapor phase at above 100 ^oC. In this severe condition, the effect of zirconia can not be exhibited enough due to the insufficient water content in the membrane. Silica content in the binary oxide provides extra water content to the membrane because silica is more attractive to water molecules than zirconia. Consequently, the binary oxide was effective to improve the proton conductivity at 120 ^oC and MZS12-10 shows the highest proton conductivity.

Conclusions

The fine powder of ZrO_2-SiO_2 binary oxide was synthesized and the composite membranes of different compositions were prepared by recasting procedure. The bonding structure of binary oxide and Si-O-Zr linkage were verified by FT-IR spectrums. Water uptake was increased with increasing silica content and proton conductivity was increased with increasing zirconia content at low temperature. However, the order of proton conductivity was reversed at 120 ^oC because silica content in the binary oxide provides extra water content to the membrane. These results are obviously confirmed by cell performance measurements. The best performance was exhibited in MZS21-10 at 80 ^oC and MZS12-10 at 120 ^oC, respectively. Consequently, the binary oxide was effective to improve the proton conductivity and water uptake at high temperature and low humidity.

Acknowledgements

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Table 1. Types and inorganic content of the tested membranes

Membrane	Inorganic filler	Inorganic content (% w/w)
Nafion® 112	-	0
Recast Nafion®	-	0
MZ10	ZrO_2	10
MZS21-10	ZrO_2-SiO_2 (Zr/Si = 2)	10
MZS11-10	ZrO_2-SiO_2 (Zr/Si = 1)	10
MZS12-10	ZrO_2-SiO_2 (Zr/Si = 0.5)	10
MS10	SiO_2	10

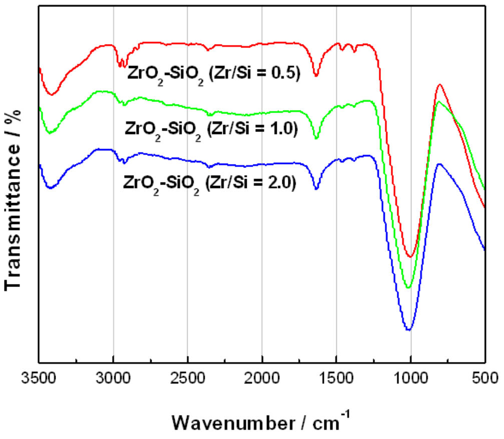


Figure 1. The FT-IR spectrums of ZrO_2-SiO_2 particles.

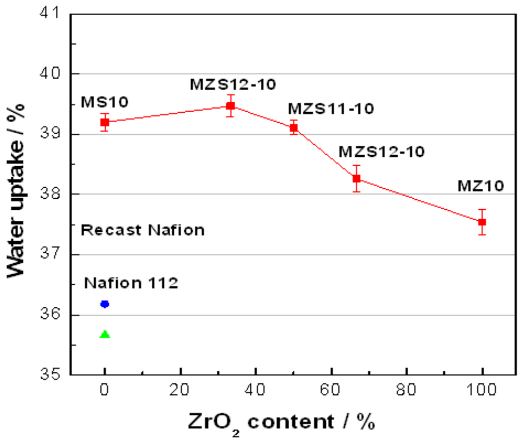
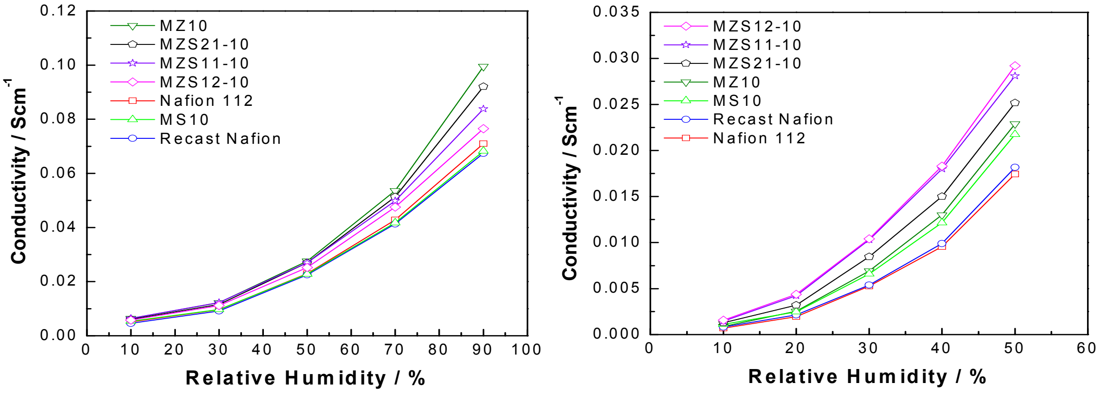
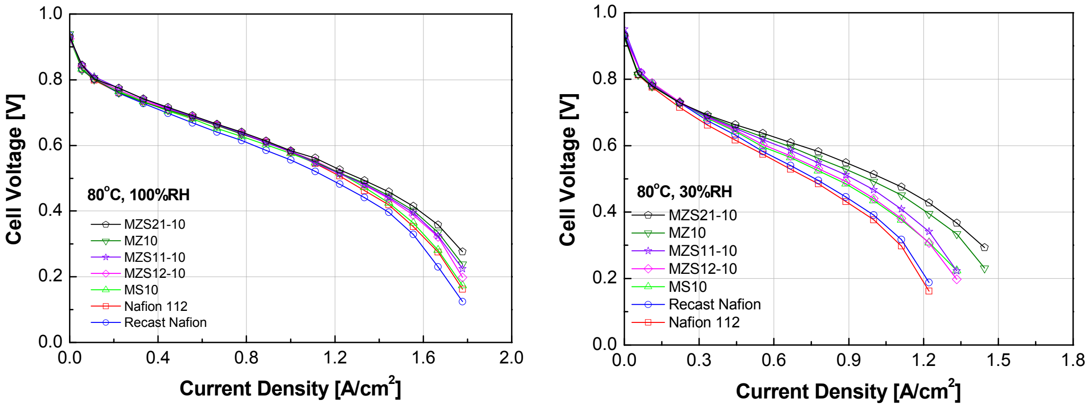


Figure 2. Water uptake of all tested membranes as a function of zirconia content.



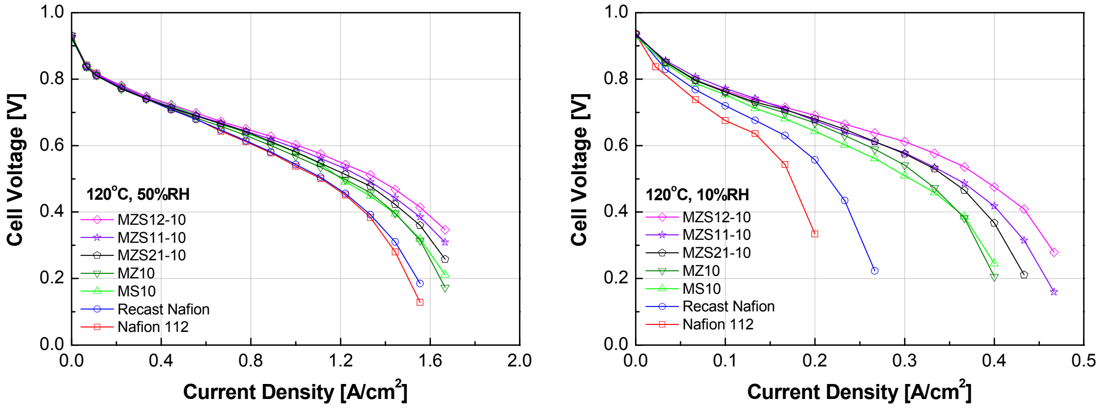
(a) (b)

Figure 3. Proton conductivity as a function of RH: (a) 80 °C, 30%RH~100%RH; (b) 120°C, 10%RH~50%RH.



(a) (b)

Figure 4. Polarization curves for all tested membranes at 80℃ (a) 100% RH; (b) 30% RH.



(a) (b)

Figure 5. Polarization curves for all tested membranes at 120℃ (a) 50% RH; (b) 10% RH.