Development of flexible solid electrolyte with high ion conductivity

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The hybrid electrolyte (HE) was prepared through the mixing of cation-exchanged polymer and ceramic electrolyte material for providing a certain flexibility to solid electrolyte (SE). To adequately utilize features of the HE with valuable ion conductivity, the electrolyte particles should be uniformly mixed with the polymer in the HE. To do that, the mixing was performed in an aqueous solution. The elasticity and hardness of each film prepared were slightly improved by increasing the contents of the electrolyte material. The ion conductivity of the HE showed the similar value with that of the pristine SE in spite of the addition of the polymer in a high level of 97.5 wt.%, resulting from the peaceful mobility of ion through the polymer, indicating that the electrolyte particles were uniformly dispersed in the polymer. As a result, the HE could be applicable to a flexible SE in a secondary battery.

Key-words: Hybrid electrolyte, Cation-exchanged polymer, Flexibility, Ion conductivity, Secondary battery

1. Introduction

A lithium secondary battery (LSB) has been growing its regions from portable electronics to electric vehicles.¹-³ The solid electrolyte (SE) has been developed and employed for aqueous lithium-air and lithium-liquid rechargeable batteries due to its high Li-ion conductivity; high structural stability, and low cost as well as environmental friendliness.⁴-⁶ The commercial LSB is usually prepared by the injection of liquid electrolyte (LE) into the membrane folded cathode and anode. However, this LE is not suitable for the flexible display and has a certain explosiveness.⁸ Even though the polymer electrolyte has been proposed to provide a certain flexibility to the electrolyte of LSB, there are limitations in real applications owing to low ion conductivity, thermal instability, and so on.⁹-¹² Therefore, the flexible electrolyte should be developed while maintaining performance.

Therefore, in this work, the hybrid electrolyte (HE) was prepared using cation-exchanged polymer having somewhat ion conductivity and a commercial SE particles. In the HE, the SE particles have to be homogeneously and independently mixed with the polymer to restrain the reduction of ion conductivity. Especially, two key points were considered to increase the independent dispersibility of SE particles in the HE; the mixture was performed in an aqueous solution and the hydrophilic polymer ionized in the aqueous solution was used. The effect of the mixture ratio of the polymer and the SE particle on the ion conductivity was investigated, and the fabrication and performance of the HE were demonstrated using various analytical techniques.

2. Experimental procedure

Nafion (Sigma-Aldrich Korea, Yongin, Korea) and Li1.3Ti1.7Al0.3(P04)3 were used as a cation-exchanged polymer and a SE material, respectively. Nafion was diluted in distilled water using an ultrasonicator (Sonifier 450, Branson Ultrasonics, Danbury, CT, USA) for 1 h at room temperature. The SE particles were added to the Nafion solution, and the mixture was sonicated for 24 h at room temperature. The mixture was dried at 80°C for 24 h, and then the HE film was prepared. The formulations of the HE prepared in this study are shown in Table 1. The schematic diagram for preparing the HE is presented in Fig. 1. In addition, heat treatment for preparing the SE was conducted at 800°C for 4 h under the atmosphere.

The phase analysis of the SE particle and the HE films was performed using an X-ray diffractometer (XRD; X-pert MPD, Model PW3040; Philips, Eindhoven, Netherlands). The microstructure of the SE sample and the HE films was observed using a scanning electron microscope (SEM; JEOL Model JSM-5610, Tokyo, Japan). Element analysis of the HE film was carried out using an energy dispersive X-ray spectrometer (EDS; energy resolution 133 eV; Oxford Inst., Oxford, UK). The samples selected for nanoindentation tests were sectioned, ground to a 10 µm finish, and then polished to a 1 µm finish. The samples were also polished with 10 nm silica colloidal solution. Nanoindentor (Nano Indenter XP, MTS Systems Corp., Eden Prairie, USA) with a Berkovich indenter tip was used to determine the elastic modulus and hardness values of the polymer used and the HE films prepared. The indenter tip drift rate and penetration depth in measurement were within ±0.05 nm/s and 1000 nm, respectively. The elastic modulus of sample (Ei) is calculated with the elastic modulus of the indenter tip (Ei) and reduced

Table 1. The formulations for preparing the hybrid electrolyte using polymer and SE material

| Run number | Polymer (wt.%) | SE material (wt.%) |
|------------|---------------|--------------------|
| Run 1      | 0             | 100                |
| Run 2      | 97.5          | 2.5                |
| Run 3      | 90            | 10                 |
| Run 4      | 100           | 0                  |

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modulus \( (E_r) \), using the following equations:

\[
E_r = \frac{1}{\gamma} \frac{S}{2} \frac{1}{\sqrt{A_x}} \\
A_x = 2.598 h_c^2 \\
\frac{1}{E_r} = \frac{1 - v_i^2}{E_i} + \frac{1 - v_s^2}{E_s}
\]

Where \( S, A_x, h_c, \gamma, v_i, \) and \( v_s \) are the contact stiffness determined from the initial part of unloading curve, the contact area, the contact depth, the correction factor, the Poisson’s ratios of the indenter and sample, respectively. The hardness \( (H) \) of sample is determined from the indentation load \( (L_{\text{max}}) \) and the contact area \( (A_x) \):\(^{13,14}\)

\[
H = \frac{L_{\text{max}}}{A_x}
\]

The impedance measurements were conducted in the frequency range of 0.1–100 kHz with a signal amplitude of 100 mV under open-circuit conditions, using a Solartron 1260/1287 electrochemical system (AC and DC).

3. Results and discussion

XRD results for the SE particle and HE films are shown in

![Fig. 2. XRD results of (a) SE particle, (b) HE film with 2.5 wt.% SE particle, and (c) HE film with 10 wt.% SE particle.](image)

![Fig. 3. Mechanical properties of polymer and HE films; (a) elasticity and (b) hardness.](image)
the cation-exchanged polymer, Naﬁon, is amorphous phase by the long hydro-carbon chains and the ponderous side chains. Thus, the polymer peak was not represented in XRD analysis. The elastic modulus and hardness values of the polymer only and HE ﬁlms prepared in this study are shown in Fig. 3. With the contents of the SE particle into the polymer, the values were slightly increased, meaning that the SE particles were well dispersed into the polymer.

The microstructures for the SE sample and HE ﬁlms are shown in Fig. 4. The SE particles before heat treatment showed a particle size less than 1 μm [Fig. 4(a)]. In the SE after heat treatment as shown in Fig. 4(b), the particle morphology was signiﬁcantly changed by sintering between particles through heat treatment, showing many and broad pores between particles. The microstructure indicated that the temperature is not enough to get a full densiﬁcation in the SE. In the SE, the lithium ion will pass through the just contact area generated between SE particles. Therefore, the extensive pores could not help to reveal ion conductivity in the SE. However, in the HE ﬁlm, the pores were strikingly reduced by the polymer.15) This means that the ion conductivity of the HE would not be expected to change despite of the addition of polymer having the relatively low ion conductivity compared with the SE material. All elements in EDS analysis were evenly detected on the surface of the HE ﬁlm (see the Fig. 5). It could be assumed again that the SE particles were uniformly dispersed in the HE ﬁlm.

Generally, in a LSB, the lithium ion moves along with the interface contacted between SE particles. The residual pores or low effective interfacial area reduces the transfer rate of the ion directly related to ion conductivity. Therefore, the SE is heat treated under a special temperature to broaden the interfaces between SE particles by the sintering phenomena. However, the only sintering is insufﬁcient to fabricate the SE having reasonable ion conductivity. Especially, the heat treatment at a higher temperature to reduce residual pores would enhance its stiffness, resulting in less ﬂexibility. For this reason, the LE is employed as a second material into the SE cell to increase the mobility of lithium ion. In the SE cell with the LE, lithium ion is easily and fast moved from the cathode to the anode without any disturbance caused by the LE ﬁlled at the space between particles. In addition, the use of the LE is possible to the uniform dispersion of SE particles in the SE cell. However, the LE has a limited application in the accordion electrolyte cell due to the low-ﬂowability of electrolyte, including a certain explosiveness.19) Consequently, in present study, the polymer was employed to provide a certain ﬂexibility to the SE and to overcome the deﬁciency and stiffness of the SE by heat treatment. However, the addition of polymer into the SE leads to the reduction of ion conductivity in the electrolyte, resulting from the self-aggregation of SE particles by the heterogeneity between bi-materials. Namely, the SE particles should be homogeneously dispersed in the polymer employed. Therefore, the HE was fabricated in an aqueous solution for providing the ﬂexibility to the SE by the uniform and independent
dispersion of SE particles into the polymer.

The ion conductivities of films were calculated with impedance values, which are shown in Fig. 6. The impedance measurement was conducted several times per a sample to obtain the accurate value. The ion conductivities were determined to be 2.43 × 10⁻⁶, 4.65 × 10⁻⁶, and 5.17 × 10⁻⁶ S/cm for the SE sample, the HE film with 2.5 wt.% SE material, and the HE film with 10 wt.% SE material, respectively, indicating that the ion conductivities were not significantly varied with the addition amount of the polymer. It is due to the reduction of pores between particles by the polymer. Also, it was shown that the electrochemical performances of the HE were not much affected by the amount of SE material in a certain level.

4. Conclusions

The cation-exchanged polymer as a secondary material was employed in preparing the HE film to provide a flexibility to the SE with a reasonable ion conductivity, and the effects of the addition amount of SE material on the ion conductivity were investigated. The HE film was prepared in an aqueous solution for homogeneously mixing between heterogeneous materials. The ion conductivity of the HE film was slightly increased in comparison with that of the SE sample, and was not significantly changed with the addition amount of SE material. It means the increase in the contact area between SE particles by the reduction in the number and size of pores existed in the pristine SE sample and the homogeneous dispersion of SE particles in the polymer. Consequently, the HE film prepared in an aqueous solution could be applied to prepare a flexible electrolyte with a reasonable ion conductivity.

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