

Electrochemical characteristics of two types of PEO-based composite electrolyte with functional SiO₂

Jong-Wook Kim, Kwang-Sun Ji, Jae-Pil Lee, Jong-Wan Park*

*Department of Metallurgical Engineering, Division of Materials Science and Engineering, Hanyang University,
17 Haengdang-dong, Seongdong-Ku, Seoul 133-791, South Korea*

Abstract

This work has investigated that the electrochemical properties of PEO–lithium bis(perfluoroethylsulfonyl)imide (LiBETI)–SiO₂ with different surface groups.

The ac impedance, cyclic voltammetry, scanning electron microscope (SEM), X-ray diffraction (XRD) were used for understanding electrochemical characteristics of prepared composite electrolytes. Composite electrolytes prepared with SiO₂ covered with trimethylsilyl exhibited good electrochemical properties. The ionic conductivity of composite polymer electrolytes (CPE) reached a maximum of about 1.5×10^{-5} S/cm at 25 °C. This result was obtained since SiO₂ covered with trimethylsilyl is suitable for increasing dispersability as well as not impeding the role of the SiO₂ surface.

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1. Introduction

In recent years, the market for consumer electronic products and the call for environmentally compatible vehicles have motivated the research and development of electrochemical power sources characterized by high energy, high power densities, good cyclability, reliability, and safety. To satisfy consumer's demands, additional improvements in the electrochemical and mechanical properties of electrolytes are needed.

However, electrochemical properties of PEO–LiX electrolyte do not satisfy the user's demands.

In order to improve the electrochemical properties of electrolytes, several approaches have been attempted by crosslinking reactions [1], copolymerization [2], addition of nano-size fillers [3] and by attachment of short chain PEO oligomers as side chains to form “comb-shaped” like structures on other polymers [4].

We investigated the addition of SiO₂ as a filler for composite electrolytes. Nano-size particles provide an order of magnitude increase in ionic conductivity over micro-size particles [5–7]. Therefore, nano-size fillers are very attractive, and there is growing interest in using surface-modified fumed silica as a filler.

An amount of related work has been performed on SiO₂.

Walls et al. [8] showed that surface groups on fumed silica determine the mechanical properties of the PEGDME-based composite polymer electrolyte (CPE). Their work also investigated electrochemical properties of prepared CPE with either hydrophilic or hydrophobic surface groups on the SiO₂ ceramic filler.

Liu et al. [9] prepared SiO₂ functionalized by 2-[methoxy-(polyethylenoxy)-propyl] trimethoxy silane and compared with untreated SiO₂ as the ceramic filler. Their work showed that treated SiO₂ used as filler could noticeably improve ionic conductivity and interfacial stability.

Chen and Chang [10] demonstrated that the addition of D-2000-modified hydrophobic montmorillonite enhanced the ionic conductivity of PEO-based electrolytes.

In this paper, one common feature of used filler was that they all had functionalized groups. Therefore, the purpose of this work is not only to investigate the electrochemical properties of PEO + lithium bis(perfluoroethylsulfonyl)imide (LiBETI) + SiO₂, but also to study the effect of the surface chemistry of SiO₂ with different functional groups.

2. Experimental

The PEO:LiN(SO₂CF₂CF₃)₂ (LiBETI)–SiO₂ composite electrolyte films were prepared by the solvent casting

* Corresponding author. Tel.: +82-2-2290-0386; fax: +82-2-2298-2850.
E-mail address: jwpark@hanyang.ac.kr (J.-W. Park).

technique using reagent grade poly(ethylene) oxide (Aldrich, $M_w = 400,000$), LiBETI (3 M), nano-size SiO_2 . Two kinds of the SiO_2 is used in this work. One type is SiO_2 (–7 nm, Degussa-Huls, R812) with trimethylsilyl $(\text{CH}_3)_3$ and silanol (Si–OH) surface groups, and the other type is SiO_2 (–7 nm, Degussa-Huls, R106) with Si–O–[–Si(CH₃)₂–O–]₄–H and silanol (Si–OH) surface groups. Poly(ethylene) oxide and LiBETI were dried before solvation in a vacuum oven for 24 h at 50 and 120 °C, respectively. Acetonitrile as a solvent was added to the PEO and LiBETI mixture to form slurries. A homogeneously dispersed emulsion, consisting of SiO_2 and the solvent, was also formed separately. The two slurries were mechanically mixed to dissolve the organic and inorganic materials in the solvents, and to achieve a homogeneous mixture. After mixing was completed, the homogeneous slurry was then transferred to a Teflon plate and the solution was cast using a doctor blade. The solvent was removed in air at room temperature for 5 h to yield a uniform film of about 80–140 μm average thickness. The attained film was dried subsequently at 50 and 25 °C in the evacuation chamber for 24 h. The final composite electrolyte films were obtained after being kept in an inert gas-filled glove box over 72 h.

Sandwich type cells (electrode/composite electrolyte/electrode) were fabricated in a glove box and then sealed up with a vacuum packer (HENKELMAN, 200A) to prevent moisture permeation.

All specimens between blocking electrodes were subjected to heat treatment at 90 °C for 24 h and then cooled down slowly to room temperature. The specimens were then sealed in a heating mantle, which guarantees a uniform temperature atmosphere before the impedance measurement.

The ionic conductivity was measured in 5 mV increments from 1 Hz to 100 kHz using an ac impedance analyzer (EG&G, M6310, M398 software). Samples were placed between two stainless steel electrodes.

The interfacial resistance between composite polymer electrolyte and lithium metal electrode was evaluated by impedance response of symmetric Li/electrolyte/Li cells in the frequency range from 10 mHz to 100 kHz. The electrode area was 1 cm^2 . X-ray diffraction (XRD) measurement was made with a Rigaku Cu K α .

3. Results and discussion

3.1. Properties of SiO_2 powders

The powder size of the SiO_2 powders was characterized using a JEOL JSM-6340F-type field emission scanning electronic microscope (FESEM).

A SEM image of the powders is shown in Fig. 1. Uniform grain size distribution is observed. Due to the ultrafine nature of the SiO_2 particles, these small particles tend to form large agglomerates [11,12].

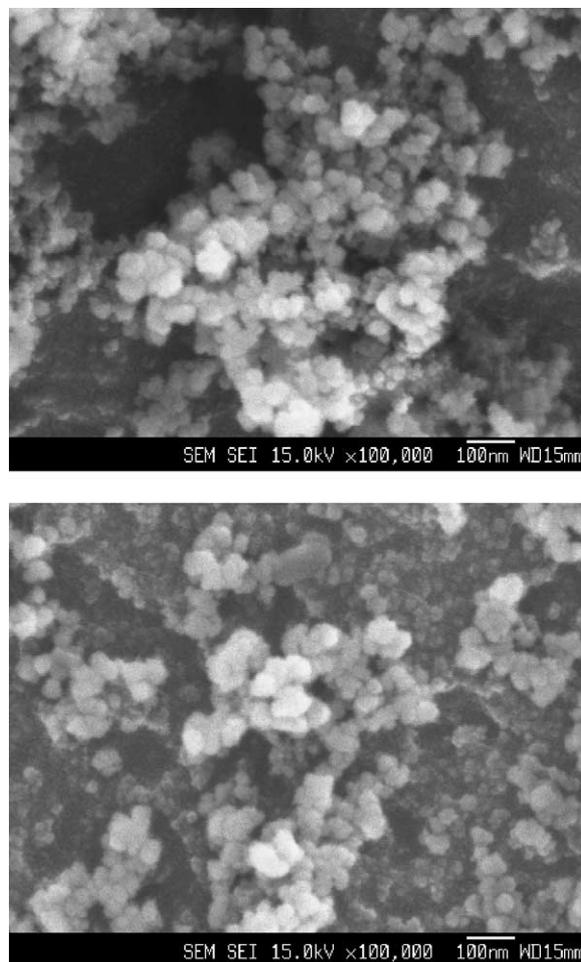


Fig. 1. Scanning electronic micrographs of the SiO_2 powders: (a) R812 and (b) R106.

3.2. XRD

With the addition of filler, it is a well-known fact that the intensity of the crystalline peaks decreases and noticeably broadens [13] and additional decrease of crystallinity is obtained through heat treatment.

Fig. 2 shows the XRD pattern for $(\text{PEO})_{16}$ -LiBETI-R106 before and after annealing. Crystallinity was reduced by additional steric hindrance caused by filler re-arrangement after the film was annealed at 90 °C for 24 h. A possible explanation is that the ceramic filler, due to its small particle size and its large surface area, prevents PEO chain reorganization with the result of freezing at ambient temperature a high degree of disorder which is likely to be accompanied by a consistent enhancement of the ionic conductivity [14].

3.3. Ionic conductivity

Previous works [6,7] have shown that the conductivity was enhanced at room temperature when nano-size ceramic fillers were added to the polymer–lithium salt complex.

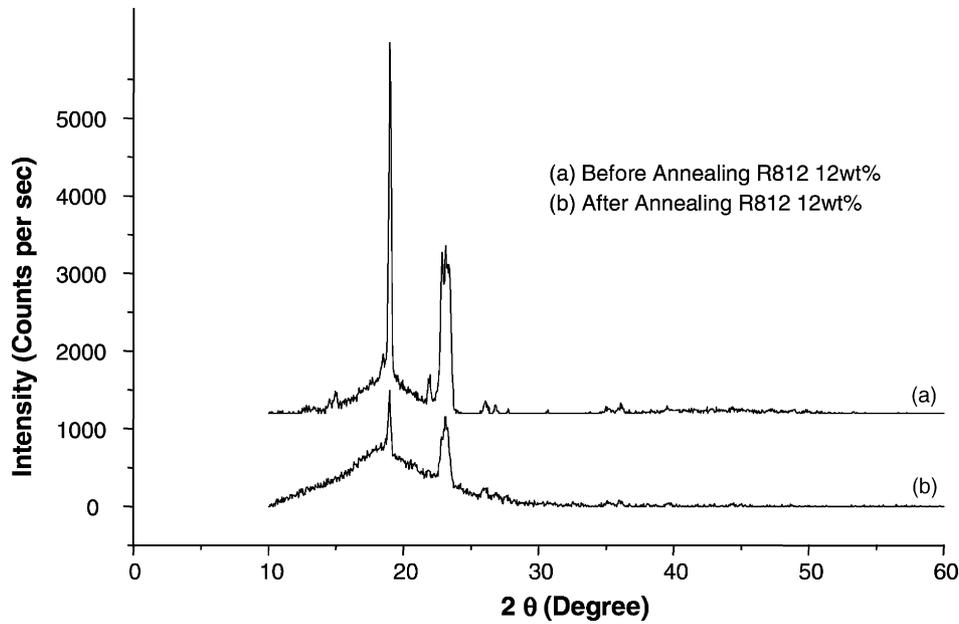


Fig. 2. X-ray diffraction patterns of the PEO–LiBETI–12% R812 composite electrolyte: (a) before annealing and (b) after annealing.

The dependence of ionic conductivity on the nano-size SiO₂ concentration is represented in Fig. 3, when the EO/Li ratio was fixed at 16. The data showed that the ionic conductivity of filler-inserted electrolyte had a maximum value of 1.5×10^{-5} S/cm at 25 °C when R812 12 wt.% added. It was higher than that of the filler-free one. In general, the ionic conductivity is increased with temperature in polymer solid electrolytes due to the higher segmental motion of polymer chains in the amorphous phase, in which the filler’s role in assisting lithium-ion conduction would be ignored. There was no significant difference in the conductivity over 60 °C in Fig. 4. For that reason, we concentrated

on the role and the enhancement mechanism of nano-size fillers at room temperature with three points of view—dielectrics, degree of crystallization and the existence of a space-charge layer at the polymer/filler interface [15]:

$$\sigma = \sum_i F|Z_i|C_i\mu_i \tag{1}$$

From Eq. (1), one can see that the conductivity of solid-state electrolyte has many determinants, such as carrier concentration (C_i), mobility (μ_i) and so on [16]. The ionic conductivity enhancement when adding high dielectric ceramic fillers (TiO₂, BaTiO₃, PbTiO₃, etc.) into PEO–Li

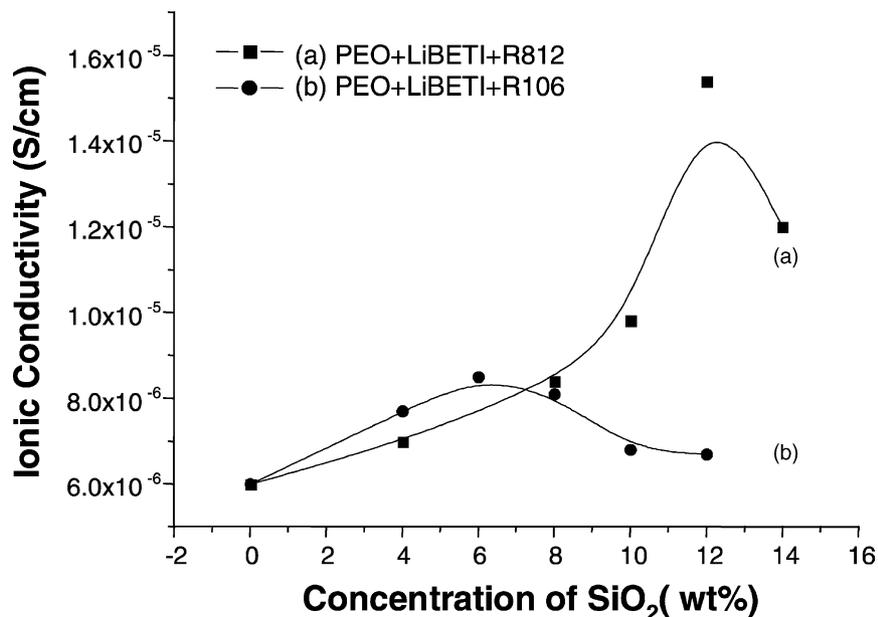


Fig. 3. Ionic conductivities vs. SiO₂ concentrations for PEO/LiBETI/SiO₂ composite electrolyte at 25 °C (where EO/Li⁺ = 16): (a) R812 and (b) R106.

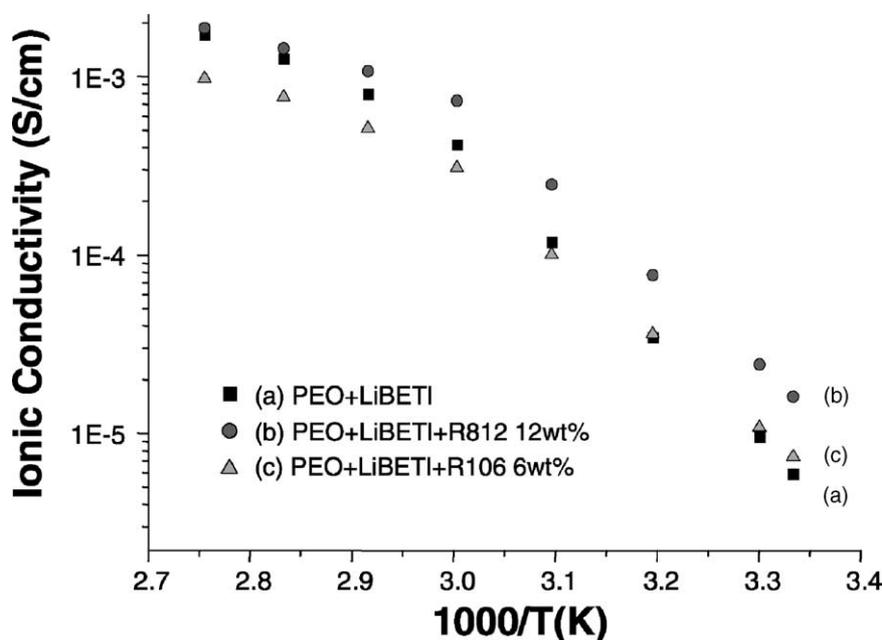


Fig. 4. Temperature dependence of ionic conductivity for the PEO–LiBETI–SiO₂ composite electrolyte.

salt complex might be due to the active dissociation of Li salt which results in increase of the mobile carrier concentration (C_i). This is the reason why many experiments have been performed not only with normal oxides but also with ferroelectric materials [17]. However, the assumption does not hold well in this experiment using SiO₂, which has a little higher dielectric constant (3.5–4.2) than PEO (2.8–3.3). Thus, the dissociating action mentioned above might not have a strong effect. Consequently, it is considered that the increase of ionic conductivity achieved by adding SiO₂ is mainly related to its mobility, which is represented by μ_i in Eq. (1), affecting the segmental motion in the free volume [13]. Therefore, we thought at first that the increase in the mobility would be more effective than the carrier's concentration for lithium conduction.

In addition to the increase of the mobility, the surface chemistry of inorganic filler is also an important factor in enhancing ionic conductivity. In a previous work, Wieczorek et al. [18] proposed acidic center on the fillers compete with the Lewis acid metal cations in the formation of complexes with the polyether chain. Croce et al. [19] presented a pictorial model of the surface interactions between three forms of dispersed nano-sized Al₂O₃ ceramic and the PEO–LiSO₃CF₃ complex.

They assumed that the differences in conductivity were directly related to differences in the extent of the specific ceramics' surface interactions.

The conductivities of composite electrolytes prepared from various surface-modified fumed silicas are shown in Fig. 4. We observed a discernable change in the conductivity of the different composite electrolytes. PEO–LiBETI–R812 composite electrolyte exhibited higher conductivity than the other samples.

It has been reported [8] that octyl groups effectively shield Si–OH because of its large size. The fillers covered with octyl groups may prevent any significant interaction between the PEO matrix and fumed silica.

From the papers as mentioned above, it is presumed that the trimethylsilyl group does not impede Si–OH group's role because the trimethylsilyl group is short and small. Additionally, because of the hydrophobic nature of R812, the dispersability of SiO₂ powders in acetonitrile was increased. This SiO₂ slurry was mixed with PEO + LiBETI slurry to dissolve the organic and inorganic materials in the solvents. Consequently, we obtained well-dispersed SiO₂ homogeneous mixture.

In case of R106, the octamethyl cyclotetrasiloxane treated functional SiO₂ has a large organized group. Accordingly, Si–OH does not interact with PEO chain.

As stated above, R812 is more effective in improving ionic transport properties (i.e. R812 > R106 > SiO₂ free). Therefore, it seems reasonable to conclude that we obtained enhanced ionic conductivity when considering both dispersibility and the extent of impeding Si–OH group's role.

3.4. Conductivity versus temperature

To characterize the transport properties of the electrolyte more fully, the study of ionic conductivity as a function of the temperature is also needed [20–22]. Fig. 4 also shows the dependence of the ionic conductivity on temperature and filler type.

Several features can be observed:

1. The conductivity–temperature plots have two obvious regions, which mean Li⁺ transport properties are

Table 1
Activation energies and pre-exponential factors of the composite electrolytes in low temperature region

| | ln A (S/cm) | E_a (kJ/mol) |
|--------------------------------------|-------------|----------------|
| (PEO) ₁₆ -LiBETI | 31 | 107 |
| (PEO) ₁₆ -LiBETI-12% R812 | 27.5 | 96 |
| (PEO) ₁₆ -LiBETI-6% R106 | 26 | 94 |

controlled by two distinct mechanisms. At lower temperatures, the linear relationship reveals that the temperature dependence of conductivity follows Arrhenius form, suggesting that the conductivity is thermally activated. While at higher temperatures, the conductivity increases with VTF empirical form.

2. The conductivity relationship can be expressed as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (2)$$

where σ_0 is the pre-exponential factor, E_a the activation energy and k is the Boltzmann's constant.

From Eq. (2), Table 1 shows activation energies and pre-exponential factors of the prepared electrolytes. The pre-exponential term in the Arrhenius equation is related to the number of charge carriers. The activation energy is related to its mobility. The ionic conductivity depends on the number of charge carriers and their mobility.

According to Table 1, the two types of composite electrolytes have similar activation energies. This suggests that the surface groups do not change the mechanism for ion conduction in PEO. However, PEO + LiBETI electrolyte has a different activation energy value. This means that the local dynamics of lithium-ion transport is somewhat different.

It is inferred from the activation energies of composite electrolyte that inorganic filler can change the mobility in a polymer matrix. On the other hand, both R812 and R106 can have relatively the same role for ion conducting properties. Therefore, it seems to verify the assumption that the difference of the surface group is not related to the conducting properties.

3.5. Interfacial property

Lithium metal is extremely attractive as a negative electrode material for secondary batteries due to its high negative electrode potential, high specific capacity, and low atomic weight. However, problems related to the use of lithium metal anode remain for polymer electrolyte-based systems. The reactivity of the lithium metal can affect the interface which forms a thick and non-uniform surface-layer. These layers may cause uneven lithium deposition in the course of the charge process, leading to a dendritic morphology which would not favor an extending cycling. Therefore, the examination of the lithium interfacial characteristics is very important for improvement of electrolyte performances. The growth of the lithium passivation layer is unpredictably influenced by the presence of liquid components and/or liquid impurities in the polymer electrolyte. The liquid phase decomposes at the surface of lithium and it affects the cyclability of the lithium electrode. The addition of ceramic powders to the polymer electrolyte is effective in reducing the effect of impurities because the ceramic powders trap traces of residual impurities [23]. Therefore, the optimization and control of the electrode/polymer electrolyte interface is a key requisite for success in LPB development.

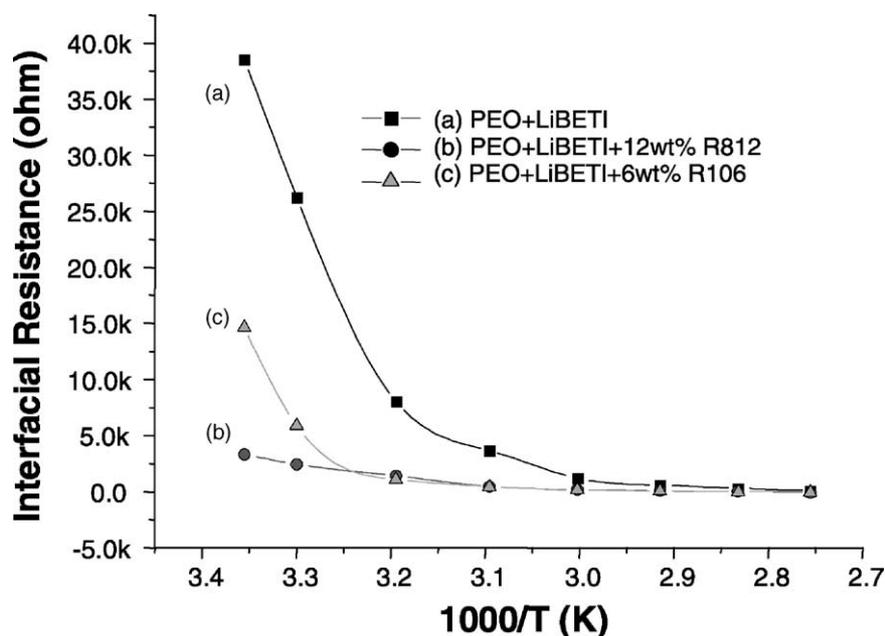


Fig. 5. Temperature dependence of interfacial resistance for the PEO-LiBETI-SiO₂ composite electrolyte.

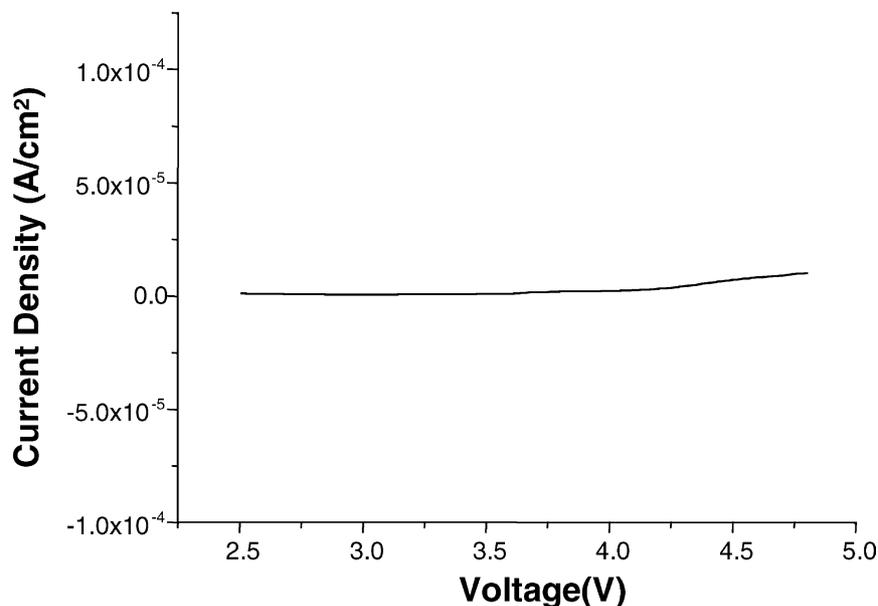


Fig. 6. Voltage sweep for a PEO-LiBETI-12 wt.% R812 electrolyte.

This study is also needed to find the proper approaches for solving or at least minimizing this drawback. It has already been reported that interface resistance of Li/composite electrolyte/Li depends on the characteristics of surface groups [9,24].

In our work, the lowest interface resistance was observed in the composite electrolyte PEO-LiBETI-R812. In the case of different surface group of the same size, R812 is most effective in trapping impurities (Fig. 5). R106 is also effective, but its surface morphology and functional groups are less suitable than R812.

3.6. Electrochemical stability

The extent of their electrochemical stability window is an important parameter for the characterization of prepared electrolytes. The electrolyte potential stability windows were determined by linear sweep voltammetry (LSV) using Li/composite electrolytes/stainless steel cells at 50 °C, in which the stainless steel was employed as a working electrode. The working potential range for highly oxidizing cathode materials such as LiCoO₂ or LiMn₂O₄ versus Li/Li⁺ is generally between +3.0 and +4.3 V. In particular, LSV of the PEO + LiBETI + 12 wt.% R812 electrolyte in the voltage range from 2.5 to 4.8 V was studied. The onset potential for degradation was not observed until a potential of 4.8 V (versus Li) is reached in Fig. 6.

4. Conclusions

This work described the preparation and the characterization of PEO-based composite electrolytes in lithium polymer batteries which could be one of the most promising

candidates for the electrochemical power sources characterized by high energy, reliability, high power densities, and safety.

A comparative study of ionic conductivity, temperature versus conductivity, interfacial properties and electrochemical stability was conducted for two different composite electrolytes.

In our work, a composite electrolyte prepared with SiO₂ covered with trimethylsilyl exhibited better electrochemical properties than other composite electrolytes. The ionic conductivity of the composite electrolyte containing 12 wt.% R812 is a maximum value of 1.5×10^{-5} S/cm at 25 °C. Temperature dependence of the ionic conductivity showed behavior close to Arrhenius equation at low temperature and VTF equation at high temperature. The study of ionic conductivity as a function of the temperature showed that difference of the surface group is not related to the conducting properties. Cyclic voltammetry indicated an electrochemical stability window of about 4.8 V. The addition of R812 is quite effective to stabilize the interface.

The improvement of the electrochemical properties was due to R812 which was suitable for satisfying not only dispersibility but it also did not disturb the interfacial surface role of the filler at the electrode.

We experimented with only two types of functional SiO₂. Further investigation of functional-filler added to a composite electrolyte is necessary to understand the effect of the surface chemistry in PEO systems.

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