

Effect of organic acids and nano-sized ceramic doping on PEO-based solid polymer electrolytes

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Abstract

Composite solid polymer electrolytes (CSPEs) consisting of polyethyleneoxide (PEO), LiClO₄, organic acids (malonic, maleic, and carboxylic acids), and/or Al₂O₃ were prepared in acetonitrile. CSPEs were characterized by Brewster Angle Microscopy (BAM), thermal analysis, ac impedance, cyclic voltammetry, and tested for charge–discharge capacity with the Li or LiNi_{0.5}Co_{0.5}O₂ electrodes coated on stainless steel (SS). The morphologies of the CSPE films were homogeneous and porous. The differential scanning calorimetric (DSC) results suggested that performance of the CSPE film was highly enhanced by the acid and inorganic additives. The composite membrane doped with organic acids and ceramic showed good conductivity and thermal stability. The ac impedance data, processed by non-linear least square (NLLS) fitting, showed good conducting properties of the composite films. The ionic conductivity of the film consisting of (PEO)₈LiClO₄:citric acid (99.95:0.05, w/w%) was $3.25 \times 10^{-4} \text{ S cm}^{-1}$ and $1.81 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C. The conductivity has further improved to $3.81 \times 10^{-4} \text{ S cm}^{-1}$ at 20 °C by adding 20 w/w% Al₂O₃ filler to the (PEO)₈LiClO₄ + 0.05% carboxylic acid composite. The experimental data for the full cell showed an upper limit voltage window of 4.7 V versus Li/Li⁺ for CSPE at room temperature.

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1. Introduction

Since the ionic conductivity of the polyethylene oxide (PEO)/Na⁺ complex was measured in 1973 [1,2], extensive research and development has been done on solid polymer electrolytes (SPE) during the past 2 decades [3]. Recently, SPEs containing dissolved metal salts have been proposed as an alternative to a liquid electrolyte in rechargeable lithium batteries. The advantages of SPEs are their capability for high-speed production of thin bipolar cells and enhanced safety due to the absence of liquid electrolytes. This has promoted development of dry, gelled, and porous types of SPEs [4,5].

PEO is one of the most promising SPEs [6]. However, due to a poor ionic conductivity ($\sigma = 10^{-8}$ to $10^{-7} \text{ S cm}^{-1}$) of these polymer electrolytes at an ambient operating temperature, various modifications have been done [7]. Recently, a group of

materials, through the addition of ceramic powders [8,9], organic acid [10], and organic/inorganic composites [11], was examined for improving composite solid polymer electrolytes (CSPEs). The addition of inert fillers, such as β -alumina [12], γ -LiAlO₂ [13] and Al₂O₃ [7,8,14] to polymer films was also attempted to improve the properties of CSPEs such as ionic conductivity, ease of fabrication of films, and improved mechanical properties. A great enhancement in the conductivity of the lithium salts-(PEO)₈ composite electrolyte was reported by using the combined action of a large surface area and the Lewis-acid character of the ceramic additive [15]. These modification techniques of adding ceramics were also applied to produce enhanced properties for proton conductive polymers. Recently, a few studies have been reported on the proton conducting membrane containing sulfonated PEO and water [11,16–18].

In the present study, the new composite CSPEs with addition of nano-sized Al₂O₃ to organic acids doped (PEO)₈ LiClO₄ were prepared to improve the characteristics of the electrolytes. Various experimental parameters affecting the characteristics of the polymer films were investigated including: ionic conductivity,

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interfacial phenomena with lithium metal, electrochemical properties, and thermal stability of SPE films employing the thermal gravimetric (TG) analysis, ac impedance, cyclic voltammetry (CV), and charge/discharge test. In addition, the effect of the doping ratio of organic acids, and the dependency of the addition of alumina on the ionic conductivity, and the grain boundary resistance were also examined.

2. Experimental

2.1. Reagents and polymer film fabrication

The starting materials, PEO (Aldrich Co., M.W. 5×10^6), LiClO_4 (Aldrich Co.), acetonitrile, maleic acid (MLEA), malonic acid (MLOA), citric acid (CA) and Al_2O_3 (particle sizes 5.8–13 nm) were obtained from Aldrich Co. (USA). The Al_2O_3 was dried at 120°C and other materials with the exception of PEO were dried at 55°C . All the experiments were performed in an Ar gas filled glove box. The polished, washed, and dried stainless steel No. 304 (SS) was cut into a specified plate, which was used as a current-collecting electrode.

To prepare the polymer electrolyte film, stoichiometric amounts of PEO and LiClO_4 (8:1) were mixed in a small glass reactor, then added to a 25 ml acetonitrile solution. The mixture was continuously stirred with a magnetic bar for 24 h. To dope organic acids into the PEO, MLEA, MLOA, and CA (0.01–0.1% mol mol⁻¹) were added to the gel suspension. Then, the mixtures were added to the 20 wt./wt.% Al_2O_3 particles (size: 5.7 nm). To make the stand-alone film, a slurry of the polymer electrolyte was spread onto a Teflon plate and allowed to dry at the room temperature. The films were dried in a vacuum oven at 60°C for 24 h. The final homogenous composite polymer films in about 100 μm thickness were stored in the glove box.

2.2. Equipments and cell construction

The surface morphology of a polymer film was observed with Brewster Angle Microscopy (BAM, BAM2 plus Co.). The thermal stability of the polymer electrolyte films was studied under the Ar gas atmosphere using thermogravimetry and differential scanning calorimetry (TG-DSC) (Labsys TG 1600, SETARAM Co.) with the heating rate of $10^\circ\text{C min}^{-1}$ from the room temperature to 400°C . Conductivities of the composite polymer electrolyte films were measured using ac impedance spectroscopy employing a PAR Model 273A Potentiostat/Galvanostat (EG&G) coupled with a EG&G 5201 lock-in amplifier, both interfaced with a personal computer. ac Perturbation of 5 mV was used and data were collected by taking 30 points decade⁻¹ over the frequency range from 1 MHz to 10 Hz for conductivity measurements and 100 kHz to 10 mHz for interface investigations at room temperature, respectively. The data were analyzed by a non-linear least square (NLLS) curve-fitting program.

To investigate cell performance with the polymer electrolyte, the thin films were inserted between two stainless steel (SS) disk electrodes. We used symmetrical non-blocking lithium electrode

cells for the study of interface phenomena. Cyclic voltammetry (EG&G PAR Model 273 Potentiostat/Galvanostat) with a three-electrode cell was performed at the scan rate of 5 mV s^{-1} in the potential range from 0.45 V to 1.0 V. Electrochemical stability of the SPE film was investigated with a SS/SPE/SS cell. All the cells were sealed in an Ar-filled glove box and the cell had an electrode area of 4 cm^2 [19,20]. Solid-state rechargeable $\text{Li/CSPE/LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ cells were constructed from laminates of the polymer electrolyte, a composite cathode of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$, and a Li metal anode. The cathode was made by coating the slurry mixture of LiNiCoO_2 (85%), graphite (10%), and PVDF (5%) onto a 304 SS Ex-met substrate to a coating thickness of $\sim 20 \mu\text{m}$ for both sides of a substrate. The anode was a 25 μm thickness Li foil pressed onto a Cu substrate.

3. Results and discussion

The surface morphologies of the CSPE films were observed using BAM as shown in Fig. 1. The BAM images obtained for PEO/ LiClO_4 films show a constantly conglomerated morphology but no crystallized images on the surface (Fig. 1). In comparison with the images shown in Fig. 1(a) $(\text{PEO})_8\text{LiClO}_4$, and (b, c, and d) the mixed electrolytes with organic acids, and (e) Al_2O_3 show uniformly spread pores on the film surface. Especially, with the addition of CA to the polymer electrolyte which significantly improved the morphology with uniform porosity, and a widely distributed texture due to decrease of crystallinity of PEO by the steric effect of PEO and strong interaction with carboxyl groups of CA (see Fig. 1(d)). Addition of Al_2O_3 to the PEO + CA composite showed a more porous surface due to a homogenous distribution of Al_2O_3 particles in the film (Fig. 1(e)). This caused the enhanced ionic conductivity and improved mechanical and thermal stabilities. These properties of the films related to an elevated conductivity measured with ac impedance spectroscopy. The results agree with that of other researchers, which suggested that the improvements in ionic conductivity of the CSPE composite with organic and inorganic fillers are caused by changes in the microstructure and morphology. Changes of the microstructure and morphology are due to the various Lewis acid–base reactions which occurred among Lewis base centers of the polyester, Lewis acid centers of alkali metal cations, and Lewis acid or Lewis base centers on the surface of Al_2O_3 [15]

Fig. 2 presents the DSC curves of (a) PEO, (b) $(\text{PEO})_8\text{LiClO}_4$, (c) $(\text{PEO})_8\text{LiClO}_4$ –0.05% CA, and (d) $(\text{PEO})_8\text{LiClO}_4$ –0.05% CA–20 wt./wt.% Al_2O_3 samples, respectively. In the TG–DTA curve obtained for PEO, an endothermic peak was observed at about 65°C due to melting of PEO. On the other hand, for a $(\text{PEO})_8\text{LiClO}_4$ film, a large exothermic peak was observed at about 250°C . The exothermic peaks shifted from 250°C to 350°C and 320°C , respectively, by adding CA and Al_2O_3 to the $(\text{PEO})_8\text{LiClO}_4$ polymer electrolyte. Addition of other organic such as, malonic acid and maleic acid produced an exothermic peak at 310°C and 325°C , respectively (not shown). This suggests that the thermal stability of the polymer film in the composites is highly enhanced by the acid and inorganic additives. This enhancement of the thermal stability of the polymer can be

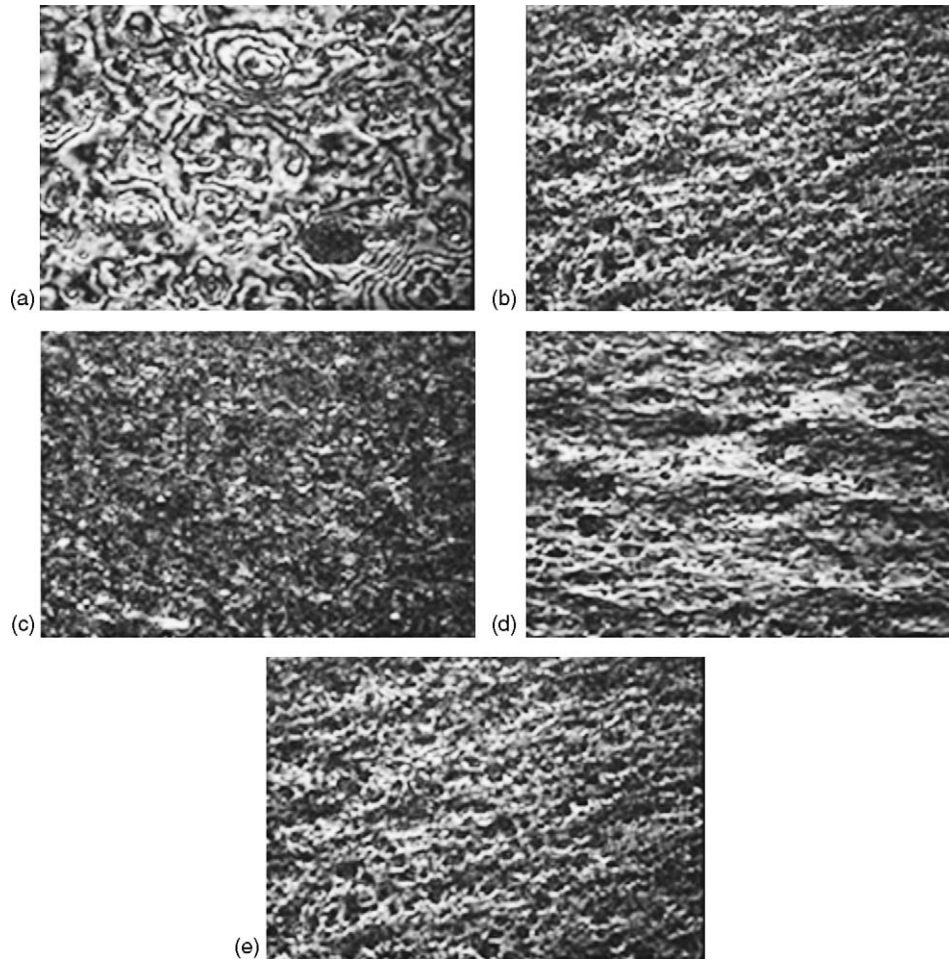


Fig. 1. BAM photographs of $(\text{PEO})_8\text{LiClO}_4$ and of the mixture of citric acid and Al_2O_3 . (a) $(\text{PEO})_8\text{LiClO}_4$, (b) $(\text{PEO})_8\text{LiClO}_4 + 0.1\%$ citric acid, (c) $(\text{PEO})_8\text{LiClO}_4 + 0.05\%$ malonic acid, (d) $(\text{PEO})_8\text{LiClO}_4 + 0.1\%$ maleic acid and (e) $(\text{PEO})_8\text{LiClO}_4 + 0.1\%$ citric acid + Al_2O_3 (image size $430\ \mu\text{m} \times 540\ \mu\text{m}$).

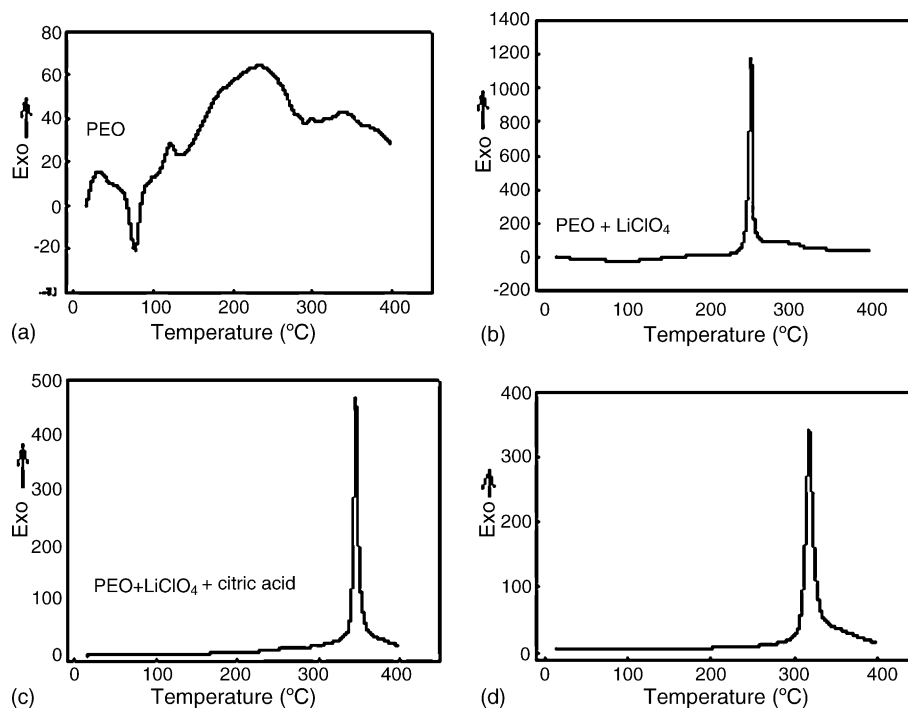


Fig. 2. The DTA curves of: (a) PEO, (b) $(\text{PEO})_8\text{LiClO}_4$, (c) $(\text{PEO})_8\text{LiClO}_4 - 0.05\%$ CA, and (d) $(\text{PEO})_8\text{LiClO}_4 - 0.05\%$ CA-20 wt.% Al_2O_3 .

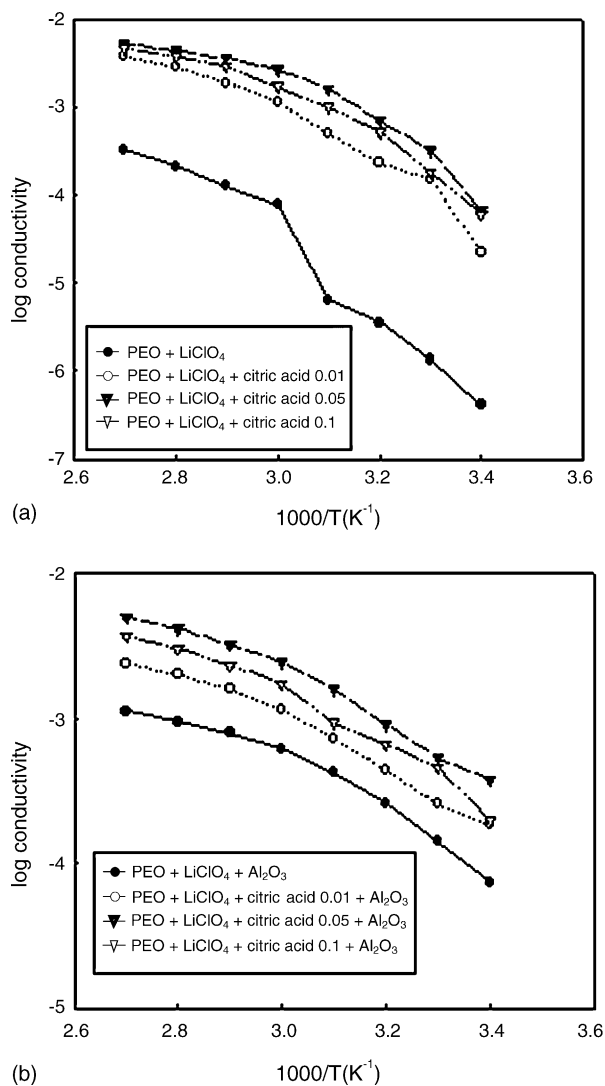


Fig. 3. Variation of the ionic conductivity with Arrhenius plots for the: (a) CA added films ((PEO)₈LiClO₄ (●), (PEO)₈LiClO₄-0.01% CA (○), (PEO)₈LiClO₄-0.05% CA (▼) and (PEO)₈LiClO₄-0.1% CA (□)) and (b) CA and Al₂O₃ added PEO films ((PEO)₈LiClO₄ + Al₂O₃ 20 wt.% (●), (PEO)₈LiClO₄ + Al₂O₃ 20 wt.% + 0.01% CA (○), (PEO)₈LiClO₄ + Al₂O₃ 20 wt.% + 0.05% CA (▼) and (PEO)₈LiClO₄ + Al₂O₃ 20 wt.% + 0.1% CA (□)).

explained by the interaction between the organic acids and the polymer matrix. The film doped with only CA was more stable and the exothermic peak appeared at higher temperatures by about 30 °C than that doped with Al₂O₃. This is comparable with the thermal behavior of PEO films based on the nano-composite electrolytes reported in the literature [7,10].

Fig. 3(a) and (b) shows the variation of conductivity of composite polymer electrolytes in a SS/SPE/SS cell with inverse temperature. Ionic conductivities obtained for a mere PEO/LiClO₄ film were reported in the range of 10⁻⁷ to 10⁻⁸ S cm⁻¹ at the room temperature and about 10⁻⁵ S cm⁻¹ at 65 °C [21]. On the other hand, ionic conductivities of (PEO)₈LiClO₄ films with three different contents of CA additives prepared in the present study were elevated dramatically to about 10⁻⁵ S cm⁻¹ at room temperature as shown in Fig. 3(a). Doping with CA made a significant increase in ionic con-

ductivities for the polymer-salt complexes, and the maximum enhancement was achieved in case of the 0.05% CA addition. The addition of 0.01, 0.05 and 0.1% of CA to (PEO)₈LiClO₄ give the conductivities of: 2.27 × 10⁻⁵ S cm⁻¹, 6.74 × 10⁻⁵ S cm⁻¹, and 6.05 × 10⁻⁵ S cm⁻¹ at 20 °C, respectively, while that of the (PEO)₈LiClO₄ electrolyte without the CA addition was 0.8 × 10⁻⁸ S cm⁻¹. All the conductivities for CA-added electrolytes were expected for a change to a more amorphous state of PEO. The conductivities of the electrolyte having the same composition increased to 1.54 × 10⁻⁴ S cm⁻¹, 3.25 × 10⁻⁴ S cm⁻¹, and 1.81 × 10⁻⁴ S cm⁻¹ at 30 °C, respectively. This increase in the conductivity by the addition of small amount of CA seems to be due to the strong ligating power of CA to the lithium ion. The three carboxylic acid groups and a hydroxyl group attached to a carbon atom can properly interact with several lithium ions due to the presence of seven ligating oxygen atoms, which give enough complexation with Li ions even in a low concentration of organic acids, and the small size of the Li ion complexes easily diffuse inside the PEO polymer networks by ion hopping such as chain hopping. Fig. 3(b) shows the variation of conductivity with inverse temperature for the addition of 20 wt./wt.% Al₂O₃ fillers to three different composites of (PEO)₈LiClO₄ containing 0.01%, 0.05% and 0.1% CA. The addition of ceramic fillers (particle diameter; 2.9–6.5 nm), such as Al₂O₃ and SiO₂, to PEO based-polymer electrolytes enhanced the conductivity, because it could act as a solid plasticizer which would inhibit crystallization and promote the retention of the amorphous phase at ambient temperature [15,22–24]. The addition of 20 wt./wt.% Al₂O₃ to (PEO)₈LiClO₄ gave an increased conductivity of 7.41 × 10⁻⁵ S cm⁻¹. On the other hand, the addition of 0.01, 0.05, and 0.1% of CA to (PEO)₈LiClO₄ containing 20 wt./wt.% of Al₂O₃ resulted in a further increase of the conductivity to 1.85 × 10⁻⁴ S cm⁻¹, 3.81 × 10⁻⁴ S cm⁻¹, and 2.00 × 10⁻⁴ S cm⁻¹ at 20 °C, respectively, as previously mentioned.

ac Impedance spectra obtained for a Li/CSPE/Li cell composed of composite polymer films and an equivalent circuit as shown in Fig. 4. The impedance spectra obtained for the Li/CSPE/Li, which consisted of 0.01%, 0.05%, and 0.1% of CAs doped (PEO)₈LiClO₄ (Fig. 4(a)) and CAs doped (PEO)₈LiClO₄ containing 20 wt./wt.% of Al₂O₃ (Fig. 4(b)), showed a semicircular arc, where the diameter corresponds to the polarization resistance (R_p) of the SPE film. The large skewed semicircle arose from the Li/SPE interfacial resistance comprised of a surface film resistance (R_{ct1}) on Li and the charge transfer resistance (R_{ct2}) of the Li⁺ + e⁻ = Li reaction. It is well known [7,25] that a passive film consisting of primary and secondary layers covers the surface of Li [25]. The resistances in terms of R_p , R_{ct1} , and R_{ct2} greatly decreased due to the addition of the organic acids to (PEO)₈LiClO₄ compared with that of (PEO)₈LiClO₄ without organic acids. This means that the addition of organic acids to the polymer film promoted the conduction of Li ions inside the polymer film. It was previously reported that this kind of compound is effective for lithium conduction with proton conduction [18]. Moreover, the addition of 20 w/w% Al₂O₃ to (PEO)₈LiClO₄ containing 0.01, 0.05, and 0.1 w/w% of CAs resulted in the decreased resistance as shown

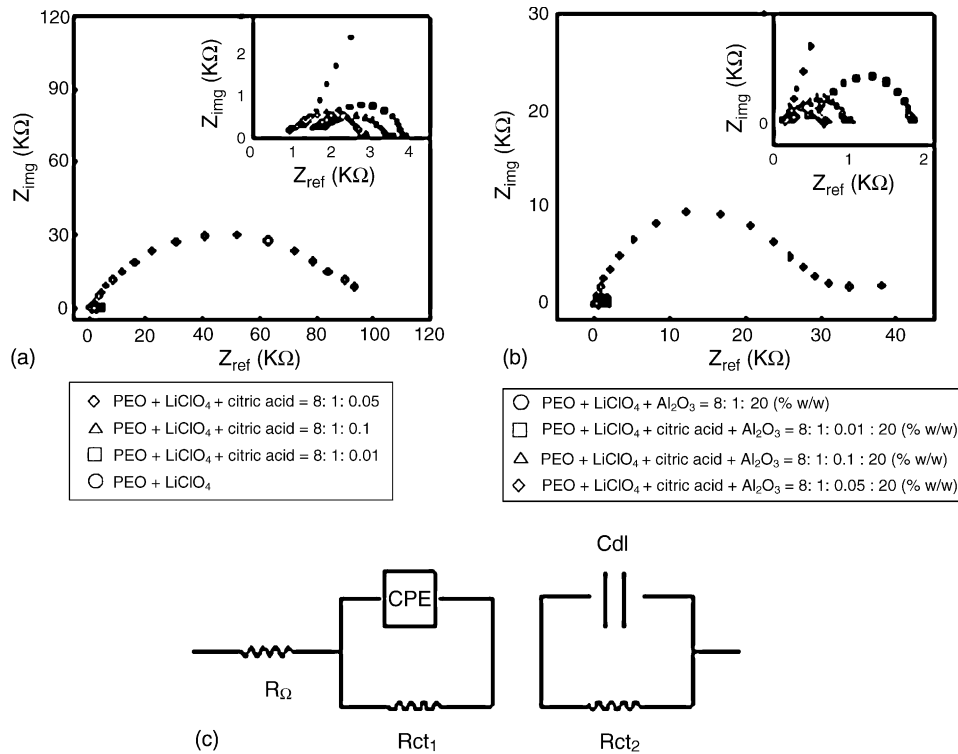


Fig. 4. ac Impedance spectra for a Li/SPE/Li cell (at 20 °C) composed of: (a) CA added PEO ((\circ) (PEO)₈LiClO₄, (\square) (PEO)₈LiClO₄ + 0.01 w/w% CA, (Δ) (PEO)₈LiClO₄ + 0.1 w/w% CA and (d) CA and Al_2O_3 added PEO (\diamond) (PEO)₈LiClO₄ + 0.05 w/w% CA, (b) (\circ) (PEO)₈LiClO₄ + Al_2O_3 20 w/w%, (\square) (PEO)₈LiClO₄ + Al_2O_3 20 w/w% + 0.01 w/w% CA, (Δ) (PEO)₈LiClO₄ + Al_2O_3 20 w/w% + 0.05 w/w% CA, and (\diamond) (PEO)₈LiClO₄ + Al_2O_3 20 w/w% + 0.1 w/w% CA), and (c) the equivalent circuit.

in Fig. 4(b). Of these composites, the composition of 0.05% CA + Al_2O_3 20 w/w% in (PEO)₈LiClO₄ gave the lowest resistance. The values of R_{Ω} , and R_{ct1} in the case of the addition of 20 w/w% Al_2O_3 to (PEO)₈LiClO₄ containing 0.05 w/w% of CA were 108.6 Ω , and 511.8 Ω , respectively. The equivalent circuit and parameters for the cell are in Fig. 4(c) and summarized in Table 1. The conductivity enhancement using the composite polymer electrolytes has been attributed to augmentation of the amorphous phase [26,27]. A review of the observations on polymer–ceramic composite electrolytes has been reported [28] previously. Concerning ionic conductivity, the incorporation of ceramic powders into a polymer matrix leads to two competing effects: (i) an enhancement of the amorphous phase that causes increase in the ionic conductivity and (ii) increasing in the T_g , which reduces the segmental motion of the polymer chain. The

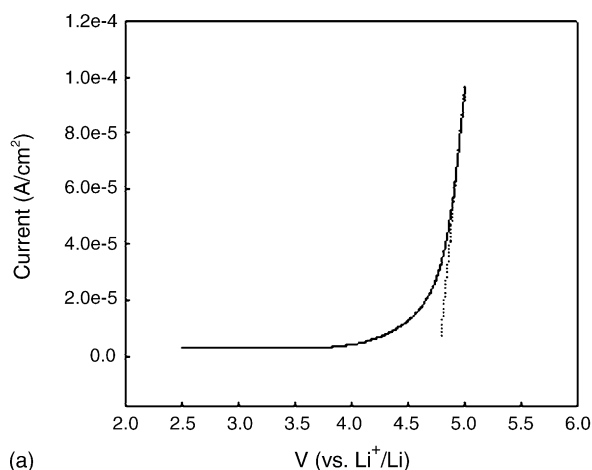
effect of nano-size alumina on the ionic conductivity and the stability of Li/CSPE interface have been reported previously [7].

For an application of CPSE to a lithium secondary battery, CSPE should not be decomposed by an oxidation/reduction reaction in the range of operating voltage. For the cathode active materials application, a CSPE should have chemical and physical stability above 4.5 V versus Li^+/Li . Thus, the stability of the composite film was tested as shown in Fig. 5(a) and displays a linear sweep voltammogram (LSV) between 2.5 V and 5.0 V versus Li^+/Li and in Fig. 4(b) a cyclic voltammogram (CV) between -0.45 V and 1.0 V versus Li^+/Li , which are recorded with a SS/Li (reference electrode)/CSPE/Li cell at a scan rate of 5 $mV s^{-1}$. The study showed that the upper limit voltage window for SPE was about 4.7 V at room temperature.

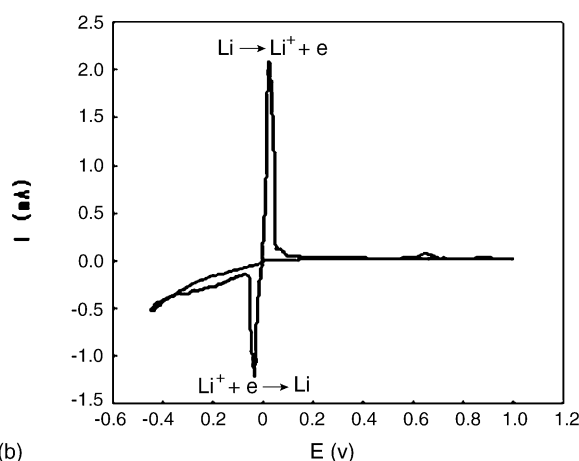
Table 1

Values of parameters for equivalent circuit used to construct the simulated curves presented in Fig. 4

| | R_{Ω} (Ω) | R_{ct1} (Ω) | Q | | R_{ct2} (Ω) | C_{dl} (nF) |
|--|---------------------------|------------------------|---------------------------|--------|------------------------|---------------|
| | | | $Y_0, mhg \times 10^{-5}$ | n_1 | | |
| (PEO) ₈ LiClO ₄ | 729.7 | 96220 | 36.00 | 0.7113 | 832.2 | 10.03 |
| (PEO) ₈ LiClO ₄ + 0.01% CA | 655.7 | 2524 | 1.12 | 0.6716 | 828.3 | 8.95 |
| (PEO) ₈ LiClO ₄ + 0.05% CA | 398.0 | 1975 | 1.87 | 0.6238 | 365.2 | 3.99 |
| (PEO) ₈ LiClO ₄ + 0.1% CA | 437.2 | 2127 | 6.53 | 0.6504 | 709.7 | 5.08 |
| (PEO) ₈ LiClO ₄ + Al_2O_3 (20 wt.%) | 218.4 | 29592 | 86.18 | 0.7423 | 245.8 | 70.91 |
| (PEO) ₈ LiClO ₄ + 0.01% CA + Al_2O_3 (20 wt.%) | 141.8 | 1441 | 2.18 | 0.6530 | 75.4 | 68.92 |
| (PEO) ₈ LiClO ₄ + 0.05% CA + Al_2O_3 (20 wt.%) | 108.6 | 511.8 | 2.56 | 0.6835 | 35.6 | 7.46 |
| (PEO) ₈ LiClO ₄ + 0.1% CA + Al_2O_3 (20 wt.%) | 112.7 | 772.8 | 2.52 | 0.6666 | 56.7 | 23.52 |



(a)

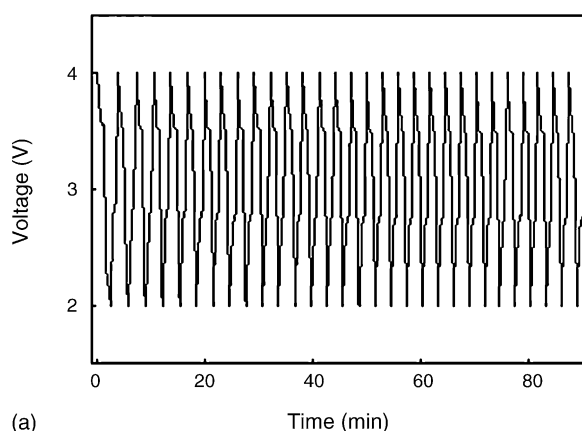


(b)

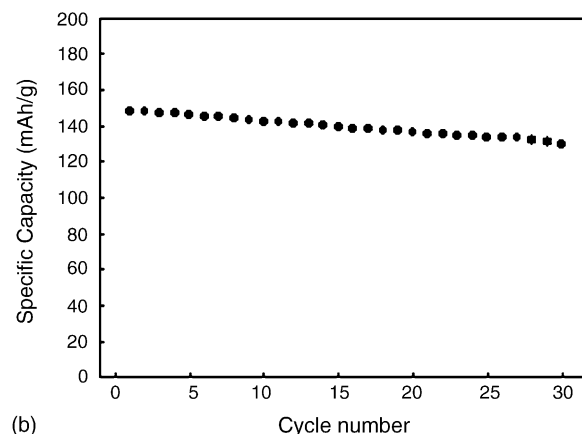
Fig. 5. (a) The linear sweep voltammogram (LSV) between 2.5 V and 5.0 V vs. Li^+/Li and (b) CV between -0.45 and 1.0 V vs. Li^+/Li for with a SS/Li (reference electrode)/CSPE/Li cell at a scan rate 5 mV s^{-1} .

This is similar to that using other PEO-based solid polymer electrolytes, which are known to possess a wide voltage stability window. The cell fabricated in the present study also showed good electrochemical stability. As shown in Fig. 5(b), the CV recorded for $(\text{PEO})_8\text{LiClO}_4 + 0.1 \text{ w/w\% CA} + \text{Al}_2\text{O}_3 \text{ 20 w/w\%}$ film in SS/SPE/Li/SS cell displayed an anodic peak for Li at $+0.03$ V, and a corresponding cathodic peak at -0.04 V. The redox peaks in the CVs are resulted from the electrochemically reversible redox reaction by enhancing the diffusion of Li^+ in the polymer matrix which is due to doping of an organic acid and ceramic into the PEO film, indicating good cyclability of the cell.

Fig. 6 shows (a) a discharge–charge cycles and (b) specific discharge–charge capacities obtained with the Li/CSPE/ $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ cell based on an electrolyte containing a mixture of $(\text{PEO})_8\text{LiClO}_4$ and CA, which cell was operated at 30°C . In this case, the current density was 0.09 mA cm^{-2} (0.12 C rate) and the cyclic numbers were 30 times. The potential range was between 4.0 V and 2.0 V. The average charge/discharge voltages of these systems are $3.81 \text{ V}/3.65 \text{ V}$. The discharge capacity on the first cycle was 148 mAh g^{-1} for the cathode. The capacity gradually dropped to 84% after 30



(a)



(b)

Fig. 6. (a) Discharge–charge cycles and (b) specific discharge–charge capacities obtained with the Li/CSPE/ $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ cell operated at 30°C and 0.09 mA cm^{-2} between 4.0 V and 2.0 V, which is based on the electrolyte containing a mixture of $(\text{PEO})_8\text{LiClO}_4$ and CA.

cycles from an initial value with a charge/discharge efficiency of 98–99%.

4. Conclusion

The performance and stability of SPEs increased when organic acid and Al_2O_3 particles were together added to PEO. Especially, when a citric acid was added, the thermal decomposition temperature increased over 350°C . The thermal stability of polymer in the composites is highly enhanced by the inorganic additive. The ionic conductivity of $(\text{PEO})_8\text{LiClO}_4$ CSPE also was enhanced by the addition of citric acid and Al_2O_3 particles. The ionic conductivity of a $(\text{PEO})_8\text{LiClO}_4$: CA (99.95:0.05, w/w%) is of the order of $3.25 \times 10^{-4} \text{ S cm}^{-1}$ and $1.81 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C , and this value has further been improved to a value $3.81 \times 10^{-4} \text{ S cm}^{-1}$ at 20°C by adding 20 w/w% Al_2O_3 ceramic oxide filler to $(\text{PEO})_8\text{LiClO}_4 + 0.05\% \text{ CA}$. The solid electrolyte composed of 0.05% CA + Al_2O_3 20 w/w% in $(\text{PEO})_8\text{LiClO}_4$ gives the lowest resistance. The SPE has a 4.7 V upper limit voltage at room temperature. The redox peaks in the CVs indicated stable oxidation and reduction reactions due to doping of organics and ceramics into films.

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