



# Effect of nano-sized barium titanate addition on PEO/PVDF blend-based composite polymer electrolytes

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## ABSTRACT

In the present study, poly(ethylene oxide) (PEO) and poly(vinylidene fluoride) (PVDF) blend based composite polymer electrolytes (CPEs) had been prepared by using a different content of nano-sized BaTiO<sub>3</sub> filler, in order to examine the filler addition effect on the structural modification and electrochemical properties. The crystallinity and thermal stability of the CPEs was evaluated using differential scanning calorimeter (DSC), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The electrochemical properties of CPEs were measured by the AC impedance method and cyclic voltammetry (CV). As a result, Both DSC and XRD results indicated that the CPE showed reduced crystallinity after the introduction of BaTiO<sub>3</sub> filler. From the ionic conductivity results, the CPE containing BaTiO<sub>3</sub> filler 15 wt.% showed the highest ionic conductivity ( $1.2 \times 10^{-4}$  S/cm) with a wide electrochemical stability window and an excellent thermal stability at room temperature. This indicated that electrochemical characteristics are dependent on the reduced crystallinity by the addition of nano-sized BaTiO<sub>3</sub> filler content.

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## 1. Introduction

Lithium polymer battery (LPB) is one of the best choices for electrochemical power source of the near future characterized by its high energy density, good cyclability, and safety [1]. Solid polymer electrolytes have received much attention as the electrolyte materials for all solid-state rechargeable lithium batteries and many polymer electrolytes have been developed [2–5].

Polymeric electrolytes have found wide application in electric or medical devices, electro-luminescence devices and photo-electric devices. Since Wright et al. discovered in 1973 that composite polymer electrolytes (CPEs) based on polyethylene oxide (PEO) with an alkaline metal salt offered ionic conductivity [6]. PEO (polyethylene oxide)-based polymer electrolyte is of current interest for high energy density and high power lithium-ion batteries due to their easy formation of complex with lithium salts, high mobility of charge carriers and stable chemical properties, etc. [7]. The order of the ion conductivity of pure polyethylene oxide is around  $10^{-7}$  to  $10^{-6}$  S cm<sup>-1</sup> at room temperature [8–12] and the order of conductivity is not suitable for practical applications. The order of ionic conductivity of  $10^{-6}$  to  $10^{-4}$  S cm<sup>-1</sup> was improved with the addition of various lithium salts (LiX; X = ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, etc.) and liquid plasticizers like ethylene carbonate (EC) or propylene carbonate (PC) and low molecular weight polyethylene glycol (PEG) to the pure PEO polymer. However, the addition of liquid plasticizer in the PEO–LiX polymer electrolyte

can improve its ionic conductivity by an order of magnitude, but their mechanical properties and potential stability of the films are not good for various applications [13,14].

Blending of different polymers provides easy preparation and feasible control of the physical properties within the miscibility compositional region. It also exhibits properties that are superior to the properties of individual component of the blend [15–17]. Recently, many efforts have been devoted to increase the ionic conductivity of blend-based polymer electrolyte membranes such as P(VdF-HFP)/PVAc [18], PEO/PAN [19], and PVDF/PEO [20]. Fan et al. [21] reported that the blend of PEO and PVDF could hinder the crystallinity of PEO, and achieve a good combination of high ionic conductivity and good mechanical strength.

On the other hand, nano-sized ceramic filler, due to its large surface area, prevents local PEO chain re-organization, which results in “locking in” at ambient temperatures, a high degree of disorder characteristic of the amorphous phase, which in turn favors high ionic transport [22–26]. Addition of ceramic fillers (TiO<sub>2</sub> [27,28], SiO<sub>2</sub> [29,30], Al<sub>2</sub>O<sub>3</sub> [31,32], BaTiO<sub>3</sub> [33,34], MgO [35]) to PEO-based electrolytes was found to increase room temperature conductivities by about 2–3 orders of magnitude, resulting increased lithium ion transference numbers, and improved interfacial [33] as well as mechanical properties [36]. Ion transport properties, thermal transitions and morphology of the composite polymer electrolytes have been dependent on the size/mass [35], surface area and surface feature of the ceramic fillers.

Although many researchers have reported the usage of various fillers for improvement of the physical and electrochemical properties

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of CPEs, the effect of nano-sized complex ceramic filler on the micro-structure and ion-conducting behaviors of polymer matrix containing PVDF polymer blend have not been fully established. Our study was focused on the ionic conductivity behaviors and the preparation of PEO/PVDF polymer matrix containing nano-sized complex ceramic (BaTiO<sub>3</sub>). In the present study, nano-sized BaTiO<sub>3</sub> was introduced into PEO/PVDF matrix based CPEs. The relationship of ionic conductivity with crystallinity was analyzed. Furthermore, the electrochemical stability and morphology for polymer electrolyte were studied.

## 2. Experimental

### 2.1. Materials

Poly (ethylene oxide) and Poly (vinylidene fluoride) with average molecular weights of  $1 \times 10^6$  (Aldrich) and  $5.34 \times 10^5$  (Aldrich), respectively, were used without further purification. Barium titanate (<100 nm particle size) was purchased from Aldrich. Lithium perchlorate (battery grade, 99.99%) was acquired from Aldrich and stored under glove box of dry Ar-atmosphere before use. Acetonitrile (ACN) also was acquired and liquid propylene carbonate (PC) was purchased from Junsei, Japan and used without further purification.

### 2.2. Preparation of composite polymer electrolytes

All of the composite polymer electrolytes (CPEs) were prepared using the solution casting technique. The CPEs system entailed the use of PEO and PVDF blend polymer matrix in a molar ratio of 8:2, PEO and LiClO<sub>4</sub> salt in a molar ratio [EO]:[Li] of 16:1, PEO and PC plasticizer in a molar ratio 1:0.1, with a different weight ratio BaTiO<sub>3</sub>. The preparation of CPE films involved the initial dissolution of PEO, PVDF and PC in ACN at room temperature for several hours, after which LiClO<sub>4</sub>, BaTiO<sub>3</sub> was added to the PEO/PVDF/PC polymer matrix solution prepared. After a homogenous mixture was obtained, it was cast onto a Petri dish and any residual solvent such as an acetonitrile were evaporated in a dry oven at 50 °C for 24 h. Finally, resultant electrolyte films were obtained. The obtained solid polymer electrolyte was peeled from the laboratory dish and stored inside the glove box.

### 2.3. Measurements

The morphology of the CPE films was investigated by SEM (HITACHI S3500N). The X-ray diffraction (XRD) patterns of CPE as functions of the BaTiO<sub>3</sub> content were obtained with a PHILIPS (Netherlands), X'Pert-MPD System equipped with a rotation anode and using line focus 3Kw Cu-K $\alpha$  X-ray tub radiation. Differential scanning calorimetry (DSC) studies were performed in the 0–100 °C range with a Perkin-Elmer (Pyris 1) system, at a heating rate of 5 °C/min and with purging nitrogen gas. The DSC studies were performed to confirm the crystallinity change of composite by peak intensity or peak area in the process of heating and cooling. Thermogravimetric analysis (TGA) were performed on the CPE using a Perkin-Elmer (TGA 7) analyzer to investigate the thermal degradation behaviors from 30 to 700 °C at a heating rate of 5 °C/min in a nitrogen atmosphere.

Measurements of electrochemical properties were carried out using a Iviumstat (IVIUM Technologies, Netherlands). The ionic conductivity measurements of the composite polymer electrolytes were carried out by means of AC impedance spectroscopy over the frequency range from 200 kHz to 10 Hz. The impedance measurements were performed by sandwiching the films between two stainless-steel (SS) electrodes. The conductivity values ( $\sigma$ ) were calculated from the bulk resistance ( $R_b$ ), which was determined by equivalent circuit analysis software.

$$\frac{1}{\sigma} = \frac{R_b A}{t} \quad (1)$$

where  $R_b$  is the resistance, and  $t$  and  $A$  are the thickness of the electrolyte film and the areas of film. The electrochemical stability of the electrolyte films was evaluated by cyclic voltammetry (CV) at a scan rate of 5 mV s<sup>-1</sup>.

## 3. Results and discussion

Fig. 1 shows SEM images of the CPE films containing various BaTiO<sub>3</sub> contents. In the case of the (a) sample, that is a PEO/PVDF/PC/LiClO<sub>4</sub> film containing no filler, a rather homogeneous morphology was shown, except some pores and rich-phases probably related to the existence of nano-sized BaTiO<sub>3</sub>. By increasing the BaTiO<sub>3</sub> content from 5 to 15 wt.%, the film morphology was changed. First of all, some of the phase, which could have been defects in the electrolyte film, disappeared in the cases of (b) to (d). This suggested that the film compactness had been improved and that the defects had been removed by adding the BaTiO<sub>3</sub> fillers. Besides, the phases and pores were made more prominent by increasing the BaTiO<sub>3</sub> content. This implied that the additional filler had been introduced into the CPE films enough to induce the Li salt, PC, nano filler rich-phases, resulting in the rather heterogeneous film morphologies. However, as shown Fig. 1(E), when filler content exceeds 15 wt.%, the phase separation was observed due to immiscibility and filler aggregation phenomena by the excessive addition of filler. This explained that a phase separation phenomena of the PEO/PVDF polymer matrix due to immiscibility and filler aggregation phenomena by the excessive addition of BaTiO<sub>3</sub>. As a result, these phenomena could be explained by improvement of the ion transport ability by miscibility increase between PEO and PVDF polymer chains by uniform particle dispersion of BaTiO<sub>3</sub> filler of 15 wt.% content in Fig. 1(D).

Fig. 2 shows the crystallinity changes in the electrolytes of varying BaTiO<sub>3</sub> contents obtained by X-ray diffraction. The characteristic diffraction peaks of the PEO crystalline phase are apparent between  $2\theta = 15^\circ$  and  $30^\circ$  [37]. In comparison with the pristine PEO sample, the diffraction peaks of the CPE containing PC, Li salt became considerably smaller and less prominent, reflecting the decreased crystallinity. With the gradual addition of the additional BaTiO<sub>3</sub> to the PEO/PVDF/PC polymer matrix system, the intensities of the characteristic peaks proportionally decreased, reaching the lowest value at a content of 20 wt.%.

To confirm the effect of filler addition on the crystalline structure of the CPEs, melting and crystallization behavior was obtained by the DSC method, as shown in Fig. 3(A) and (B). With the addition of the BaTiO<sub>3</sub> to the PEO/PVDF polymer matrix, the intensities of the characteristic peaks decreased, reaching the lowest value at 20 wt.%. The melting and crystallization transition, corresponding to the crystalline to amorphous transition, was very sluggish, and the endothermic reaction was shown to start from below the melting and crystallization point. The curves moved to a low-temperature region as a result of the addition of BaTiO<sub>3</sub>. It was found that the melting temperature ( $T_m$ ) of crystalline PEO was around 54–61 °C(a) and the crystallization temperature ( $T_c$ ) of crystalline PEO was around 28–35 °C(b), which was slightly degraded when the content of BaTiO<sub>3</sub> was increased. Also, the CPE crystallinity was decreased with the addition of increasing amounts of BaTiO<sub>3</sub>. Consequently, it could be stated that the presence of BaTiO<sub>3</sub> improved the ionic conductivity of the CPE by slightly decreasing the CPE crystallinity [38].

The value  $\chi_c$  has been defined as the enthalpy ratio of PEO samples to the complete crystalline PEO. It can be calculated by the equation:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^\circ} \quad (2)$$

where  $\Delta H_f^\circ$  (147.76 J/g) is the melting enthalpy of a completely crystalline PEO sample and  $\Delta H_f$  is the experimental enthalpy. The crystallinity value can describe the relative change of the crystalline or

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