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Effects of 1-hexyl-1-methylimidazolium iodide ionic liquid to poly(vinyl alcohol)–based solid polymer electrolyte

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Abstract

A solid polymer electrolyte (SPE) membrane has been fabricated using poly (vinyl alcohol) (PVA) as polymer host dissolved in deionized (DI) water. Lithium bis(oxalato) borate (LiBOB) electrolyte salt and 1-hexyl 1-methylimidazolium iodide (HMII) are incorporated into the membrane to contribute free ions, enhancing ionic conductivity. SPE was produced using the solution cast technique on Petri dishes. Then these slurries were dried at room temperature. The final product is a self-standing opaque membrane with visually homogenous surfaces. Further observation using FE-SEM revealed magnified images of membrane surfaces and cross-sections. Molecule interaction and crystallinity were observed using FT-IR and XRD. Impedance measured using EIS was used to calculate ionic conductivity. It was found that ionic conductivity of pure PVA film was 3.9×10^{-7} S/cm while ionic conductivity of SPE before and after ionic liquid addition was 4.77×10^{-7} S/cm and 2.66×10^{-6} S/cm.

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INTRODUCTION

The advancement of portable electronic devices and electric vehicles demands more reliable energy storage in terms of performance and safety. Secondary lithium-ion (Li-ion) battery has come into business since the early '90s and is still leading the market today. The basic scheme of Li-ion battery consists of a positive and negative electrode, an insulating separator between both electrodes, and a liquid electrolyte. Liquid electrolytes in commercial batteries consist of electrolyte salts dissolved in carbonate solvents. This system is prone to leaking and fire, especially during high-temperature applications. Solid polymer electrolytes (SPEs) were introduced to answer this challenge; taking a solid form relies on inorganic electrolyte salts as charge carriers. Having polymer as its matrix eliminates conventional separators; therefore, SPEs are more flexible and versatile to adapt to various devices.

The disadvantage of SPE membranes is their low conductivity compared to a liquid electrolyte, mostly due to relatively high crystallinity in the SPE complexes. In addition, crystalline structure in the SPE membranes results in the Li+ ion movement across the polymer chain being hindered, reducing its capability to travel between electrodes. Therefore, few additives such as ceramic fillers, plasticizers, and ionic liquids are mainly incorporated in the SPEs to decrease crystallinity.

The ionic liquids attract many eyes, especially in electrochemical applications owing to their high chemical and thermal stability and non-volatility and non-flammability [1, 2, 3, 4] being in a liquid state at room temperature. It also possesses high ionic conductivity and a wide potential window. These properties make ionic liquids highly explored in polymer electrolytes to boost their ionic conductivity along with the electrolyte salt.

The ionic liquid can be a strong contender to replace liquid electrolyte since its free ions could promote Li-ion movements and enhance the Li-ion battery's performance [5, 6, 7, 8]. However, on a commercial scale, that could be less desirable in terms of feasibility due to the high price. Therefore, we hereby explored the possibility of using ionic liquid as an addition to solid polymer electrolyte membrane for Li-ion battery application. In this study, deionized (DI) water was used to replace hazardous solvents such as N-methyl pyrrolidone (NMP), N, N-Dimethylacetamide (DMAc), and dimethylformamide (DMF) which are categorized as hazardous substances due to their reproductive toxicity [9]. Poly(vinyl alcohol) (PVA) was used as the polymer host because it is easily soluble in water and versatile to form SPE complexes with various electrolyte salts and additives [10].

METHOD

Material

PVA powder, lithium bis(oxalato) borate (LiBOB) electrolyte salt, and 1-hexyl-1 methylimidazolium iodide (HMII) ionic liquid were purchased from Sigma Aldrich. PVA (MW = 89,000) and LiBOB were heated prior to the experiment to remove trace moisture. HMII was used without further treatment. Table 1 lists the sample identification

Methods

The solution casting technique was employed to fabricate a solid polymer electrolyte membrane. First, PVA powder was dissolved in deionized water using a magnetic stirrer on a hot plate set at 90°C for 3 hours until a clear solution was obtained. LiBOB salt of 20% w/w with respect to polymer weight was then added and mixed for another 2 hours before adding HMII in the slurry.

The beaker glass containing SPE slurry was sonicated (Elmasonic, 37 kHz) for 20 minutes and cast on Petri dishes. The slow evaporation method was used to dry the samples at room temperature. After 48 hours, free-standing membranes were easily peeled off the Petri dishes. FTIR spectroscopy (Thermoscientific Nicolet iS-10, wavenumber range of 4000-400 cm^{-1}) was performed to observe functional groups in the polymer-salt complex and its interaction.

Table 1. Sample identification

Sample	PVA (g)	LiBOB (g)	HMII (g)
PVA00	5	0	0
PVA20	5	1	0
PVA20IL	5	1	0.1

Polymer crystallinity and complexation were studied with X-ray diffraction (Rigaku Smartlab) on CuKα cathode gun in the 2θ range of 10°-80°. Impedance was measured with Electrochemical Impedance Spectroscopy (EIS, Autolab) with a working frequency of 10 Hz–50 kHz. Field Emission Scanning Electron Microscope (FE-SEM) was performed using JEOL JIB 4610F at 5 kV acceleration voltage. Nyquist plot of real versus imaginary impedance was then utilized to calculate ionic conductivity σ using formula $\sigma = R_b \times L/A$, where A is the contact area between electrode and electrolyte, L is membrane thickness, and Rb is bulk resistivity, obtained from the intercept value of the curve with real impedance axis. SPE membranes used for EIS measurement were cut in identical circular shapes with 16mm in diameter. These membranes were stacked between SS plates in the CR2032 coin cell case.

RESULTS AND DISCUSSION

Stacked FT-IR spectra of LiBOB powder and sample PVA00, PVA20, and PVA20IL are shown in Figure 1. A prominent peak around 3300 cm^{-1} indicates the O-H bond contributed by PVA substrate [11]. On samples PVA20 and PVA20IL, these peaks were slightly shifted in position and into more narrow peaks, indicating a weakening of hydrogen bond. Typical vibration peak of C=O stretching around 1733 cm^{-1} [12] was also seen to diminish in samples PVA20 and PVA20IL. CH2 asymmetric stretching around 2900 cm^{-1} was even disappeared completely upon salt and ionic liquid addition, indicating good complexation on the solid polymer electrolyte system. The small shoulder peak on 1160 cm^{-1} corresponds to the C-N stretching of HMII [12].

Vibrational peaks of LiBOB salt appeared on wavenumber 1372 cm^{-1} and 1081 $cm^{-1,}$ which correspond to B-O and O-B-O stretching, respectively [13]. Small peak around 3513 $cm^{-1,}$ which usually indicates the hydrate phase of LiBOB salt did not appear on samples PVA20 and PVA20IL, which suggests LiBOB-based SPE is able to prevent hydrate formation [14].

Crystallinity tells a lot about the degree of structural order in a material. For example, crystalline materials with strong, sharp peaks tend to have intact grains that highly influence Li-ion migration in the Li-ion battery system. Conversely, the lower the crystallinity, the more defects exist, and grains are more scattered. XRD characterization results are presented in Figure 2.

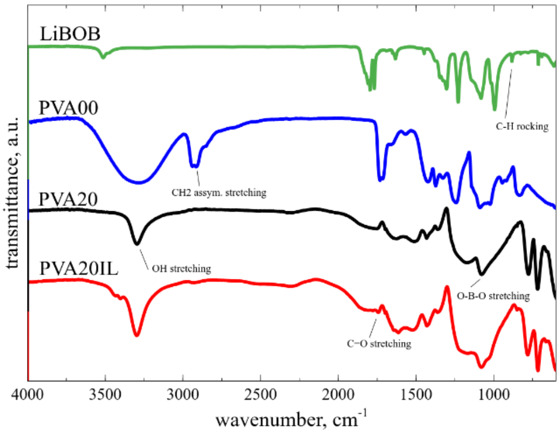


Figure 1. FT-IR spectra of LiBOB powder, PVA film, SPE before (PVA20) and after (PVA20IL) ionic liquid addition

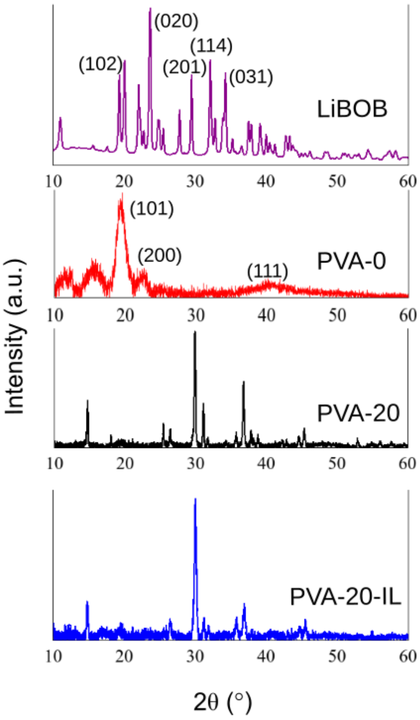
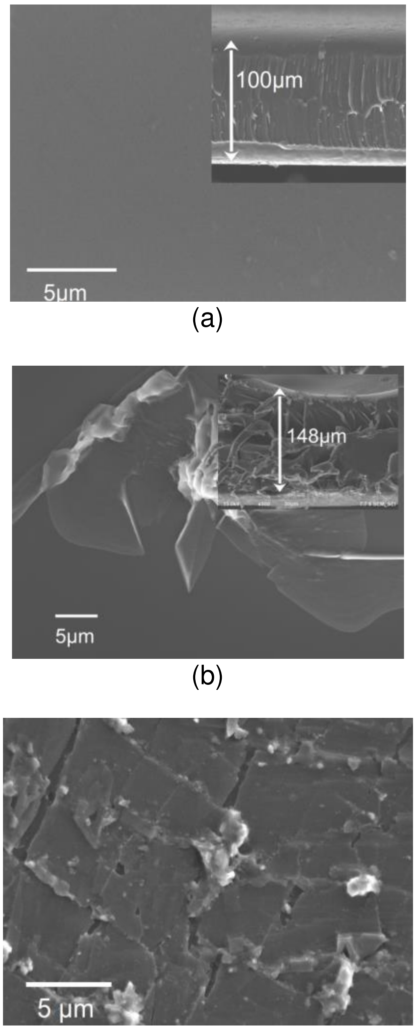


Figure 2. XRD patterns of LiBOB powder, PVA film, SPE before (PVA20) and after (PVA20IL) ionic liquid addition

PVA-0 exhibits semicrystalline structure, where typical peaks would appear at 2θ of 19.5°, 23°, and 41° which correspond to [101], [020], [111] planes. The Formation of SPE complex as indicated by reduced overall crystallinity of LiBOB salt in PVA polymer host shown on PVA-20. A few strongest peaks indicated LiBOB powder at 23°, 29°, and 32°, which corresponds to (020), (201), and (114), respectively [15]. Only (201) peak was identified on the SPE complex of both samples, suggesting the salt has dissociated and blended well into the polymer matrix [16].

Further decrease in overall crystallinity was observed on the PVA20IL sample. It can also be seen that (101) and (111) peaks of the PVA host have disappeared completely on samples PVA20 and PVA20IL.

Micrographs of pure PVA film without electrolyte salt and ionic liquid addition is shown in Figure 3(a). It presents a smooth and homogeneous film as expected. However, upon LiBOB addition, as shown in Figure 3(b), flakes of salt particles were found scattered but spread evenly both on the surface and across the cross-section.



(a)

(b)

(c)

Figure 3. SEM micrograph of (a) PVA00, (b) PVA20, and (c) PVA20IL

The incorporation of ionic liquid, however, resulted in cracked surface and particle agglomeration, as illustrated in Figure 3(c), which usually obstructs any attempts to enhance the ionic conductivity of solid polymer electrolytes [17]. The Sonication procedure should be explored further to prevent agglomeration, as presented in the research done by Dhatarwal et al. [18].

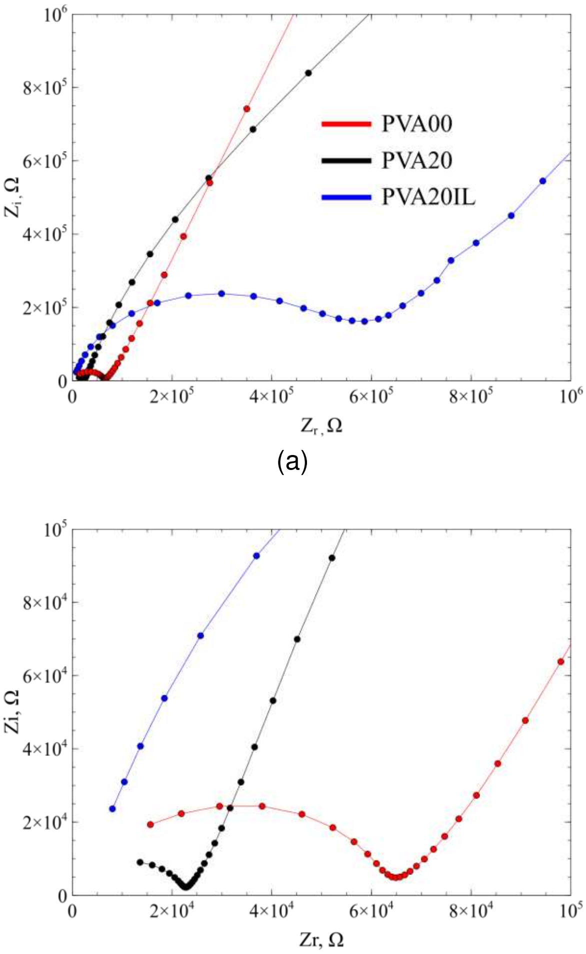
Nyquist plots presenting impedance measurement from high to low frequency are shown in Figure 4. Typical characteristics of impedance plot can be observed on all SPE membranes: semicircle in the high-frequency range contributed by bulk region of the electrolyte, and the tilted line attributed to the blocking electrode.

The intercept of the plot with the real impedance axis denotes bulk resistivity. Ionic conductivity σ could then be calculated and summarized in Table 2.

Table 2. Ionic conductivity of SPE membranes

Sample	**Conductivity (S/cm)**
PVA00	3.90×10^{-7}
PVA20	4.70×10^{-7}
PVA20IL	2.66×10^{-6}

The addition of LiBOB salt into polymer substrate hardly increased the ionic conductivity. This is possible because, in the all-solid condition, the ionic movement has been slightly impaired. Highly crystalline electrolyte salt added to the polymer has increased the crystallinity of the overall complexation, therefore rendering the structure more intact [19]. However, this environment impedes lithium ions from freely moving between electrodes. This can be improved by increasing salt concentration to a certain number; too high a concentration would result in salt aggregates within the complex, which would hinder free ion movement [20].



(a)

(b)

Figure 4. Nyquist plot of SPE membranes in (a) full range and (b) close up view on a high-frequency range

Incorporation of HMII ionic liquid resulted in the increasing ionic conductivity by order of magnitude. This is because ionic liquid provides free cations and anions, adding free charge carriers. Ionic conductivity is then expected to increase following general relation for conductivity $\sigma = nq\mu$, where "n" is the number of charge carriers, q is "charge of the ion", and "μ" is the mobility of the carriers[1]. It is, however, noted that ionic conductivity around 10^{-6} S/cm is not sufficient to be applied in Li-ion batteries as it needs at least 10^{-3} S/cm to substitute conventional liquid electrolyte, as revealed by recent research such as poly-imide/poly(ethylene oxide (PEO) /lithium bis (trifluoro methanesulfonyl) imide SPE which reach 2.3×10^{-4} S/cm or work by Gonzalez et al. The incorporate 1-Butyl- 1-methyl pyrrolidinium bis(trifluoromethanesulfonyl) imide (PYR14TFSI) ionic liquid in PEO/LiTFSI complex, generating ionic conductivity of 5×10^{-4} S/cm [21][22].

CONCLUSION

Water-based solid polymer electrolyte has been fabricated using the solution cast technique. PVA was employed as the polymer host, LiBOB and 1-hexyl-1methyimidazoliium iodide as electrolytes salt and ionic liquid additive, respectively. XRD and FT-IR characterization has shown that these components have blended well in the membranes. EIS measurement results in the Nyquist plot were employed to calculate the ionic conductivity of 3.90×10^{-7}, 4.7×10^{-7}, and 2.66×10^{-6} S/cm for pure PVA film and SPE before and after ionic liquid addition, respectively.

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