Interfacial Properties of Solid Polymer Electrolyte for Lithium-Ion Battery

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Abstract. The problem in developing solid electrolyte is the interface between solid electrolyte and electrode in an all solid lithium-ion batteries (LIB). Due to this reason, the interfacial properties of solid polymer electrolyte (SPE) for LIB have been studied using scanning electron microscopy (SEM), and electrochemical impedance spectrometry (EIS). The aim of this study is to elucidate the effect of interfacial structure onto the properties of SPE for LIB. Two kind different electrolyte / cathode interfacial arrangements were constructed by coating and stacking Chitosan based SPE onto lithium permanganate based cathode. The effect of interfacial structure onto the impedance has been studied. It was found that in case the SPE stacked on the electrode, micro-gap appeared at the interface and resulted in the existence of Warburg impedance or interfacial resistance. However, when the SPE was coated using solvent casting onto the electrode the micro-gap did not appear and the interfacial resistance could be neglected.

Keywords: Solid Polymer Electrolyte, Interfacial Properties, Lithium-ion Battery

1. Introduction
Lithium-ion batteries [LIB], having a high voltage and a high energy density, are widely used in various mobile devices such as smart phone and tablet PC. However, due to using a flammable liquid electrolyte, there is a risk of explosion or fire accidents. To reduce the risk, the liquid electrolytes are substituted by solid ones, making all-solid-state lithium batteries are proposed as the best solution [1]. An all-solid-state battery is also safer and more easily packaged [2].

Solid-state electrolyte (SSE) can be divided into inorganic solid electrolytes (ISE) and solid polymer electrolytes (SPE). The ISE are mostly based on ceramic or glassy material such as NASICON type phosphates, lithium phosphorus oxynitride (LiPON), garnet, and so on [3]. In this last decade, we have also studied the synthesis and characterization of solid-state electrolyte based on silver-lithium phosphate [4]. While SPE are formed by the incorporation of inorganic such as lithium salt into polymer matrices which are having functional groups such as polyether, polyacrylonitrile, polyester, polysiloxane and soon. Compared with ISEs, SPE have several advantages: They are lightweight and flexible, have interfacial compatibility, and are very processable. Previously, several efforts to obtain Chitosan based SPE have been done [5-7].
One of the problems in developing SSE is the interface between solid electrolyte and electrode [8]. Recent computational studies have shown that various interfaces are not always stable chemically or electrochemically leading to loss of capacity and increase in impedance [9, 10]. Other study showed that proper engineering of the electrode/electrolyte interface was essential for long term cell performance [11]. Several approaches had been applied to reduce interfacial impedance between SSE and cathodes, including surface coating [12], interface softening [13] and so on. It is known that the interfacial properties are affected by the physical as well as chemical structure at the interface.

In this study, we will elucidate the relationship between interfacial structure and properties of SPE for LIB. Two kind different electrolyte - cathode interfacial arrangement were constructed by coating and stacking Chitosan based SPE onto lithium permanganate based cathode. Scanning electron microscopy (SEM) and electrochemical impedance spectrometry (EIS) were used to study the structure and properties, respectively.

2. Experimental method

2.1. Materials

The chitosan (low molecular weight, 86% deacetylated degree) was purchased from Bogor Agricultural Institute Laboratory. Analytical grade of acetic acid as solvents was purchased from Merck, and used without further purification. Deionized water was used to make 1 wt.% acetic acid solution. Lithium perchlorate (LiClO$_4$) as lithium salt and lithium permanganate (LMO, LiMn$_2$O$_4$) as cathode material were purchased form Sigma-Aldrich and used as-received. The LMO however, was dried using vacuum oven at 80°C for 12 hours priory.

2.2. Sample preparation

The Chitosan powder was dissolved into the acetic acid to make a 4 wt. % polymer solution. A certain amount of LiClO$_4$ was then added to get a 30 wt.% polymer electrolyte solution. The SPE film was prepared as in previous method, i.e. by casting the electrolyte solution in a cast mold and kept for two days to evaporate the solvent [5-7]. The obtained SPE film, (a) sample, was then stored under vacuum condition at room temperature to complete the solvent evaporation. The cathode was prepared by mixing 1.5 g. LMO powder into 28 g. polymer electrolyte solutions to get 15 : 85 solid to solid proportion. The mixing solution was then casted onto 17 µm Aluminum foil and kept for one hour under heating temperature at 100°C to remove the solvent. The obtained LMO cathode film, (b) sample, was stored under vacuum. SPE coated LMO cathode, (c) sample, was prepared by coating polymer electrolyte solution on the surface of LMO cathode and followed by drying process under heating temperature at 100°C for one hour. The stacking sample, (d) sample, was prepared by stacking and pressing SPE film on the surface of LMO cathode. The samples thickness was controlled to be about 100µm and the structure are illustrated as in Table 1. The cross section was observed by fracturing them after immersed in liquid nitrogen.

| Samples | Illustration | Remarks |
|---------|--------------|---------|
| (a) SPE | ![Illustration](image1.png) | Chitosan based SPE film; (Chitosan + LiClO$_4$) |
| (b) LMO | ![Illustration](image2.png) | LMO cathode, composed of LMO : SPE = 85:15 wt% : (LMO+SPE) |
| (c) SPE coated LMO | ![Illustration](image3.png) | SPE coated LMO cathode, prepared by casting technique; ((LMO+SPE)/SPE) |
| (d) SPE stacked LMO | ![Illustration](image4.png) | SPE stacked LMO cathode, prepared by pressing method ; (LMO+SPE)&SPE |

Table 1. Samples name and their illustration.
2.3. Sample characterization

A Scanning Electron Microscope (SEM, JEOL JSM 6510 LA) equipped with Energy Dispersive X-ray Spectrometer (EDS) were used to study the surface as well as the cross section structures. While the impedance characteristic was studied by using a computer controlled impedance analyzer (HIOKI LCR Hi-Tester Model 3532, Japan) within frequency range of 42 Hz to 5 MHz. Data fitting were performed using EIS Spectrum Analyzer (EISSA) software.

3. Results and discussion

SEM photograph were observed to confirm the surface as well as the cross section morphologies of each sample. Figure 1 shows the surface micrograph of SPE film, LMO cathode, SPE coated on LMO, and SPE stacked on LMO samples with 200X magnification except SPE stacked on LMO (500X). As in previous study, the Chitosan based SPE film (Figure 1(a)), shows relative smooth surface exhibits the domination of Chitosan polymer on the surface [5-7]. LMO cathode (Figure 1(b)) shows the existence of LMO particle on the surface. The SPE stacked on LMO sample (Figure 1(d)), was completely same with SPE film (a), except a small effect of pressing in the stacking process. In contrast with SPE film sample, the surface of SPE coated on LMO cathode (Figure 1(c)), was not smooth even if dominated by Chitosan film and some agglomeration of the lithium salt, as confirmed by EDS (Figure 2). This difference can be due to the difference of drying method that is the sample of SPE film was dried slower than SPE coated on LMO.

![Figure 1](image1.jpg)

**Figure 1.** SEM micrograph from surface of (a) SPE, (b) LMO, (c) SPE coated on LMO, and (d) SPE stacked on LMO samples.

Figure 2 shows the EDS results of the sample SPE coated on LMO. It was found that the surface was dominated by carbon (60.83 atom%) which is originated from Chitosan. However, an interesting phenomena was found in which Manganese (the main component of LMO) was observed on the surface (3.76 atom%). It means that some part of cathode material dissolved into the SPE layer. Of course, it is unexpected since it will contact with the anode and cause short contact.
Figure 2. EDS spectrum from surface of Chitosan SPE coated on LMO cathode ((c) sample).

Figure 3. SEM micrograph from cross section of (c) SPE coated on LMO and (d) SPE stacked on LMO.

The different between coated and stacked sample was observed from the cross sectional micrograph as shown in Figure 3. When SPE was coated on the cathode, the SPE was completely contacted with cathode and some part of cathode dissolved in the SPE layer as shown in sample of SPE coated on LMO. In other hands, when SPE was just stacked on the cathode surface micro-gap or void was found at the SPE cathode interface as indicated on sample of SPE stacked on LMO. In other word, the coated sample has better SPE cathode interface than that of stacked one.

Electrochemical Impedance Spectroscopy (EIS) is a technique currently used to study the electrical properties of the bulk materials and their interfaces (i.e., electrode electrolyte interfaces) over a wide range of frequency and temperature. The bulk and interface contributions can be separated by using this technique [14]. Therefore, effect of the interface onto the electrical properties was studied by impedance measurement as shown in Figure 4. The Nyquist plots of the impedance spectra, shown in Figure 4, consist of semicircle alike in appearance for all samples. The SPE film shows the appearance of semicircle at high frequency and smallest size. The LMO cathode shows two semicircles at high and medium frequency. The semicircle of coated sample seems to be similar in appearance but smaller in size compared to the LMO cathode only. In contrast, the stacked sample shows the appearance of a big semicircle. However, all samples show the existence of capacitance and resistance.
In order to investigate the difference in the EIS spectra, we employed equivalent circuits and fitted to the data as displayed in Table 2. The EIS data was interpreted by fitting them to equivalent circuit models. The model was constructed by using resistor (R) and constant phase element (CPE). CPE was commonly introduced to the circuit when using pure capacitor could not fit in simulation. CPE has no physical meaning. It is just a calculated parameter when circuit element behaving in between capacitor and resistor [15]. Therefore, we consider mostly on the role of resistance (R). The experimental data was fitted and matched with the equivalent circuit as shown in the Table 2. The model was taken account based on the experimental data and the sample system. The EIS spectra of SPE film for example, show the appearance of 2 semicircles. Therefore, we constructed an equivalent circuits composed of a single CPE and a parallel circuit of CPE and resistor. We assumed that the SPE sample was composed of lithium salt (LiClO₄) dissolved in polymer (Chitosan) matrix. Thus, the impedance of SPE was affected by the distribution of lithium salt in the matrix. Similarly, the LMO cathode also showed 2 semicircles spectra, can be originated from SPE matrix and dissolved LMO particles.

![Nyquist Plot](image_url)

**Figure 4.** Nyquist Plot of (a) SPE film, (b) LMO cathode, (c) SPE coated LMO, and (d) SPE stacked LMO.

Table 2 clearly shows that the equivalent circuit model can be fitted on the experimental data. Having initial resistance, the LMO cathode seems to be different with SPE film, it may due to the existence of LiMn₂O₄ powder as cathode active material. The SPE coated LMO ((c) sample), however, appear to be same with the LMO cathode rather than SPE film only. While the SPE stacked LMO matched with different circuit, in which Warburg impedance must be involved. Comparing the equivalent circuit between (c) and (d) sample, it was clear the source of difference between coating (c) and stacking (d) samples. The SPE coated LMO shows a similar circuit with the uncoated LMO. It means that there was no effect of solid electrolyte cathode interface. While, at SPE stacked LMO (d sample) the effect of interface seems to appear in form of Warburg impedance (1.5x10³kΩ) result in high resistance. The stacked sample also have a higher initial resistance (R₁ = 0.6 kΩ) than the coated one which is mostly zero (R₁ = 1.1 x 10⁻³kΩ). It can also be due to the existence of micro-gap at the interface of the stacked sample. In other word, the problem in the interface between SPE and electrode in an all solid lithium-ion batteries can be reduced by casting the electrolyte solution on the cathode surface.
Table 2. Equivalent circuits, Nyquist Plot and fitting results of EIS spectra.

| S.N. | Circuits | Fitting result | Sample remarks |
|------|----------|----------------|----------------|
| (a)  | [CPE1, CPE2, R1] | ![Experimental](#) ![Fitted result](#) | [SPE (Chitosan + LiClO4)](#) |
|      | R1 = 19.7 kΩ | ![Z’(Ohm)](#) ![X’(Ohm)](#) |  |
| (b)  | [R1, CPE1, CPE2, R2, R3] | ![Experimental](#) ![Fitted result](#) | [LMO (SPE + LiMn2O4)](#) |
|      | R1 = 3.8 x 10^{-16}kΩ, R2 = 57.3 kΩ, R3 = 8.9 kΩ | ![Z’(Ohm)](#) ![X’(Ohm)](#) |  |
| (c)  | [R1, CPE1, CPE2, R2, R3] | ![Experimental](#) ![Fitted result](#) | [Coated (SPE coated on LMO)](#) |
|      | R1 = 1.1 x 10^{-15}kΩ, R2 = 45.6 kΩ, R3 = 3.9 kΩ | ![Z’(Ohm)](#) ![X’(Ohm)](#) |  |
| (d)  | [R1, CPE1, Wa1, R2] | ![Experimental](#) ![Fitted result](#) | [Stacked (SPE stacked on LMO)](#) |
|      | R1 = 0.6 kΩ, R2 = 56.9 kΩ | ![Z’(Ohm)](#) ![X’(Ohm)](#) |  |
The effect of interfacial structure to the properties can be illustrated as in Figure 5. Micro-gap between electrolyte and electrode was observed when the Chitosan based SPE just stacked on the cathode surface result in the appearance of Warburg impedance. The results of this study recommend how to control the interfacial structure and the properties of SPE in all solid battery system. That is, we must eliminate the gap in the interface and make the SPE stick to the cathode. Surface coating is one of the methods to reduce the interfacial effect and agree with previous study [12].

![Figure 5](image)

Figure 5. Schematic illustration for two types difference SPE cathode interfacial arrangements (a) SPE coated LMO and (b) SPE stacked LMO.

4. Conclusion
The interfacial structure and properties of solid electrolyte and the cathode for battery application have been studied. LiClO₄ containing Chitosan were used as the solid electrolyte and LiMn₂O₄ (LMO) was the cathode active material. Two kind different interfacial arrangements were constructed by coating and stacking method. SPE coated and stacked cathode was used as the sample to study the effect of interfacial structure to the resistance. When the Chitosan SPE stacked on the LMO cathode, micro-gap appeared at the interface and resulted in the existence of Warburg impedance or interfacial resistance. However, when the SPE was coated using solvent casting onto the cathode the micro-gap did not appear and the interfacial resistance could be neglected.

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