

PREPARATION AND PROPERTIES OF NAFION[®] NANOCOMPOSITE BASED ON ZIRCONIUM PHENYLPHOSPHATE LAYERD COMPOUND

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1 Introduction

PEMFC operating at high temperatures ($> 90\text{ }^{\circ}\text{C}$) has advantages such as higher system efficiency, flexibility in fuel selection and simplification in water management. However, most commercialized membranes are based on sulfonic-acid moieties, which are not dissociable at anhydrous conditions. But phosphonic acids could be conductive at higher temperatures due to their self-dissociation nature.

Therefore, we synthesized solid proton conductors by grafting alkyl phosphonic acids to zirconium phosphate. The synthesized zirconium diphosphophenyl phosphate (Zr3P) showed the very high conductivity over 10^{-2} S/cm at anhydrous conditions above $120\text{ }^{\circ}\text{C}$.

In our previous research, to solve the poor proton conductivity of Nafion[®] at high temperature, we developed the nanocomposite membranes of Nafion[®]/inorganic particles. Zirconium phosphate (ZrP) is one of the most promising high temperature proton conductors because of high ion exchange capacity, thermal stability, insolubility in concentrated acid, but the proton conductivity of ZrP was very low (10^{-5} S/cm at $120\text{ }^{\circ}\text{C}$). So we developed nanocomposite membrane of hydrocarbon polymer containing layered inorganic filler with phosphonic acid, and then we developed Nafion[®]/Zr3P nanocomposite membrane. Nanocomposite membrane is predicted to improve proton conductivity of Nafion[®] under anhydrous condition at high temperatures (0.01 S/cm at $120\text{ }^{\circ}\text{C}$). Zr3P will be expected for using nanocomposite membrane material for PEMFC to improve the proton conductivity at high temperature.

2 Experimental

2.1 Preparation of zirconium diphosphophenyl phosphate

1,3,5-Tribromobenzene and 1,3-diisopropylbenzene were heated to $155\text{ }^{\circ}\text{C}$ for 15 min. After the reaction mixture was cooled to Room Temperature, nickel(II) bromide was added and Triisopropyl phosphite was added at $150\text{ }^{\circ}\text{C}$ during 3 hr. Then volatile components were distilled off to obtain a dark viscous residue. Chromatography of the residue was performed on a column of silica gel eluted with ethyl acetate. And obtained hexaisopropyl 1,3,5-benzenetriphosphonate. Concentrated hydrochloric acid, hexaisopropyl 1,3,5-benzenetriphosphonate, and distilled water were refluxed for 24 hr. The hydrolyzed solution was evaporated to dry. Then the residue was dissolved in distilled water; the solution was treated with charcoal, and the filtrate was evaporated to 1,3,5-Benzenetriphosphonic acid (BTP) as a white solid.

BTP was dissolved in distilled water in a plastic bottle by heating and stirring at $60\text{ }^{\circ}\text{C}$. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in distilled water in another plastic bottle, to which HF was added. The bottle was kept at $80\text{ }^{\circ}\text{C}$. The two bottles of solutions were then combined and stirred in a single plastic vessel. The plastic vessel was left open to the atmosphere to reduce the liquid volume. Heating was carried out over a three-day period, during which time a fine white precipitate formed. The solution was filtered and washed with distilled water several times. The resulting precipitate was dried in a vacuum.

2.2 Preparation and characterization of Nafion[®]/Zr3P nanocomposite membrane

The Nafion[®] gels were precipitated from commercial 5 wt% Nafion[®]/H₂O/propanol solution

(Solution Technology, EW= 1100) by removing solvents at room temperature under vacuum. After they were dissolved in N,N-dimethylacetamide (DMAc, Aldrich) at 80 °C, 5 wt% Nafion®/DMAc solution was ultrasonically mixed with Zr3P dispersed in distilled water for 4 hr at 50 °C, and it was cast onto a glass plate above 100 °C in a convection oven. Nafion®/Zr3P nanocomposite membranes were placed in 1M phosphoric acid for 24 hr at 80 °C and boiled in 3% H₂O₂ solution for 1 hr to remove organic impurities then thoroughly rinsed with distilled water.

In order to compare with Zr3P, we synthesized zirconium phenyl phosphate (ZrPP). ZrPP was similar structure with Zr3P except phosphonic acid which was chemically bonded with benzene ring.

The chemical structure of Zr3P was confirmed by Transformation Infrared (FT-IR) spectra (Thermo Electron Corp./Nicolet 380) in the range of 4000 ~ 400 cm⁻¹. ³¹P Nuclear Magnetic Resonance (NMR) (Varian/UnityInvor-500) was applied to verify chemical changes of phosphonic acid group.

X-ray diffraction (XRD) measurement was carried out with a Rigaku Rad-C 4037A1 diffractometer in symmetrical reflection geometry using Cu K emission ($\lambda = 1.5406 \text{ \AA}$) to observe exfoliated state of nanocomposite membrane.

Proton conductivity of the membrane was determined by ac impedance spectroscopy (Solartron impedance analyzer). The sample membranes were placed in the coaxial BEEKTech conductivity cell, which was put between the unit cell hardware and connected to the humidity bottle in order to control humidity and temperature. The frequency range varied from 1 MHz to 1 Hz at a perturbation voltage of 5 mV at galvanostatic mode.

3 Results and Discussion

In ¹H-NMR, BTP showed that was substituted terminal site for phosphoric acid groups. PPA showed 3 peaks at 7.6, 7.4 and 7.3 ppm by phenyl groups. The peak at 7.3 ppm corresponds to phosphoric acid groups, which indicates that phosphoric acid groups were chemically bonded with phenyl groups.

Fig. 1 shows FT-IR spectra of ZrPP and Zr3P. We synthesized Zr3P particles in order to increase proton conductivity at high temperature. Zr3P

contained -PO₃H₂ peak at 1189 ~ 980 cm⁻¹. This peak confirmed the phosphonic acid group which was placed in Zr3P. And IR peak of Zr3P was at 748 and 496 cm⁻¹, corresponding to the C-P bonds to show phenyl ring and zirconium were reacted by phosphonic acid group.

Fig. 2 illustrates ³¹P NMR spectra of ZrPP and Zr3P. In ZrPP, phenyl phosphate group peaks were shown at -6.2 ppm. Whereas, both phenyl phosphate group peaks and phosphonic acid peaks to substituted in benzene ($\delta = 1.65$) were existed in Zr3P. This fact showed proton conducting mechanism was very activated as well as phosphonic acid groups were chemically bonded in benzene.

Fig. 3 shows XRD patterns of Zr3P. ZrPP had layered structure with narrow interlayer distance (ca. 14.4 Å), but that of Zr3P increased to ca. 16.2 Å, because the pendent phosphoric acid groups were introduced in the interlayer region. We confirm that phenyl phosphoric acid was inserted into ZrP interlayer successfully. It resulted in improving the proton transport through the interlayer region by the self dissociation of protons from the strong acidic groups (-PO₃H₂). The proton transport in Zr3P is dominated by the surface -PO₃H₂ groups, it expected to give much higher conductivity (10⁻⁴ S/cm at 120 °C) than ZrPP.

As given Fig. 4, the proton conductivity of Nafion® and Nafion®/Zr3P nanocomposite membrane as a function of temperature from 20 °C to 120 °C. The relative humidity was checked using a measuring instrument certainly. Fig. 7 described all proton conductivities increase until 90 °C, however, because of the dehydration of membrane, Nafion® declined rapidly above 90 °C which was the boiling point of water. Water retention of the membrane is the most important parameter in determining the proton conductivity of Nafion®. At high temperature, the vapor pressure is less than the saturation vapor pressure so net evaporation form the liquid phase in the membrane to air occurs until chemical potentials are equal. This phenomenon causes a dramatic drop in the proton conductivity which is dependent on water content.

On the other hand, the proton conductivity of Nafion®/Zr3P nanocomposite membrane showed similar value compared with that of Nafion® below 90 °C. But above 90 °C, They maintained more than 10⁻² S/cm unlike Nafion®. These proton conductivities originated in proton conducting

mechanism of phosphonic acid as well as sulfonic acid. As stated above strong acids have a special character that they can store some water molecules. These results were caused that function of phosphonic acid was revealed from keeping high proton conductivity. Although the dehydration of the membrane interfered with proton conducting mechanism of sulfonic acid group of Nafion[®], this implied that phosphonic acid in Zr3P might work as a proton conductor at elevated temperature instead of sulfonic group of Nafion[®]. The highest proton conductivity is 0.012 S/cm of Nafion[®]/Zr3P 10 wt% at 120 °C, below 25% RH.

As these results, Nafion[®]/Zr3P could be used for high temperature proton conducting membrane at low humid conditions due to proton conducting mechanism of phosphonic acid.

4 Conclusions

In order to increase proton conductivity at high temperature, we developed Nafion[®] nanocomposite membrane with nano-sized phosphonic acid functionalized zirconium phosphate.

We successfully synthesized Zirconium diphosphophenyl phosphonate (Zr3P) as a solid proton conductor. Zr3P was obtained by precipitation of ZrOCl₂ and 1,3,5-Benzenetriphosphonic acid that has two phosphonic acids. ¹H-NMR, XRD results showed that inorganic particle has layered structure, and strong chemical bonds occurred between them. Zr3P was higher ion conductivity due to its proton conducting nature than ZrPP.

And then we developed Nafion[®]/Zr3P nanocomposite membrane. Nanocomposite membrane is predicted to improve proton conductivity of Nafion[®] under anhydrous condition at high temperatures (0.01 S/cm at 120 °C, <25% RH). Zr3P will be expected for using nanocomposite membrane material for PEMFC to improve the proton conductivity at high temperature.

Due to such high proton conductivity Nafion[®]/Zr3P nanocomposite membrane could be used at high temperature and low humid conditions due to conducting mechanism of phosphonic acid groups at these conditions.

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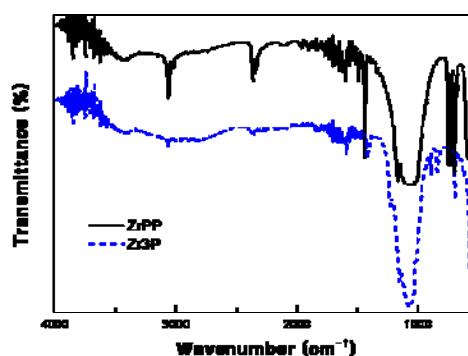


Fig.1. FT-IR spectra of ZrPP and Zr3P

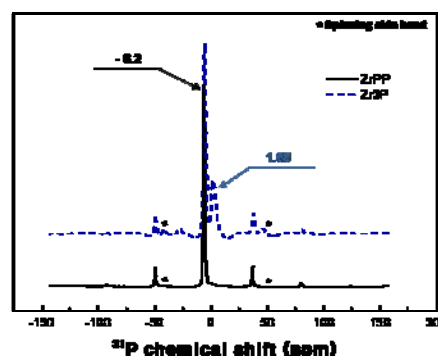


Fig.2. ³¹P NMR of ZrPP and Zr3P

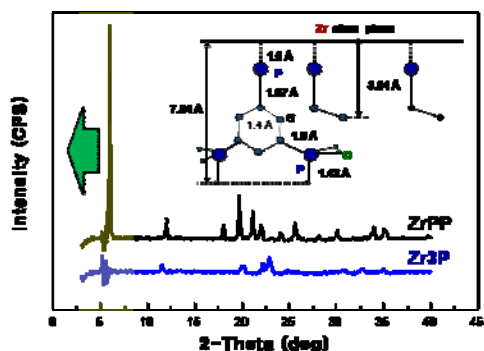


Fig.3. X-ray diffraction patterns of Solid proton conductors.

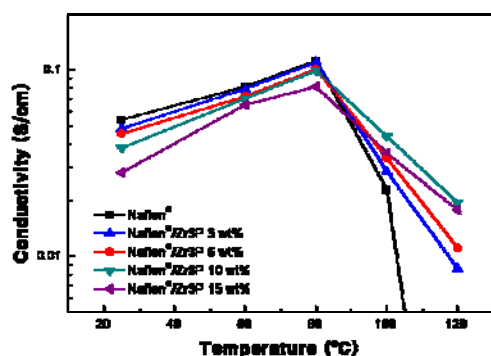


Fig.4. Proton conductivity of Nafion® and Nafion®/Zr3P nanocomposite membrane.

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