

Article

Preparation and Characterization of Organic-Inorganic Hybrid Hydrogel Electrolyte Using Alkaline Solution

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Abstract: Organic-inorganic hybrid hydrogel electrolytes were prepared by mixing hydrotalcite, cross-linked potassium poly(acrylate) and 6 M KOH solution. The organic-inorganic hybrid hydrogel electrolytes had high ionic conductivity ($0.456\text{--}0.540\text{ S cm}^{-1}$) at $30\text{ }^{\circ}\text{C}$. Moreover, the mechanical strength of the hydrogel electrolytes was high enough to form a 2–3 mm thick freestanding membrane because of the reinforcement with hydrotalcite.

Keywords: hydrogel electrolyte; organic-inorganic hybrid; alkaline electrolyte

1. Introduction

Solid polymer electrolytes permitted safer, thinner and more flexible battery designs [1], but their ionic conductivity was insufficient to use in practice. Polymer gel electrolytes, which can stably hold considerable amount of electrolyte solution within polymer matrices, significantly improved ionic conductivity [2,3]. Thus lithium polymer secondary batteries with polymer gel electrolytes have actively been researched and developed. Meanwhile, alkaline secondary batteries such as nickel-metal hydride (Ni-MH) batteries are well-known as safe and environmentally friendly systems compared to

lithium ion batteries and lithium polymer secondary batteries. Moreover, nickel-zinc and silver-zinc batteries are promising systems for their high energy density.

Several researchers have tried applying polymer electrolyte or gel electrolyte to alkaline secondary batteries [4-7]. Iwakura *et al.* firstly prepared a polymer hydrogel electrolyte (PHE) in which a KOH aqueous solution was held in a network structure of the cross-linked potassium poly(acrylate) (PAAK). They found that the PHE had liquidlike ionic conductivity, and applied it to all solid state Ni-MH batteries [8-10]. Inoue *et al.* developed a clay-based inorganic hydrogel electrolyte using hydrotalcite (HT) and KOH aqueous solution, and clarified that it had ionic conductivity comparable to the PHE [11]. However, these hydrogel electrolytes showed too low mechanical strength to form a freestanding membrane. In this work, we tried preparing organic-inorganic hybrid hydrogel electrolytes using PAAK, HT and KOH aqueous solution to realize not only high ionic conductivity but also high mechanical strength. Dispersing carbon black or silica as nanofiller is a popular strategy to reinforce rubber or organic polymer materials [12,13]. In addition, Croce *et al.* found that the nanocomposite polymer electrolytes using polyethylene oxide and LiClO₄ containing TiO₂ and Al₂O₃ nanoparticle had high ionic conductivity [14]. Therefore, it is reasonable to apply HT as nanofiller to reinforce the PHE.

2. Experimental Section

2.1. Preparation of Organic-Inorganic Hybrid Hydrogel Electrolytes

KOH and HT were purchased from Wako Pure Chemical Industries, Ltd. PAAK whose potassium content was 11 wt% was purchased from Sigma-Aldrich. Milli-Q (Millipore) water with resistivity of 18.2 M Ω cm was used in this study. Three kinds of organic-inorganic hybrid hydrogel electrolytes were prepared according to the following procedure: 0.8, 1.6 or 2.4 g of HT was added to 10 mL of 6 M KOH aqueous solution. After being stirred for 5 min, 1 g of PAAK was added to the resultant suspension, followed by stirring for a few minutes and standing for 3 days, resulting in homogeneous milky hydrogel. After that, air bubbles in the gel were removed under a vacuum. All procedures were performed at room temperature. Each hydrogel electrolyte is called hybrid hydrogel(0.8), hybrid hydrogel(1.6) and hybrid hydrogel(2.4), respectively.

2.2. Electrochemical Measurements

Electrochemical measurements were carried out using a potentiostat (SI1287 and SI1260; Solartron Analytical) with a three-electrode configuration cell. An Hg/HgO electrode was used as the reference electrode. Two Pt plates with apparent surface area of 1 cm² were used as the counter and working electrodes, respectively. Ionic conductivity of 6 M KOH solution and three hydrogels was evaluated by ac impedance measurement at a frequency of 100 kHz with the perturbation of 5 mV. A handmade two-electrode conductivity cell consisted of two Pt black-coated Pt electrodes with apparent surface area of 1 cm² was used.

2.3. X-Ray Diffraction Analysis

X-ray diffraction (XRD) spectra of HT and hybrid hydrogel electrolytes were measured by using an X-ray diffractometer (XRD-6100; Shimadzu) equipped with a Cu $K\alpha$ source ($\lambda = 0.1541$ nm, 50 kV, 30 mA).

3. Results and Discussion

Figure 1 shows pictures of the hybrid hydrogel(1.6) and its freestanding membrane. The hybrid hydrogel(1.6) showed white color and tolerance to alkali. The hybrid hydrogel(1.6) kept its shape for hours when it was put on a flat surface (Figure 1(a,b)). In addition, it was possible to form a freestanding membrane with a thickness of 2–3 mm (Figure 1(c,d)). These strongly suggest the hydrogel electrolyte has high mechanical strength. The mechanical strength of the hydrogel electrolyte using only PAAK or HT was too low to form a self-standing membrane. Conventional polymer-clay composites containing aggregated nanolayer tactoids ordinarily improve rigidity, but they often sacrifice elongation and toughness [15]. However, the present hybrid hydrogel electrolytes keep both viscosity and elasticity. Thus, HT is homogeneously dispersed in PAAK matrix and HT works well as nanofiller to reinforce the PHE. Moreover, it should be noted that the hybrid hydrogel electrolytes are prepared just by mixing organic polymer, clay and KOH aqueous solution for only a few minutes. In this way, the hybrid hydrogel electrolytes are readily and quickly prepared.

Figure 1. Photographic images of hybrid hydrogel(1.6) and its freestanding membrane. (a) Top and (b) side views of the hybrid hydrogel(1.6); (c) front and (d) side views of the freestanding membrane.

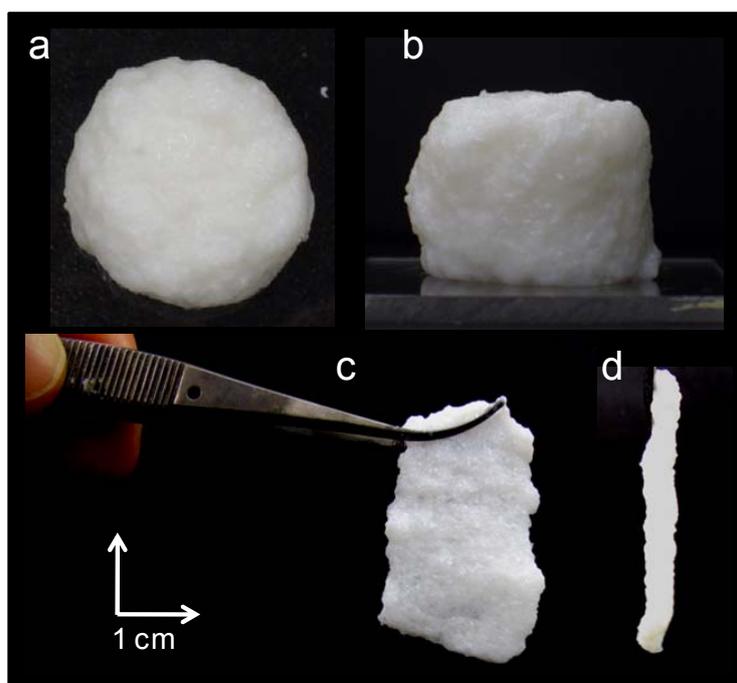


Figure 2 shows XRD spectra of the hybrid hydrogel(1.6) and pristine HT. The hybrid hydrogel(1.6) had diffraction peaks similar to the pristine HT. The lattice distance of the pristine HT was evaluated

as 0.78 nm from the (003) peak and that of HT in the hybrid hydrogel(1.6) was 0.77 nm. In the case of the inorganic hydrogel electrolyte with only HT, lattice distance was increased to 0.81 nm because carbonate was replaced with OH^- upon ion exchange or the degree of hydration increased [11]. In the present case, it is deduced that the hybrid hydrogel(1.6) has lower degree of hydration than the inorganic hydrogel electrolyte. Another is less replacement of carbonate in the interlayer of HT lamellae with OH^- ion. According to the Scherrer's equation, the crystallite size of HT was evaluated as 26.7 nm for the pristine HT and 24.6 nm for the hybrid hydrogel(1.6). Therefore, the number of HT lamellae is estimated to be 35 for the pristine HT and 33 for the hybrid hydrogel(1.6), indicating that most of the HT lamellae were not delaminated in the hybrid hydrogel.

Figure 2. X-ray diffraction (XRD) patterns of hybrid hydrogel(1.6) and pristine hydrotalcite (HT).

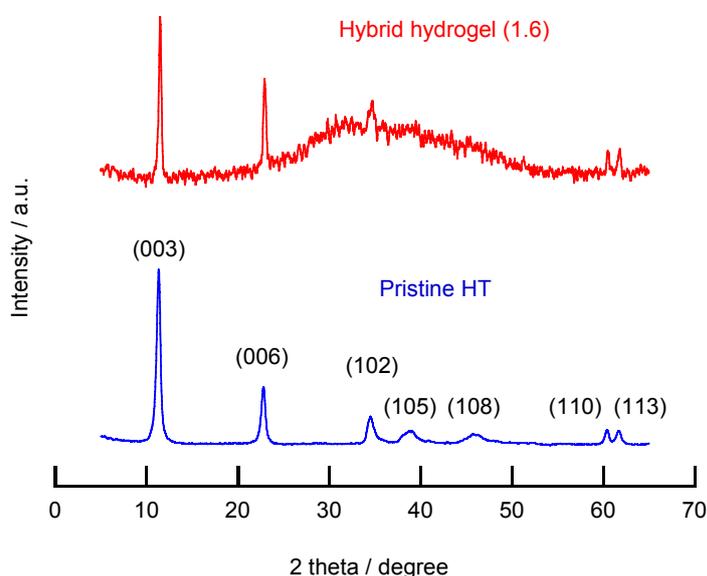
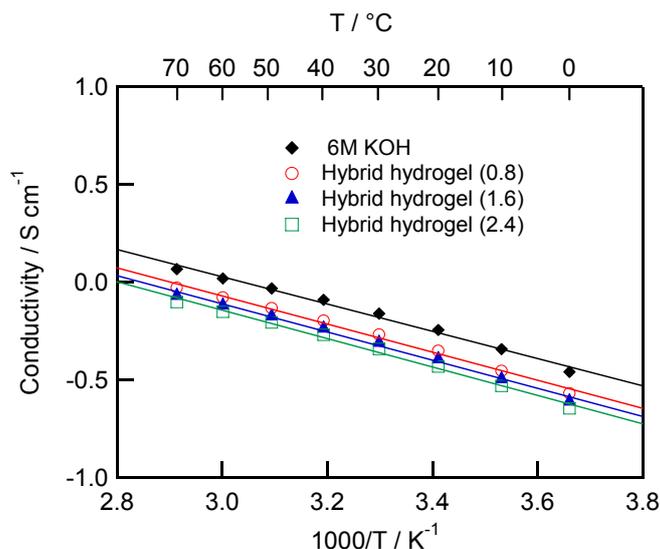


Figure 3 shows temperature dependence of ionic conductivity for 6 M KOH aqueous solution and three hybrid hydrogel electrolytes. Arrhenius equation is given as follows:

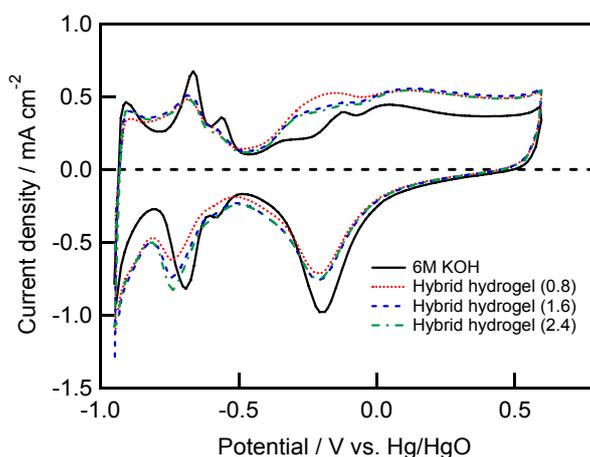
$$\ln(\kappa) = \ln \sigma_0 + \frac{\Delta E_0}{R} \cdot \frac{1}{T} \quad (1)$$

where κ is ionic conductivity, R is the gas constant, σ_0 is frequency factor, ΔE_0 is activation energy and T is absolute temperature. In each case, logarithm of ionic conductivity in the range of 0 to 70 °C showed linear dependence on the reciprocal of absolute temperature. This suggests that the Arrhenius-type ionic conduction mechanism holds in the hybrid hydrogel electrolytes in the range of 0 to 70 °C. Table 1 shows κ at 30 °C, ΔE_0 and $\ln \sigma_0$ values for three hybrid hydrogel electrolytes. The κ at 30 °C, ΔE_0 and $\ln \sigma_0$ values for the 6 M KOH aqueous solution were 0.691 S cm⁻¹, 13.4 kJ mol⁻¹ and 4.89, respectively. For the hybrid hydrogel electrolytes, ionic conductivity decreased with increasing HT content, while activation energy was independent of HT content, suggesting that the mobility of OH^- ion did not change with HT content. On the other hand, $\ln \sigma_0$ gradually decreased with increasing HT content. This can be ascribed to the decrease of free OH^- ions because carbonate anions adsorbing electrostatically on the HT particle surface with positive charges were replaced with OH^- ions.

Figure 3. Arrhenius plots of 6 M KOH solution and three hybrid hydrogel electrolytes.**Table 1.** Ionic conductivity (κ), activation energy for ionic conductivity (ΔE_0) and logarithm of frequency factor ($\ln \sigma_0$) for three hybrid hydrogel electrolytes.

	Hybrid hydrogel(0.8)	Hybrid hydrogel(1.6)	Hybrid hydrogel(2.4)
κ at 30 °C/S cm ⁻¹	0.540	0.491	0.456
ΔE_0 /kJ mol ⁻¹	13.8	13.8	13.9
$\ln (\sigma_0$ /S cm ⁻¹)	4.80	4.72	4.69

Figure 4 shows cyclic voltammograms (CVs) of a Pt working electrode in 6 M KOH aqueous solution and three hybrid hydrogel electrolytes. Typical oxidation and reduction peaks due to the formation of Pt oxide and its reduction and hydrogen adsorption and desorption were observed in the CV in each hybrid hydrogel electrolyte. However, there was no significant current for any other reactions in each voltammogram. Therefore we can say the electrochemical window of Pt in the hybrid hydrogel electrolytes is comparable to that in 6 M KOH aqueous solution, which clearly indicates the hybrid hydrogel electrolytes are promising solid electrolytes for alkaline batteries, capacitors and fuel cells compatible with 6 M KOH aqueous solution.

Figure 4. Cyclic voltammograms of a Pt electrode in three hybrid hydrogel electrolytes at 30 °C. Scan rate: 100 mV s⁻¹.

4. Conclusions

The mechanical strength of the hybrid hydrogel electrolytes containing both PAAK and HT is high enough to form freestanding membranes. Their ionic conductivity is 0.456–0.540 S cm⁻¹ at 30 °C and their potential window is comparable to that in KOH solution. Moreover, the hybrid hydrogel electrolytes can be prepared just by mixing the HT, PAAK and KOH solution without polymerization and thermal treatment. The hybrid hydrogel electrolytes have potential for safe, economical and environmentally friendly energy applications like batteries, capacitors and fuel cells.

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