Application of LiBOB-PVdF-co-HFP solid polymer electrolyte in Li-ion battery and Comparison to Its Conventional Counterpart

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Abstract. Solid polymer electrolyte is widely introduced as the safer, more effective alternative to the liquid electrolyte of conventional lithium-ion battery. It incorporates polymer as the matrix, with electrolyte salt and additive filler to boost its conductivity. In this research, an experiment has been performed to compare solid polymer electrolyte to its conventional counterpart, i.e. lithium-ion battery with liquid electrolyte. Solid polymer electrolyte was synthesised using PVdF-co-HFP as polymer matrix, LiBOB as electrolyte salt, and nano-TiO2 as additive filler. Despite good results from the characterisation of the free-standing polymer membrane, its performance in coin cell battery application is still less than favourable when compared to coin cell battery with liquid electrolyte.

1. Introduction
Since its early development circa 1990, lithium-ion battery has been through many improvements in performance and wide applications. The turn of the century marked new era of technology advancement, in which electronic devices are getting smaller and becomes portable. This demands better performance of energy storage these devices relied on [1].

Former generation of lithium-ion battery employed NiCd (nickel-cadmium) and NiMH (nickel metal hydride) which was later found to have memory loss effect. The unrechargeable properties of these primary batteries also gave way to the development of secondary battery. So far, lithium-ion battery has been commercially made available worldwide for various applications of electronic devices.

Conventional lithium-ion battery comprised of positive and negative electrode separated by a separator membrane made from polyethylene (PE) or polypropylene (PP) or tri-layer PP/PE/PP namely commercial Celgard separator. Lithium ions were transmitted between electrodes through liquid electrolyte which was essentially electrolyte salt dissolved in carbonate solvent [2], [3]. The disadvantage of having liquid-phase electrolyte is the risk of leakage which can be serious because the solvent is flammable and toxic, which could be dangerous if released to environment [4].

First introduced around 1980s, electrolyte made of polymer was entering the research and development of primary and secondary lithium-ion battery [5]. Instead of dissolving electrolyte salt into carbonate solvent, it is dispersed in polymer matrix, forming free-standing film. This film then acted as separator in lithium-ion battery system. Early development of solid polymer electrolyte
employed polyethylene oxide (PEO) as polymer matrix. In this research, we used poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) which was proven to possess better dielectric constant and suitable for various electrolyte salt for lithium battery application [6]. Moreover, PVdF-co-HFP can also reduce polymer crystallinity, therefore allowing membrane to absorb more electrolytes and hence result in higher conductivity [7].

2. Experimental Methods

Lithium bis(oxalato)borate (LiBOB) salt was obtained from Sigma Aldrich and underwent heating at 80°C for 24 hours prior to experiment to remove moisture. Polymer PVdF-co-HFP and filler titanium oxide (TiO₂, Sigma Aldrich) were used without preliminary treatment. PVdF-co-HFP was dissolved in N,N-Dimethylacetamide (DMAC) solvent and stirred using magnetic stirrer on a hot plate set at 50°C temperature. After it was thoroughly dissolved, LiBOB salt and TiO₂ filler were added subsequently until it formed homogeneous slurry. Various amount of TiO₂ was added to the slurry to observe the effect of total TiO₂ content towards the conductivity. Solid polymer electrolyte membrane was formed by casting the slurry on a glass substrate using doctor blade method. It was then dried in room temperature until dried and solidified, forming free-standing film. The membrane was then put in plastic wrap container and stored in a dry box with 30% relative humidity to preserve the membrane from moisture and impurities from the atmosphere.

Surface morphology and element distribution was observed using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDXS) while ionic conductivity was derived through Cole-Cole plot obtained from impedance measurement using Electrochemical Impedance Spectroscopy (EIS). Finally, to evaluate its performance as secondary battery we assembled 2032CR lithium-ion battery coin cells using commercial lithium iron phosphate (LiFePO₄) and metallic lithium as electrodes. Conventional Celgard separator was replaced using solid polymer electrolyte obtained from above mentioned experiment. In cell A, the solid polymer electrolyte membrane was used as it is while in cell B it was soaked in organic solvent ethylene carbonate/ethyl methyl carbonate (EC/EMC) commercially used in liquid electrolyte. Cyclic voltammetry test was performed in Wonatech WBCS3000 automatic battery cycler, with working voltage range of 2.5 - 4.2 V.

3. Results and discussion

3.1. SEM

Secondary electron method of SEM was performed at low acceleration voltage (5 kV) to avoid charging therefore minimizing image artefacts. Variation of TiO₂ content showed little to no difference towards surface morphology, as seen on Figure 1a, b and c. Generally, all samples possess micropores which may aid lithium transfer between electrodes. These micropores were most probably formed by the assistance of TiO₂ which lower overall crystallinity of the polymer membrane.

EDXS on surface and cross-section area have shown that the electrolyte salt and the filler were distributed evenly within the polymer matrix. Electrolyte salt was represented by atom B, polymer matrix PVdF-co-HFP by atom F, and TiO₂ filler by atom Ti. This also helps micropore formation throughout the membrane. In this observation, TiO₂ addition of 5% (Figure 1a) has smooth surface with definite pore and matrix barrier. EDXS mapping of this sample also displayed uniformly distributed particle with no distinct agglomeration. Different results were found in sample with TiO₂ addition of 10% and 20% (Figure 1b and c, respectively) where lumps of filler and probably lithium salts were found on the surface due to agglomeration.

3.2. FT-IR

The possibility of change in polymer structure were observed using FT-IR (Fourier Transform Infra Red) spectroscopy which detects functional group within the compounds in the sample. From all spectrum, as shown on Figure 2, it can be seen that the fingerprints of all functional groups existed without any signs of shifting, confirming that the method used to synthesis solid polymer electrolyte does not alter the chemical bonds of the membrane.
PVdF-co-HFP can be observed on peak number 840, 875, 1175, and 1401 cm\(^{-1}\) which are assigned to CH\(_2\) rocking and assymmetric stretch of CF\(_2\), C-C skeletal vibration, CF\(_2\) symmetrical stretching, and C-F stretching, respectively. LiBOB salt fingerprints were found on peak number 604, 1070, and 1811 cm\(^{-1}\) representing B-O deform, O-B-O symmetric stretch, and C=O out-of-phase oscillation, respectively. TiO\(_2\) filler can be observed on wave number around 500-900 cm\(^{-1}\), representing Ti-O stretching vibration.

![Figure 1. SEM micrographs of (top row) surface and (bottom row) cross section of solid polymer electrolyte with (a) 5%, (b) 10%, and (c) 20% TiO\(_2\) filler addition.](image)

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![Figure 2. FT-IR spectrum of polymer electrolyte membrane, compared to LiBOB salt.](image)

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3.3. EIS  
EIS measurement result shown on Figure 3 displayed Cole-Cole plot where bulk resistivity can be estimated from the semicircle formed during test. Further calculation to obtain conductivity was performed using formula \( \tau = L / (R_b \times A) \), where \( R_b \) is bulk resistivity, \( L \) is sample thickness, and \( A \) is sample area in contact with EIS stainless steel test plate. These calculations resulted in highest conductivity of \( 4.33 \times 10^{-11} \text{ mS/cm} \), possessed by solid polymer electrolyte sample with 20% \( \text{TiO}_2 \) filler addition. Aside from the aid of relatively high amount of \( \text{TiO}_2 \) filler, good distribution of lithium salt and filler in this sample are considered crucial factor to increase ionic conductivity of the solid polymer electrolyte membrane, as confirmed by SEM and EDXS analysis.

3.4. Cyclic voltammetry  
Performance of the solid polymer electrolyte was evaluated by cyclic voltammetry of a coin-cell battery in Figure 4. Two samples were assembled and tested as a comparison: battery cell using commercial Celgard separator and solid polymer electrolyte membrane containing 20% \( \text{TiO}_2 \). This sample was taken among three membranes as it has highest ionic conductivity, according to the EIS measurement result mentioned previously.

![Figure 3. Cole-cole plot showing impedance value of the electrolyte membrane.](image)

![Figure 4. Cyclic voltammetry curve of cell with solid polymer electrolyte and celgard as electrode separator.](image)
To boost the conductivity, two drops of LiBOB liquid electrolyte (LiBOB salt dissolved in EC/EMC solvent) were added on the separator during assembly process. It can be seen from the CV curve that the cell with solid polymer electrolyte did not exhibit as good oxidation-reduction path as the cell with liquid electrolyte and celgard separator. Oxidation curve formed single peak, which was expected from secondary battery, but no significant peak was shown where reduction should have occurred. This indicates lithiation and delithiation between electrodes did not perform properly.

4. Conclusions

Solid polymer electrolyte was synthesised using doctor blade method, resulting in free-standing membrane of PVdF-co-HFP and LiBOB salt with nano-TiO$_2$ filler. Material characterisation using SEM, FT-IR, and EIS showed that the polymer electrolyte membrane was blended homogeneously, and exhibited conductive behaviour as shown by impedance test. However, cyclic voltammetry test resulted in imperfect curve of reduction-oxidation path in the battery cell. Despite the boost from liquid electrolyte, all-solid-state battery still needs major improvement in regards to its electrolyte membranes. Conductivity must be increased as high as possible to accommodate lithium ion movement between electrodes to advance the performance of the secondary battery.

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