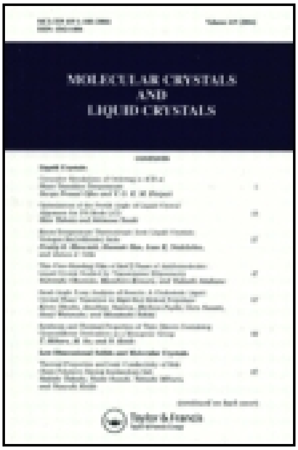

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Preparation of Heteropoly Acid Entraped in Nano Silica Matrix

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Heteropoly acid entraped in nano silica matrix was prepared by the microemulsions method. The primary particle size was less than 400nm and it decreased with the content of the heteropoly acid. When these silica particles were blended with sulfonated polyethersulfone, the HPA could be effectively immobilized in aqueous environment. The conductivity of this composite electrolyte was 1.4×10^{-3} S/cm with the 15% HPA.

Keywords microemulsion; heteropoly acid; proton conductivity; fuel cell

1. INTRODUCTION

HPAs show the high proton conductivity, which is suitable to be used as solid electrolytes and applicable to solid electrolyte, etc.[1,2]. In our previous work[3], the polymer electrolyte containing the HPA showed high proton conductivity, but dissolved in water resulting in the decrease of the fuel cell performance. In this study, to overcome this stability problem, HPA was immobilized in the micropore of nanosized SiO_2 by the microemulsion method[4]. The composite electrolyte was prepared by the mixing the nanosized silica particles with polyethersulfone to measure the proton conductivity.

2. EXPERIMENTAL

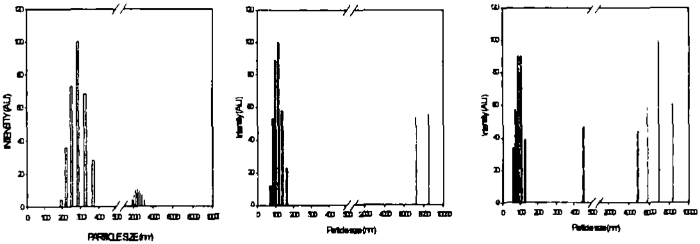
Sodium bis(2-ethylhexyl) sulfosucinate(AOT) as surfactant, cyclohexane as an oil phase, tetraethyl orthosilicate(TEOS) and 12 tungsto(VI) phosphoric acid (PW) were used as received. AOT was dissolved in cyclohexane at 0.3M, and the specified amount of 7.5 wt% PW solution in water was added to form well-defined microemulsion phase. And then, TEOS was dropped in this phase. SiO_2 particles with HPA were obtained after 12hr stirring at room temperature. Dispersed SiO_2 particles in cyclohexane were centrifuged with 15,000 rpm and the particles were rinsed with acetone several times.

Sulfonated polyethersulfone was dissolved in DMF. The polymer solution was mixed with the SiO_2 nano particles immobilized with HPA. And, *the polymer membrane was prepared by* using doctor *blade*. After the film casting, sulfonated polyethersulfone composite membrane was dried in vacuum oven at 80°C. The thickness of membrane was controlled to 45μm.

The composite membrane was characterized by FT-IR, AC impedance apparatus and extraction test of the heteropoly acid in the aqueous solution.

3 . RESULTS AND DISCUSSION

Figure 1 shows the particle size distribution of silica with the various content heteropoly acid(H). At 10% heteropoly acid, the size of silica shows main peaks at 300nm with small intensity at 2000-3000nm. At 20% heteropoly acid, the main peaks appear at 120nm with relatively large peaks at 7000-8000nm. At 30%, the main peak appears at 90nm with large peaks at 450nm and 4000-9000nm. If we assume that these main peakes appeared at the small size(< 400nm) are originated from primary silica particles, the increasing contents of heteropoly acid seems to reduce the primary size of silica. Simultaneously, it also increases the aggregation of primary particles to yield large peaks above few thousand nanometers. These suggest that the amount of the heteropoly acid affects the size of silica due to changing the stability of microemulsion



(a) (b) (c)

FIGURE 1 Particle size distribution of silica
(a) 10% HPA, (b) 20% HPA, (c) 30% HPA

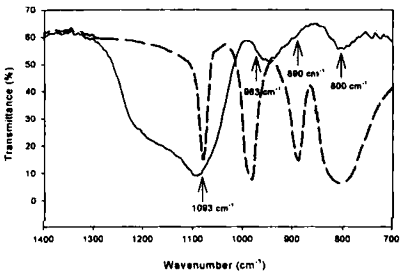


Figure 2 The IR spectra of pure heteropoly acid (dashed line) and the silica containing the 30% heteropoly acid (solid line)

The infrared spectra of the silica particle containing the heteropoly acid was presented in figure 2. 1093cm^{-1}, 983cm^{-1}, 890cm^{-1}, and 900cm^{-1} bands are the characteristic band of the 12 tungsto(VI) phosphoric acid. all the bands representing characteristic bands of heteropoly acid are preserved also in the spectra of SiO_2 particles. The SiO_2 particles prepared by microemulsion method successfully preserve the heteropoly acid and expected to have the proton conducting behavior.

Figure 3 shows the result of elution test of the polymer composite membrane containing the heteropoly acid. When the heteropoly acid was directly mixed with PES without immobilization in silica, the pH of water drastically decreased with immersion time. The decrease of pH in figure 3 was mainly due to the dissolution of heteropoly acid in the composite membrane. On the other hand, PES containing the heteropoly acid immobilized in nano silica particle shows no change of pH with time. Heteropoly acid immobilization in silica was effective to inhibit the dissolution of heteropoly acid in aqueous media.

Conductivity of PES composite membrane containing the immobilized heteropoly acid was presented by the frequency-dependent complex impedence spectra in figure 4. The conductivity of the pure

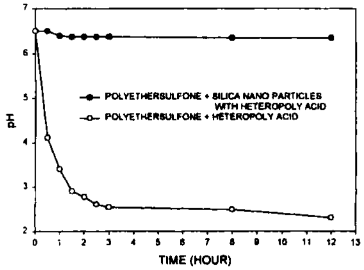


Figure 3 The elution rate of heteropoly acid in the polymer composite membrane

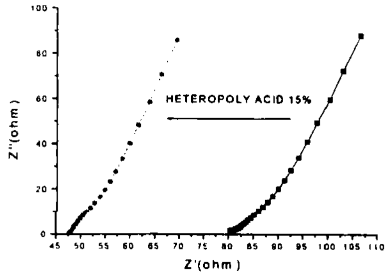


Figure 4 The impedence spectra of the PES composite membrane containing the immobilized heteropoly acid in nanosized silica

sulfonated polyethersulfone membrane was 6.5×10^{-5} S/cm. When the nano silica particles containing the 15% heteropoly acid was added to sulfonated polyethersulfone, the conductivity was drastically increased to 1.4×10^{-3} S/cm. It clearly shows that heteropoly acid enhanced the proton conductivity of the composite polymer membrane.

4. CONCLUSION

Heteropoly acid was successfully immobilized in nano silica matrix. The microemulsion process was promising to produce proton conductive silica. Composite polyethersulfone membrane with this silica showed high stability in the aqueous environment. The conductivity of the sulfonated polyethersulfone membrane was increased to 1.4×10^{-3} S/cm from 6.5×10^{-5} S/cm by the 15% heteropoly acid.

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