

Fabrication and characterisation solid polymer electrolyte based polyvinylidene fluoride - lithium bis (oxalato) borate

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Abstract. The aim of this research is to fabricate and investigate the properties of solid polymer electrolyte (SPE). This kind of electrolyte can take place as electrolyte and separator for LIB in order to prevent leakage of its package caused by employing liquid electrolyte. SPE based on Lithium Bis (Oxalato) Borate or LiBOB and Polyvinylidene Fluoride (PVDF) was carried out by simple casting techniques. SPE preparations were performed by varying the ratio of PVDF and LiBOB compositions (90:10, 85:15, 80:20, 75:25) dissolved in DMAC solvents at 50 °C. Characterization of Electrochemical Impedance Spectroscopy is used to observe ionic conductivity of the SPEs, and that of Cyclic Voltammetry is used to investigate the performance of the battery as well. The obtained sheets have a thickness from 40 to 140 μm . Sample having 90:10 ratio of PVDF-LiBOB has the highest ionic conductivity, namely $4,97 \times 10^{-5} \text{ S cm}^{-1}$. The sample which has good performance is exhibited by the sample D investigated by the existence of oxidation and reduction peaks which reveal the reversible system.

1. Introduction

Lithium-ion battery (LIB) is a battery which is widely used as a source of electricity in various electronic devices such as camera, laptops, mobile phones, laptops, and other electronics. Lithium batteries have excess strength such as lighter weight, larger storage capacity, and long-life cycle [1]. Recently, researchers are trying to develop lithium battery system called all solid state batteries whose components are solid, including electrolytes. With this system, the battery will be avoided from electrolyte leakage and has better packaging efficiency [2].

In developing all Solid State Batteries, the solid polymer electrolyte (SPE) is being developed by recent researchers. SPE consists of salts dissolved in a polymer matrix. Besides taking place as Li ion conductor, it also acts as a separator dissociating the electrodes to avoid getting short circuit. SPE has many advantages, such as having good flexibility, not easy to react with electrode, lighter, and easier to fabricate [3]. In addition to its advantages, SPE has a lower ionic conductivity compared to a commercial electrolyte (LiPF_6).

Sharma and Tharuk tried to develop SPE based Poly(acrylonitrile)-Lithium hexa-flour phosphate (PAN-LiPF_6) which exhibit ionic conductivity ranges from 10^{-3} Scm^{-1} [4], nevertheless capacitance stability of LiPF_6 is less stable than lithium bis(oxalate) borate (LiBOB) [5]. SPEs based poly (vinyl alcohol) (PPA) - LiBOB salt were successfully manufactured with ionic conductivity ranging from 10^{-5}



⁴ Scm⁻¹ [6]. In addition to PPA, Polyvinylidene Fluoride (PVDF) - LiBOB is fabricated with fillers such as Polyethylene Oxide (PEO) [7], Titanium Oxide (TiO₂) [8], Aluminum Oxide (Al₂O₃) [9], and ZrO₂ [10]. The addition of these fillers can decrease crystallinity and improve the mechanical properties of SPE. Preparation of SPE with the PVDF polymer matrix due to the polymer has several advantages, such as its high dielectric constant (8.5), which can affect the solubility of lithium salt [11], and good insulators. Some researchers have attended greatly PVDF as a membrane or composite for developing LIBs or Lithium-Sulfur batteries (LSBs). It's regarded to its good properties such as thermal stability, high mechanical strength, high hydrophobicity, and chemical resistance.

This paper discusses the results of research on the characterization of solid polymer electrolyte (SPE) fabricated by PVDF as the polymer matrix and LiBOB as lithium salt with different ratios and without addition of filler. The solvent used is N, N-Dimethyl Acetamide (DMAC). SPE drying is done at room temperature. The SPE was assembled into a half cell. Characterization is performed to see impedance by using Electrochemical Impedance Spectroscopy (EIS) and to see electrochemical performance in coin cell by using Cyclic Voltammetry.

2. Methods

2.1. Materials

The electrolyte salt used in this preparation was Lithium bis (oxalato) borate (LiBOB, Sigma Aldrich). The polymer matrix was Poly (vinylidene) fluoride (PVdF, Sigma Aldrich) with purity > 98% and a molecular weight >180,000 (GPC). The solvent was N, N-dimethylacetamide (DMAC, Merck) purity > 99%. The activator of LiBOB was EC: EMC with the ratio 1:1 purchased from Merck with purity > 98%.

2.2. Sample solid polymer electrolyte preparation

SPE preparation was carried out by using casting solution technique. Initially, PVDF was heated at 70 °C for 24 hours in order to evaporate its air content. The heated PVDF was dissolved in 5 mL DMAC on a hotplate (KA C- MAG HS-7) at 50 °C while stirred at 1 rpm for 45 min. The mixture was added LiBOB and kept stirring at 1 rpm on the hotplate at 50 °C for 45 minutes. After homogeneously dissolved LiBOB, the slurry was cast on the glass and dried at room temperature. The composition of the mixture was shown by table 1.

Table 1. Composition of PVdF-LiBOB.

Sample	PVdF (gr)	LiBOB (gr)
A	0.90	0.10
B	0.85	0.15
C	0.80	0.20
D	0.75	0.25

2.3. Preparation of half coin cells

The coin cell was assembled by a cathode, lithium metal, and an anode, lithium titanium oxide (Li₄Ti₅O₁₂) (LTO). The anode is widely studied because of being a low expense and owning safe material, and theoretically exhibit a high specific capacity (175 mAh/g) as well. It pays attention for applications in lithium-ion batteries. Before crimped into the coin cell, the SPEs, which were shaped like a disk with diameter 19 mm, were dropped by EC: EMC (1: 1 ww%) in order to activate the lithium salt. The assembling process was carried out in glove box filled by argon gas.

2.4. Sample characterisation

The dried SPEs were characterized by an EIS (HIOKI 5322-50 LCR HiTESTER) to measure the ionic conductivity under frequency 0.6 kHz - 50 kHz. The coin cells were tested by cyclic voltammetry

(CV) within the scan rate 0.05 mV/s over the voltage range, 0,05 – 3,0 V for three cyclics. This is conducted to evaluate its electrochemical occurred in the system.

3. Result and discussions

3.1. EIS

The result of EIS characterization is presented in a Cole-cole plot. From the plot, there are two parts, semicircle and linear line. The semicircle indicates bulk resistivity while the linear line indicates the diffusion process in the SPE. The functions of solid polymer electrolyte in battery system are not only to contribute ionization process but also to separate anode and cathode in order to prevent short circuits. Separator resistance affected of internal resistance of the battery so that it can effect to the performance of the battery. Figure 1 shows cole-cole plot which could be analysed for calculating the impedances of the coin cell. They can be counted by determining the intersection of semicircle form with the Z' axis.

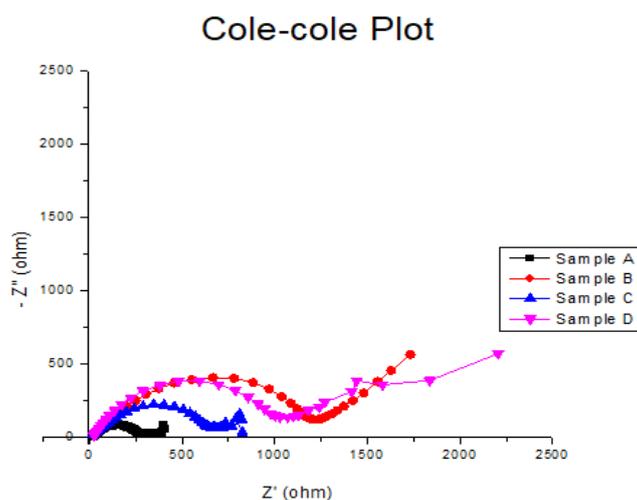


Figure 1. Cole-cole Plot of SPE based PVDF-LiBOB.

The black, blue, pink, and red lines respectively represent the sample A, C, D, and B. EIS assay accompanied by the ionic conductivity value of the coin cell. Based on the semicircle graph, the impedances obtained in sample A, B, C, and D are respectively 2.82×10^2 ohm, 1.21×10^3 ohm, 6.58×10^2 ohm, and 1.07×10^3 ohms, respectively. The equation, $\sigma = t / (R_b * A)$ is used to calculate the ionic conductivity, where σ means the ionic conductivity, t means the thickness of SPE, R_b means SPE bulk resistance, and A means the area of the SPEs. Table 2 shows the ionic conductivity of each sample. The highest ionic conductivity was achieved by sample A. Theoretically sample D should have the highest one because it has lithium salt the most [6]. This condition can be caused by the solubility of LiBOB as lithium salt in the solvent. Each sample has time in common to be stirred, namely 45 minutes. Because they consist of lithium salt differentially so that the sample D, 25% LiBOB, perhaps owns dissolutive lithium salt more than the others. The more the sample contains LiBOB, the longer it should be stirred.

Table 2. Ionic conductivity of SPEs based PVdF-LiBOB

Sample	Conductivity (S cm ⁻¹)
A	4.97×10^{-5}
B	2.06×10^{-6}
C	7.55×10^{-6}
D	6.50×10^{-6}

3.2. Cyclic Voltammetry

Figure 2 shows the CV characteristic of coin cells with the PVDF-LiBOB based SPEs. The CV measurements were performed with a voltage range of 0.05 - 3.0 volts and a scan rate 50 mV / s for three cycles. The current response is represented as a function of the applied potential. The current in the overall process of this system is brought by two steps, the migration of electroactive material to the surface and the reaction of electron transfer.

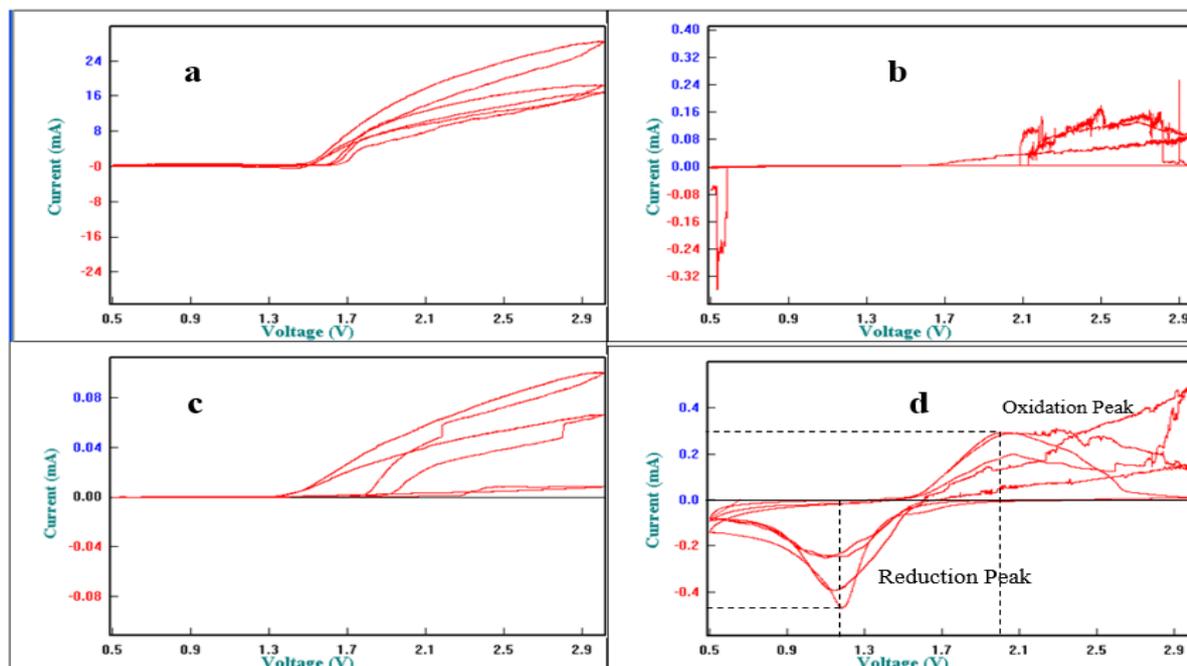


Figure 2. Cyclic voltammetry (CV) curves of Li/LTO cell with SPEs, (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

This method, cyclic voltammetry, has been used widely by the amount of inorganic researchers, because the ligands affecting the potential of cyclic voltammetry on the reduction and oxidation process of central metal ion is interested in investigating. The graphs of Sample B and D are rougher than those of sample A and C. This may be caused by the existence of impurities as SPEs were prepared. In addition, the lithium salt (LiBOB) is hygroscopic [12], wherein the lithium salt readily binds to water in the air, which can cause short-circuit cells. The oxidation peak of the sample D graph lies at a current around 0.3 mA to 0.35 mA and voltage around 1.9 to 2.1 volts. The reduction peak lies at a current (-0.45) to (-0.50) mA and voltage around 1.18 to 1.2 volts. The difference voltage of the peaks for sample D was obtained around 0.72 to 0.9 volts. When we analyse the cyclic voltammogram based on the peak current of the anode and cathode, the characteristics of the electrochemical process can be determined, such as reversible or irreversible [13]. That the reaction is quite fast to maintain the concentration of the oxidized and reduced forms in equilibrium with each other at the electrode surface can be meant as reversible electrochemistry. The four cyclic voltammograms show that sample A, B, and C possess the oxidation peak only. It means that the samples can be classified into an irreversible system while the sample D includes the reversible system due to the couple peaks.

4. Conclusions

SPE based PVDF-LiBOB was successfully carried out by simple solution casting. From the characterisation employed to the samples we can infer that the highest ionic conductivity of SPEs prepared was achieved to the sample with the PVDF-LiBOB ratio 90:10, namely $4.97 \times 10^{-5} \text{ S cm}^{-1}$. The result is not encouraged by cyclic voltammetry characterization which exhibits that sample D has two peaks, oxidation and reduction.

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