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Heteropolyacid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) Incorporated Solid Polymer Electrolyte for PEMFC

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1 INTRODUCTION

In the last twenty years, much efforts have been carried out to develop the proton exchange membrane fuel cell (PEMFC). The PEMFC have several advantages: high power density, compactness, high performance, quick and stable operation at low temperature, non electrolyte leakage, and so on¹⁾. Due to these advantages, the PEMFCs have already applied to the military and aerospace sectors. PEMFCs are expected to be utilized in terrestrial transportation in near future.

Even with the latest advances of the fuel cell technology, in this PEMFC system, Nafion is mainly used for polymer electrolyte due to its high conductivity, high permselectivity, physicochemical stability and mechanical strength. Because Nafion structure consists of chemically stable hydrophobic ($-\text{CF}_2-\text{CF}_2-$) and hydrophilic groups (SO_3F), the superacidity is attributed to the electron-withdrawing effect of the perfluorocarbon chain acting on the sulfonic acid group and promotes the fast proton transfer in the Nafion structure²⁾. But the PEMFCs showed some drawbacks that have prevented these systems from large-scale applications, due to the high cost of the polymer membrane (perfluoro sulfonic acid membrane, Nafion) and novel electrocatalyst (Pt based catalysts)³⁾.

Instead of high cost Nafion membrane, new alternative membrane showed low conductivity or unstability⁴⁾.

In addition, several heteropoly compounds have long been used as good cluster models of mixed oxide catalysts and widely used as catalysts for various industrial processes, such as oxidation, hydration, esterification and etheration⁵⁾. Heteropolyacids are acid forms of heteropolyanions formed with condensation of different kinds of oxoacids. The heteropolyacids with the Keggin type anions such as $\text{PW}_{12}\text{O}_{40}^{3-}$ (Fig. 1) are soluble in polar solvent and stable. The strong acidity of heteropolyacid is attributable to the large size of polyanion having low and delocalized charge density. Some researches were carried out to investigate how heteropoly compounds influenced the electrocatalytic activity. The hydrate form of $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{nH}_2\text{O}$ has high proton conductivity ($0.18 - 0.17 \text{ Scm}^{-1}$). The activation energy of proton conduction is much lower than that of the other solid proton conductors. Savadogo⁶⁾ reported that improvement in the overpotential and current density of the hydrogen evolution reaction using modified Ni electrode with $\text{H}_3\text{Mo}_{12}\text{O}_{40}^{3-}$, $\text{PW}_{12}\text{O}_{40}^{3-}$, and $\text{SiW}_{12}\text{O}_{40}^{4-}$. The 2%Pt-1% H_2WO_4 based electrode was found to result in a performance several times better for the oxygen reduction reaction⁷⁾. But no study has been performed to improve the performance of polymer electrolyte by using heteropolyacid.

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Fig. 1 The structure of the Keggin anion ($\text{PW}_{12}\text{O}_{40}^{3-}$).

In this study, a new composite electrolyte membrane for PEMFC was prepared with blending of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and the sulfonated polysulfone polymer, and the unit cell performance of PEMFC system was investigated.

2 EXPERIMENTAL

2.1 Preparation of membrane

The schematic preparation procedure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ incorporated membrane and electrode assembly are shown in Fig. 2. 12-Tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, abbreviated as PW) was commercially obtained from Junsei Chemical Co.. For the purification, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was recrystallized with deionized water after extraction with ethyl ether. Sulfonated polysulfone (abbreviated as SPSF) was prepared with sulfonation reaction suggested by Johnson et al.⁸⁾. The unit chemical structure of SPSF is shown in Fig. 3.

PW and SPSF were blended with common solvent, dimethyl formamide ($\text{HCON}(\text{CH}_3)_2$, Aldrich Chem.) and stirred for 24 hours at room temperature. The $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and sulfonated polysulfone were completely soluble in dimethyl formamide. The weight ratio of PW to SPSF was varied into PW (0%):SPSF(100%), PW(15%):SPSF(85%), and PW(30%):SPSF(70%), respectively. The PW-SPSF membrane was prepared by spin coating the PW-SPSF mixture on a glass plate to form a thin film of 30-200 μm thickness. The prepared PW-SPSF membrane was dried for 24 hours under vacuum condition at 80 $^{\circ}\text{C}$.

Fig. 2 Schematic preparation procedure of PW-SPSF and electrode assembly.

2.2 Preparation of electrode assembly

In this work, commercial electrodes (Vulcan XC-72, Globe Tech. Inc.) were used. Membrane and electrode assemblies were

prepared with the following steps; (i) brushing a 5% Nafion solution into the commercial electrode, (ii) evaporation of solvent(isopropyl alcohol) in the Nafion solution at 80°C for 2hr, and (iii) hot pressing a pair of these electrodes on both sides of a PW-SPSF membrane with a pressure of 120kg/cm² at 120°C.

Fig. 3 Unit structure of sulfonated polysulfone.

2.3 Performance test

The gases (O₂ and H₂) were controlled with mass flow controller. The flow rate of H₂ and O₂ were 100ml/min and 200ml/min, respectively. The gases were passed through a water bath kept at a constant temperature (80°C). The DC electrical parameters of the cell were controlled with an electronic load (HP6050A).

3 RESULTS AND DISCUSSION

Figure 4 shows the FT-IR spectra of PW-SPSF membranes having different PW contents. The primary structure(Keggin structure) of H₃PW₁₂O₄₀ can be identified by the characteristic bands of IR spectra. The FT-IR bands at 810cm⁻¹, 895cm⁻¹, 980cm⁻¹, and 1080cm⁻¹ can be attributed to the interaction of W-O-W, W-O-W, W=O, and P-O bonds, respectively. As shown in Fig. 4, it shows that the characteristic bands of Keggin structures in heteropolyacid incorporated membrane(b,c), and the intensities of characteristic bands of

primary structure at PW(30%)-SPSF(70%) is stronger than that of PW(15%)-SPSF(85%) membrane. Due to the effect of SPSF polymer and SO₃ bands in SPSF, the other bands of PW-SPSF membranes are found in Fig. 4. These FT-IR results shows that the H₃PW₁₂O₄₀ keeps its Keggin structure after blending with SPSF polymer. As a result, Keggin structure and sulfonic acid group in SPSF polymer form a proton conducting layer in composite membrane.

Fig. 4 FT-IR spectra of (a) PW(0%)-SPSF(100%), (b)PW(15%)-SPSF(85%), and (C) PW(30%)-SPSF (70%) membranes.

The SEM photographs of PW(30%)-SPSF(70%) membrane is shown in Fig. 5. There was no cracks or shrinkage of polymer on the surface of PW-SPSF membrane. H₃PW₁₂O₄₀ was not crystallized into large particles after membrane preparation. It shows that the H₃PW₁₂O₄₀ with SPSF polymer

blended homogeneously in a composite membrane.

With the FT-IR and SEM results, we found that the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is highly dispersed in the membrane structure. To evaluate the gas permeability of composite membrane, permeation tests of O_2 and H_2 gas using standard permeation cell were carried out⁹⁾. The gas permeabilities of O_2 and H_2 gas were almost negligible and it may be attributed to the dense micro structure of membrane as shown in Fig 5.

Fig. 5 SEM image of PW(30%)-SPSF(70%) membrane.

Figure 6 shows the effect of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loading on the cell voltage versus current density relations. To obtain the curves in Fig. 6, the cells were operated at 70°C and atmospheric pressure. The current density of SPSF membrane without $\text{H}_3\text{PW}_{12}\text{O}_{40}$, PW(0%)-SPSF(100%), was $14\text{mA}/\text{cm}^2$ at 700mV. The current densities of composite polymer membranes, PW(15%)-SPSF(85%) and PW(30%)-SPSF(70%), were $26\text{mA}/\text{cm}^2$ and $55\text{mA}/\text{cm}^2$, respectively. The current density of PW(30%)-SPSF(70%) was three times higher than that of PW(0%)-

SPSF(100%) membrane. Also, the maximum value(990mV) of the open circuit voltage (OCV) was achieved at the PW(30%)-SPSF(70%) membrane. Consequently, the heteropolyacid incorporated membrane showed high current density and the current density was increased linearly with the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loading.

Fig. 6 Cell voltage vs. current density plot for various PW weight ratio (Globe tech's electrode, electrode area = 2cm^2 , PW membrane thickness = $30\mu\text{m}$, operating at 70°C , and $\text{H}_2/\text{O}_2 = 1/1$ atm.).

The impedance spectra of heteropolyacid incorporated membrane was shown in Fig. 7. From the Nyquist plot, it showed that the membrane resistance of PW(0%)-SPSF(100%) was 1.6 ohm and the interfacial resistance was 4.7 ohm. These impedance results of sulfonated polysulfone electrolyte were compared to that of commercial Nafion 115 at the same condition (Globe Tech's electrode and 700mV). The Nafion had lower membrane resistance (0.21 ohm) and interfacial

resistance(0.19 ohm) than that of SPSF electrolyte. On the other hand, the membrane and interfacial resistances of PW(30%)-SPSF(70%) membrane decreased to 0.96 ohm and 1.04 ohm, respectively. These results clearly showed a significant effect of $H_3PW_{12}O_{40}$ on the membrane and interfacial resistance. Namely, super acidity in $H_3PW_{12}O_{40}$ increased the proton conductivity in the electrolyte and also decreased the interfacial resistances between polymer electrolyte and Pt/C electrode (anode /cathode).

Fig. 7 Nyquist diagram for various PW weight ratio(Globe tech's electrode, electrode area=2cm², PW membrane thickness=30μm, operating at 70 °C, and $H_2/O_2=1/1$ atm.).

The current-voltage characteristics(Fig. 6) and impedance results(Fig. 7) of PW-SPSF membrane show the promotion effect of $H_3PW_{12}O_{40}$ on PEMFC performance. Based on these results, the main promotion effect of heteropolyacid on the cell performance can be attributed to the increased proton conductivity of PW-SPSF membranes. Namely, in our humidity condition of PEMFC, the hydrate form of heteropolyacid acted as high proton conductor¹⁰⁾, which resulted in the decreased

charge-transfer overpotential of interfacial resistance between membrane and electrode. Also, the activation overpotential was decreased by the addition of $H_3PW_{12}O_{40}$ in the sulfonated polysulfone electrolyte. The Tafel slope(0.370V/decade) of PW(30%)-SPSF(70%) was lower than that of other membranes(more than 0.400V/decade).

The PW-SPSF electrolyte showed lower performance than that of commercial Nafion electrolyte at given potential. It can be due to the lower proton conductivity of PW-SPSF than that of Nafion, and PW-SPSF electrolyte have higher resistances compared to Nafion membrane. However, these problems might be solved and the heteropolyacid incorporated polymer electrolyte would be very promising as a alternative material of the Nafion membrane. More improvements on the heteropolyacid compounds as well as SPSF electrolyte polymer materials should be attempted for practical utilization in PEMFC system.

4 CONCLUSION

A new composite polymer membrane for proton exchange membrane fuel cell(PEMFC) was prepared with the incorporation of $H_3PW_{12}O_{40}$ (PW) into sulfonated polysulfone(PSPF). $H_3PW_{12}O_{40}$ homogeneously incorporated in the SPSF matrix(PW-SPSF) and the Keggin structures of $H_3PW_{12}O_{40}$ were maintained during the process of polymer blending. The addition of $H_3PW_{12}O_{40}$ increased the ionic conductivity and showed the lower resistance of proton transfer in PW-SPSF composite membrane. The current density of PW(30%)-SPSF(70%) membrane

was 55mA/cm² at 700mV, which is three times larger than that of PW(0%)-SPSF(100%) membrane.

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