Improved properties of LiBOB-based solid polymer electrolyte by additive incorporation

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Abstract. Solid polymer electrolytes comprising of poly(vinylidene fluoride) (PVdF) and lithium bis (oxalato) borate (LiBOB) have been prepared using solution casting technique. Having an important role in lithium-ion battery system, electrolyte is required to have high ability to transfer lithium ions between electrodes. Safety aspect is the main reason for the development of solid polymer electrolyte as advancement from conventional liquid electrolyte. Nevertheless, solid polymer electrolyte generally has lower conductivities compared to liquid electrolyte. In this research, ceramic additives, as well as plasticiser materials, have been incorporated within the solid polymer electrolyte system to improve its conductivity. Addition of TiO2 filler has proven to increase ionic conductivity by two orders of magnitude. Further improvement was seen in the incorporation of PEG plasticiser, where ionic conductivity was enhanced by three orders of magnitude.

1. Introduction
A particular urgency has been raised from the rapid advancement of electrical/electronic technologies. Portable electronic devices are in requirement of energy storage system in order to sufficiently power them. Lithium-ion batteries have been widely developed since the early 1990’s because of its high capacity and notably longer shelf-life compared to the predecessors such as NiMH and NiCd batteries.

A lithium-ion battery consists of positive and negative electrode where intercalation of lithium ions and exchange of electron takes place. A separator exists between those electrodes to prevent short-circuit. The movement of lithium ions is governed by electrolyte, which acts as a transfer media. Early implementation of lithium-ion battery used liquid electrolyte, i.e electrolyte salt dissolved in carbonate-based solvent.

Along the way, it has been discovered that liquid electrolyte in the lithium-ion battery system possessed disadvantages [1–3] such as the potential of solid electrolyte interface (SEI) layer formation caused by reaction which decreases intercalation potential of Li-ion between electrodes. In addition, reliability in high temperature is highly required because lithium-ion battery is widely used in heated environments such as electric vehicle or oil and gas application.

Solid polymer electrolyte system employs polymer host as a solid solvent for metal cations. Electrolyte salts and additive materials are dissolved in the polymer matrix. In this experiment, poly(vinylidene fluoride) or PVdF was used as the main polymer matrix because of its relatively high dielectric constant [4] compared to other polymers. In the early years of the development of polymer electrolyte, Wright et.al [5] utilised poly(ethylene oxide) or PEO as the matrix due to its desired properties i.e proper blending and good mechanical characteristics. These properties were found to be
in accordance with research conducted by M. Jacob [6], whom experiment yielded in conclusion that blending of PVdF and PEO as a polymer matrix in solid polymer electrolyte system resulting in 80:20 composition as optimum ratio. Proper blending, good plasticity, and free-standing film was obtained. Any other composition resulted in unstable and fragile thin film. In this experiment, incorporation of additive materials [7] was observed to understand how they affect crystallinity level and ionic conductivity of solid polymer electrolyte system.

2. Experimental methods

2.1. Materials
Electrolyte salt lithium bis(oxalato) borate (LiBOB, Sigma Aldrich), was used after heating treatment to remove water. Poly(vinylidene) fluoride (PVdF, Sigma Aldrich), was used as polymer matrix. Interchangeably, polyethylene glycol, (PEG, Merck), and polyethylene oxide (PEO, Merck), was used in addition to PVdF. Additive materials titanium oxide (TiO$_2$, Merck) and aluminium oxide (Al$_2$O$_3$, Merck), were used without further purification. As the solvent, N,N-dimethylacetamide (DMAC, Merck) was utilised as the other materials have excellent solubility in DMAC compared to other solvents such as N-methyl pirrolidone, NMP, or dimethyl furan, DMF.

2.2. Sample preparation
Solid polymer electrolyte sample was prepared using solution cast technique. Polymer materials were dissolved in DMAC using magnetic stirrer on a hot plate. PVdF:LiBOB concentration was fixed throughout this investigation while additive content was varied as shown in table 1. Electrolyte salt and additive materials were subsequently added into the polymer solution until homogeneously mixed and a clear slurry has been formed. The slurry was cast onto a glass substrate and air-dried in atmospheric condition until a polymer membrane was obtained. To remove any possible remaining solvent, the membrane was heated in a vacuum oven for 24 hrs in 50°C temperature. A small section of the membrane was cut out for characterisation, then the rest of the sample was stored in a dry box with less than 40% relative humidity (RH) to maintain its properties.

| Table 1. Sample Preparation of Solid Polymer Electrolyte using Various Additives. |
|----------------------------------|
| Content                         |
| Sample A PVdF + PEO + LiBOB + TiO$_2$ |
| Sample B PVdF + PEO + LiBOB + Al$_2$O$_3$ |
| Sample C PVdF + PEG + LiBOB |
| Sample D PVdF + PEO + LiBOB |
| Sample E PVdF + PEO |
| Sample F PVdF + LiBOB |

2.3. Sample characterisation
Surface morphology was observed using Scanning Electron Microscopy (SEM) Hitachi SU-3500. To preserve sharpness and focus, low acceleration voltage of 5 kV was used. However, 20 kV acceleration voltage was employed while performing Energy Dispersive X-ray Spectroscopy (EDS) to examine element distribution. Phase shifting and change, as well as crystallinity level, was observed using X-Ray Diffractometer (XRD) analysis, using CuK$_\alpha$ radiation between 20 of 10° to 50°. Room temperature conductivity of the polymer electrolyte membrane was determined from AC-impedance measurement using Hioki 3520 LCR with data acquisition obtained over the frequency range of 1 Hz.
and 1 MHz. The membrane was sandwiched between two stainless steel plates acting as blocking electrodes.

3. Results and discussion

3.1. SEM
Figure 1 shows the surface morphology of solid polymer electrolyte membrane observed using SEM Hitachi SU-3500. Without salt and additives, surface of the polymer matrix appears to be smooth and flat as shown in figure 1(e). Addition of LiBOB electrolyte salt results in porous membrane across the surface (figure 1(f)).

![SEM pictures of (a) Sample A, (b) Sample B, (c) Sample C, (d) Sample D, (e) Sample E, and (f) Sample F](image1)

TiO$_2$ addition results in uneven blending of solid polymer electrolyte system, as shown in figure 1(a), in contrast, figure 1(b) shows homogeneously blended Al$_2$O$_3$ additive and LiBOB salt in the polymer matrix. The ionic conductivity of the solid polymer electrolyte system can be partly attributed to this phenomena; this would be discussed further in the next section. Surface morphology of sample C and D are presented in figure 1(c) and (d), respectively. The porous surface of the polymer membrane is observed on these samples, with grains of electrolyte salt dispersed throughout the layers.

3.2. XRD
Phase identification was performed using PDXL software; beta-PVdF phase was identified in all samples, as observed on 2θ of 20.47° and hkl of (220).

The prominent diffraction peak of porous film with TiO$_2$ and Al$_2$O$_3$ are shown in figure 2(a) and 2(b), respectively, indicating an unsuccessful blending of TiO$_2$ and Al$_2$O$_3$ filler. In addition, it also indicates that the crystallinity levels of both samples are still relatively high, which impact to the ionic conductivity is in good agreement with the EIS measurement. High crystallinity level could hinder the lithium-ion movement between electrodes, hence decreasing the ionic conductivity of the solid polymer electrolyte system [8].
The diffraction patterns of other samples are almost similar, demonstrating that the additive and electrolyte salt has been mixed homogeneously into the porous PvdF substrate (figure 2(c), 2(d), 2(e), and 2(f)). It is also observed that addition of PEG and PEO does not lead to higher crystallinity level of the solid polymer electrolyte system, which is desired properties from these additives.

3.3. EIS

Results of impedance measurement using LCR meter was presented in a Cole-Cole plot. Ionic conductivity of solid polymer electrolyte system was calculated using simple equation τ = t / (Rb * A), where τ is ionic conductivity, t is membrane thickness, Rb is bulk resistivity, and A is surface area of the membrane in contact with stainless steel plate of LCR meter, functioned as a blocking electrode. The value of Rb was taken from the intercept of the first semicircle on the X axis. Generally, Cole-Cole plot has two parts; first semicircle represents bulk/grain resistance while the linear line represents grain boundary resistance.

Figure 3 presents value of -log ionic conductivity of all sample. Highest ionic conductivity (lowest -log value) is indicated by sample B followed by sample C, D, A, and F. Naturally, sample E possess the lowest conductivity value as it only contains polymer substrate with neither electrolyte salt nor additive materials. Poorly blended sample A was causing high crystallinity of PEO phase, which in turn resulting in ionic conductivity that was less than expected. Solid polymer electrolyte system using
PEO and PEG without metal oxide additive materials does not appear to show a significant difference in terms of ionic conductivity, in accordance with XRD diffractogram which presents relatively similar pattern of these two samples.

4. Conclusions
Solid polymer electrolyte has been prepared via solution cast technique, producing a free-standing conductive membrane. From the characterisation performed on the sample, it can be concluded that incorporation of additive materials contributes highly to the ionic conductivity of the membrane due to the crystalline-amorphous phase transition. This condition would increase lithium-ion mobility between electrodes, hence improving the ionic conductivity of the solid polymer electrolyte.

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