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ORIGINAL PAPER

# Effect of additives in PEO/PAA/PMAA composite solid polymer electrolytes on the ionic conductivity and Li ion battery performance

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**Abstract** Polyethylene oxide (PEO) based-solid polymer electrolytes were prepared with low weight polymers bearing carboxylic acid groups added onto the polymer backbone, and the variation of the conductivity and performance of the resulting Li ion battery system was examined. The composite solid polymer electrolytes (CSPEs) were composed of PEO, $LiClO_4$, PAA (polyacrylic acid), PMAA (polymethacrylic acid), and $Al_2O_3$. The addition of additives to the PEO matrix enhanced the ionic conductivities of the electrolyte. The composite electrolyte composed of PEO:$LiClO_4$:PAA/PMAA/$Li_{0.3}$ exhibited a low polarization resistance of 881.5 ohms in its impedance spectra, while the PEO:$LiClO_4$ film showed a high value of 4,592 ohms. The highest ionic conductivity of $9.87 \times 10^{-4}$ S cm$^{-1}$ was attained for the electrolyte composed of PEO:$LiClO_4$:PAA/PMAA/$Li_{0.3}$ at 20 °C. The cyclic voltammogram of $Li^+$ recorded for the cell consisting of the PEO:$LiClO_4$:PAA/PMAA/$Li_{0.3}$:$Al_2O_3$ composite electrolyte exhibited the same diffusion process as that obtained with an ultramicroelectrode. Based on this electrolyte, the applicability of the solid polymer electrolytes to lithium batteries was examined for an Li/SPE/$LiNi_{0.5}Co_{0.5}O_2$ cell.

**Keywords** Polymer electrolyte · Polyethylene oxide · Additives · Lithium ion battery

## 1 Introduction

Since the ionic conductivity of PEO containing alkaline salts was reported in 1973 [1], diverse studies have been conducted on the complexes of Li, Na, and K ions with PEO to enhance the conductivity of the polymer electrolyte [2, 3]. However, the PEO containing the alkali metal ions still exhibits a relatively low ionic conductivity at room temperature, which showed a conductivity of $\sim 10^{-5}$ S cm$^{-1}$, due to its high crystalline ratio. This restricts the use of PEO containing alkaline salts in real applications. Thus, various methods of minimizing the crystallization degree on the polymer electrolyte have been tried since the middle of the 1980s. Various materials, such as ceramic powders [4], organic acids [5], and organic/inorganic composites [6], have been examined for the purpose of producing composite solid polymer electrolytes (CSPEs). The addition of some inert additives, such as $\beta$-alumina [7], $\gamma$-$LiAlO_2$ [8], and $Al_2O_3$ [9], to polymer films was also attempted to improve the properties of CSPEs, such as their ionic conductivity, film process ability, mechanical properties, etc. Of using these additives, a large improvement in the conductivity of a lithium salt-$(PEO)_8$ composite electrolyte was reported by using the combined action of the large surface area and the Lewis-acid characteristics of the ceramic additive [10]. Similar techniques using additives have also been applied to enhance the properties of proton conductive polymers. Recently, the effect of organic acids and nano-sized ceramic doping agents on the properties of a PEO-based solid polymer electrolyte was reported [11].

Besides PEO based electrolytes, gel electrolytes based on PMMA or PAA were studied for their applications to Li batteries, electrochromic devices, and solid-state chemical sensors [12, 13]. In addition, the improvement in the proton conductivity of polymer electrolytes based on PAA has

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been reported [14]. The influence of the complexation between PMMA and PEO on the relaxation behavior of the polymer chains was also studied by $^{13}C$ solid state high resolution NMR spectroscopy [15, 16]. Especially, PMAA and PAA bear carboxylic acid groups in the polymer structure that may increase their interaction with $Li^+$ ions. This may result in an increase in their conductivity through the easier transfer of the $Li^+$ ions by the carboxylic acid groups in the polymer. PMMA is the closest to polyacrylic acid, but the availability of $–CH_3$ groups in the α-position causes hydrophobic interactions and, as a result, the more compact conformation of the macromolecules is revealed in solution [17]. However, until now there have been no reports on the study of PEO based polymer electrolytes containing PMAA and PAA as an additive. Thus, we tried to improve the properties of CSPEs by using composite PEO films together with PMMA, PAA, and ceramic additives.

In the present study, the various experimental parameters affecting the characteristics of a solid electrolyte membrane were examined for a composite electrolyte based on PEO containing $LiClO_4$, PAA (polyacrylic acid),PMAA (polymethacrylic acid), citric acid, and$Al_2O_3$ as additives. The ionic conductivity, the interfacial phenomena with the lithium metal, and the electrochemical characteristics of the polymer electrolyte were studied using ac impedance, cyclic voltammetry, and charge/discharge experiments. In addition, the effects of the doping ratio of the organic acids and the addition of $Al_2O_3$ on the ionic conductivity and the grain boundary resistance were also examined.

## 2 Experimental

### 2.1 Reagents and fabrication of the polymer film

Poly(ethylene oxide) (PEO), lithium perchlorate ($LiClO_4$), acetonitrile, and alumina ($Al_2O_3$, 5.6 μm) were purchased from Aldrich Co. (USA) and citric acid was purchased from Yakuri Pure Chemicals Co. (Japan). PAA/PMAA/$Li_{0.3}$ was prepared in a glove-box filled with Ar gas. To prepare the polymer electrolyte film, stoichiometric amounts of PEO and $LiClO_4$ (mol ratio 8:1) were mixed in a small glass reactor, and then added to an acetonitrile solution. The mixture was continuously stirred with a magnetic bar for 24 h and then $Al_2O_3$ powders were added. PAA/PMMA was firstly copolymerized and mixed with LiOH (mol ratio 0.3:0.6) in water, then dried in a vacuum oven for 24 h. To make the stand-alone film, the slurry of the polymer electrolyte was spread onto a Teflon plate and left to stand at room temperature to allow the solvent to evaporate slowly. The films were dried in a vacuum oven at 60 °C for 24 h. The final homogeneous composite polymer films with a thickness of about 100 μm were stored in a glove box under an Ar atmosphere.

### 2.2 Equipments and cell construction

The ionic conductivity of the solid polymer electrolyte was measured using a SS/SPE/SS (SS = Stainless Steel, SPE = Solid Polymer Electrolyte) cell, which was assembled by sandwiching the polymer electrolyte between two stainless steel (SS) disk electrodes. The interface phenomena of the SPE film were investigated with a Li/SPE/Li cell. The ionic conductivity of CSPE was evaluated with the impedance data obtained by employing a PAR Model 2263 potentiostat (E.G&G). In this case, an AC perturbation of 5 mV was used over the frequency range from 1 MHz to 1 Hz for the temperature range from 20 to 90 °C. The data were displayed in the form of a Nyquist plot and a log conductivity vs. temperature curve. Cyclic voltammetry (Kosentech PT-1 Potentiostat/Galvanostat, (S. Korea)) with a three-electrode cell was performed between −1.0 and 1.0 V at various scan rates from 0.1 to 500 mV $s^{-1}$. The discharge capacity test for the Li/SPE/$LiNi_{0.5}Co_{0.5}O_2$ cell was carried out with a battery cycler (Won A Tech. Model WBCS 3000 (S. Korea)), where the positive electrode was $LiNiCo_{0.5}O_2$ and the negative electrode was a Li foil (cell area: 4 $cm^2$). The current density was 0.25 μA $cm^{-2}$ (10 μA $g^{-1}$), and the potential range was between 2.5 and 3.7 V at 30 °C. All procedures were carried out under an argon atmosphere in a glove box.

## 3 Results and discussion

Figure 1A shows the measured ionic conductivity of the polymer electrolytes, PEO/$LiClO_4$ (at a mol ratio of 8:1), with different compositions containing the additives, citric acid, $Al_2O_3$, PAA, and PMAA, in the temperature range from 20 to 90 °C. The ionic conductivity measured for the pure PEO/$LiClO_4$ film was $5.65 \times 10^{-7}$ S $cm^{-1}$ [18]. On the other hand, the ionic conductivity of the polymer film with only $Al_2O_3$ additives was slightly increased to $9.42 \times 10^{-7}$ S $cm^{-1}$ [19, 20]. The addition of citric acid to PEO resulted in a slightly greater to be $6.24 \times 10^{-6}$ S $cm^{-1}$, and the conductivity of the films to which only PAA was added was increased to $7.96 \times 10^{-6}$ S $cm^{-1}$. As can be seen, the ionic conductivities of the PEO:$LiClO_4$ films to which a single additive was added were similar to each other at 20 °C. However, the ionic conductivity of the film, to which PAA was added, was higher than that of the polymer doped with only citric acid at temperatures above 30 °C. The ionic conductivities of the polymer doped with the additives were measured, where the polymer films were composed of PAA/PMAA, PAA/PMAA/$Li_{0.6}$, and PAA/PMAA/$Li_{0.6,}$

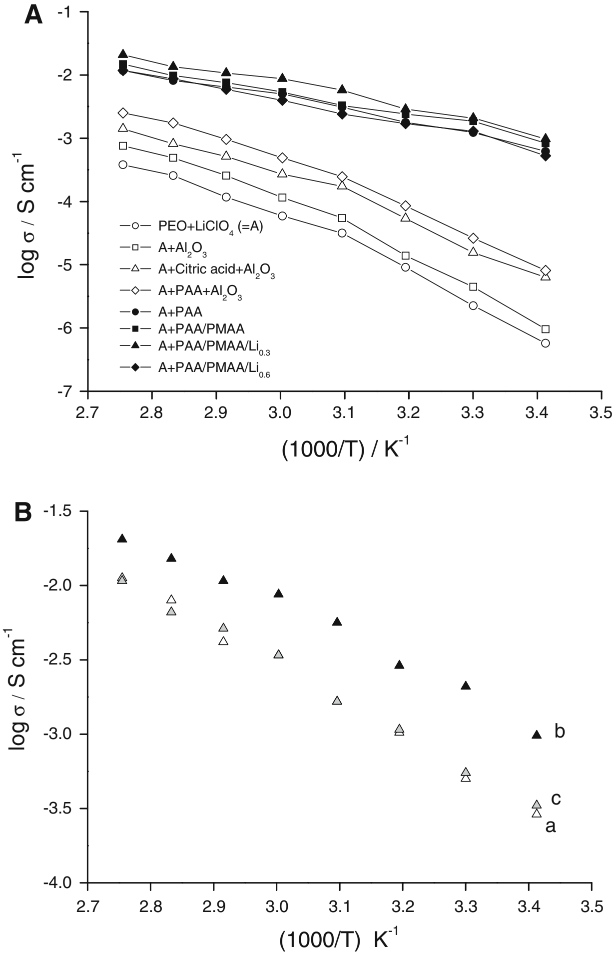

**Fig. 1** **A** Ionic conductivity of the polymer electrolytes, PEO/LiClO$_4$ (at a mol ratio of 8:1), with different compositions containing the additives, citric acid, Al$_2$O$_3$, PAA, and PMAA, in the temperature range from 20 to 90 °C. **B** Temperature dependency of the ionic conductivity for the polymer electrolyte composed of PEO:LiClO$_4$ and PEO:LiClO$_4$:PAA/PMAA/Li$_{0.3}$, where the compositions are a) PEO:LiClO$_4$:PAA/PMAA/Li$_{0.3}$ = 8:1:0.05, b) PEO:LiClO$_4$:PAA/PMAA/Li$_{0.3}$ = 8:1:0.1, c) PEO:LiClO$_4$:PAA/PMAA/Li$_{0.3}$ = 8:1:0.15

respectively. The ionic conductivity of the electrolytes composed of PEO:LiClO$_4$:PAA/PMAA, PEO:LiClO$_4$:PAA/PMAA/Li$_{0.3}$, and PEO:LiClO$_4$:PAA/PMAA/Li$_{0.6}$ increased greatly to 8.24, 9.87, and 5.28 × 10$^{-4}$ S cm$^{-1}$, respectively. As shown, the ionic conductivity was enhanced by changing the additive components as the following order; PAA < PAA/PMAA < PAA/PMAA/Li$_{0.3}$ < PAA/PMAA/Li$_{0.6}$. The enhanced ionic conductivity should be related to the lowing crystallinity by increasing the amorphous region and increasing the number of pores by adding the additives. In this case, the movement of Li ions in the film is easier and the ionic conductivity is therefore increased. Figure 1B shows the variation of the ionic conductivity with the inverse of the temperature for the different mole ratios of PEO:LiClO$_4$:PAA/PMAA/Li$_{0.3}$. The mole ratios were (a) 8:1:0.05, (b) 8:1:0.1, and (c) 8:1:0.15. The temperature dependence of the ionic conductivity exhibited Arrhenius behavior in the entire temperature range of the measurements (20–90 °C). The observed tendency suggests that the charge transport is independent of the segmental movement of the PEO/PAA/PMAA composite solid polymer electrolytes. The best result was obtained for the ratio of PEO:LiClO$_4$:PAA/PMAA/Li$_{0.3}$ = 8:1:0.1.

The impedance spectra in the form of two semicircles for the Li/SPE/Li cells consisting of the solid polymer electrolytes and the equivalent circuit are shown in Fig. 2. Where, R$_1$ is the resistance of the bulk solid polymer film, R$_2$ is the interface polarization resistance between the film and Li electrode, R$_3$ is the charge transfer resistance. Table 1 shows the extracted parameters for the circuit elements evaluated by fitting the impedance data to the equivalent circuit [21–23]. The bulk resistance values (R$_1$) of the film were similar for all of the electrolyte compositions. On the other hand, the polymer electrolyte composed only of PEO + LiClO$_4$ gave the highest resistance values of R$_2$ and R$_3$, viz. 4,592 and 1,437 ohms, respectively. The corresponding values of the PEO:LiClO$_4$:Al$_2$O$_3$ composition were 2,871 and 317.7 ohms and those of the PEO:PAA/PMAA/Li$_{0.3}$ composition were 881.5 and 267.1 ohms, respectively, where the values of R$_2$ and R$_3$ decreased upon the addition of Al$_2$O$_3$ and PAA/PMAA/Li$_{0.3}$. Of these additives, the addition of PAA/PMAA/Li$_{0.3}$ showed the greatest decreasing in the impedance.

Figure 3A shows the CVs recorded for the Li/SPE/SS cell at a scan rate of 20 mV s$^{-1}$, where the electrode area was 2 × 2 cm$^2$. The composition ratio of the solid electrolyte composed of PEO:LiClO$_4$:citric acid:Al$_2$O$_3$ was 8:1:0.05: 10 wt%. As shown in the figure, the CV recorded for the cell

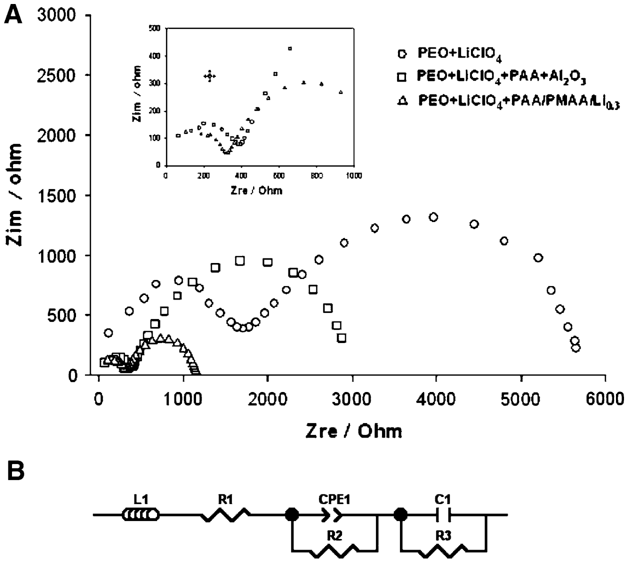

**Fig. 2** **A** Ac impedance spectra obtained for a Li/SPE/Li cell and **B** equivalent circuit of the cell

**Table 1** The extracted parameters for the circuit elements evaluated by fitting the impedance data to the equivalent circuit

| Sample | L (H) | $R_1$ (Ω) | CPE | | $R_2$ (Ω) | C (F) | $R_3$ (Ω) |
|---|---|---|---|---|---|---|---|
| | | | $Y_0$ (S) | *n* | | | |
| PEO + $LiClO_4$ (=A) | 1.94E−12 | 58.76 | 1.80E−6 | 0.6316 | 1,437 | 4.19E−10 | 4,592 |
| A + PAA + $Al_2O_3$ | 2.79E−13 | 40.89 | 3.51E−6 | 0.7239 | 317.7 | 1.45E−9 | 2,871 |
| A + PAA/PMAA/$Li_{0.3}$ | 7.91E−7 | 38.84 | 3.85E−6 | 0.7447 | 267.1 | 9.46E−10 | 881.5 |

composed of SS and Li electrodes with the PEO:$LiClO_4$:citric acid:$Al_2O_3$ (8:1:0.05:10 wt%) film without PAA and PMAA displayed redox peaks. Figure 3B shows the CVs recorded for the Li/SPE/SS cell without $Al_2O_3$ at different temperatures. In this case, the composition of the SPE of PEO;$LiClO_4$:PAA/PMAA/$Li_{0.3}$ was 8:1:0.1 wt%. As shown in the figure, the anodic and cathodic peaks were not observed below 50 °C, however, a pair of redox peak was clearly observed at 70 °C, showing the anodic peaks at +380 mV and the cathodic peak at 740 mV, which is comparable to the previous result [24]. This indicates that both the anodic and cathodic processes were promoted by the easy movement of the Li ions at temperatures above 70 °C, because the melting point of PEO is 64 °C and it changes into the amorphous state at this temperature, thus facilitating the movement of the Li ions.

On the other hand, the CV recorded for the Li/SPE/SS cell composed of PEO:$LiClO_4$:PAA/PMAA/$Li_{0.3}$:$Al_2O_3$ (8:1:0.1:10 wt%) at different scan rates shows a sigmoidal shape, as shown in Fig. 4, which is the same pattern as that of the CV obtained using an ultra-microelectrode. Here, the anodic peak appeared at +280 mV due to the reaction of $Li \rightarrow Li^+ + e$, and the corresponding cathodic peak at −210 mV due to the reaction of $Li^+ + e \rightarrow Li$. In this case, the movement of the ions through the sub-micro holes formed in the electrolyte film due to the addition of $Al_2O_3$ showed the same behavior as that in the diffusion process of an ultra-microelectrode [25].

To examine the cyclability of the redox process of the cell, fast cyclic voltammetry was carried out for the Li/SPE/$LiNi_{0.5}Co_{0.5}O_2$ cell. The CV shown in Fig. 5 revealed the good cyclability and characteristics [26]. As shown in Fig. 5A, the peak current decreased to be stabilized by early 10 cycles among 100 cycles, and it entered a steady state, indicating the cell might be stable during the potential cycles. To ascertain the effective application of the polymer electrolyte in a lithium polymer battery, the Li/SPE/

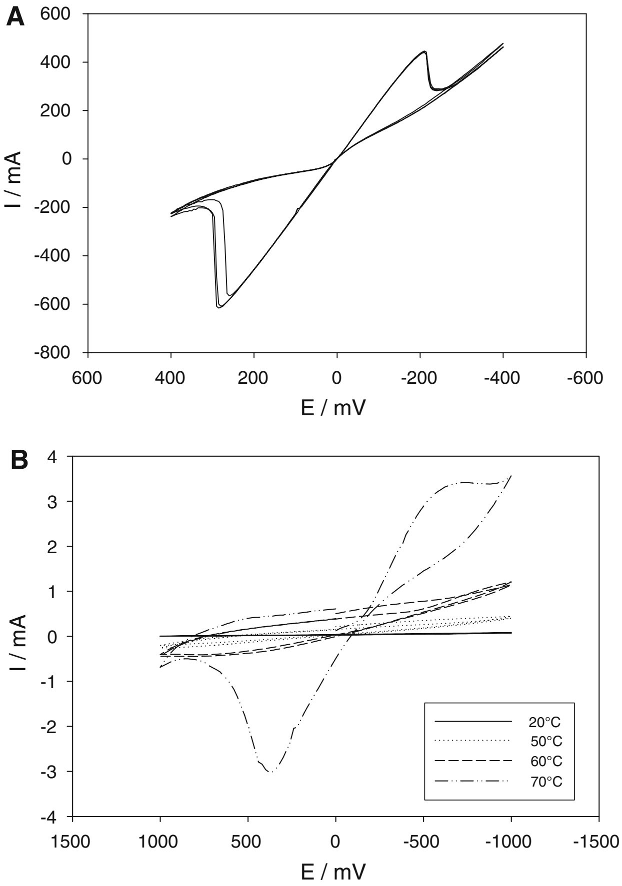

**Fig. 3** **A** CVs recorded for a Li/SPE/SS cell (the electrode area was 2 × 2 $cm^2$, and the scan rate was 20 mV $s^{-1}$). Composition of SPE was PEO:$LiClO_4$:citric acid :$Al_2O_3$ = 8:1:0.05:10 wt%. **B** CVs for a Li/SPE/SS cell containing PEO:LiClO4:PAA/PMAA/$Li_{0.3}$ = 8:1:0.1 wt%

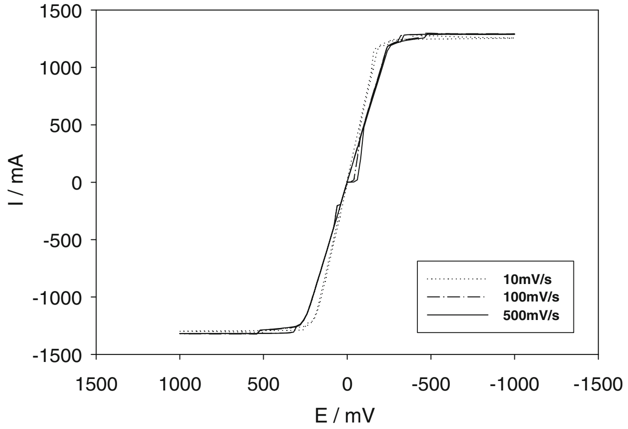

**Fig. 4** CVs for the Li/SPE/SS cell at different scan rates. The electrode area was 2 × 2 $cm^2$. The composition of SPE was PEO:$LiClO_4$:PAA/PMAA/$Li_{0.3}$:$Al_2O_3$ = 8:1:0.1:10 wt%

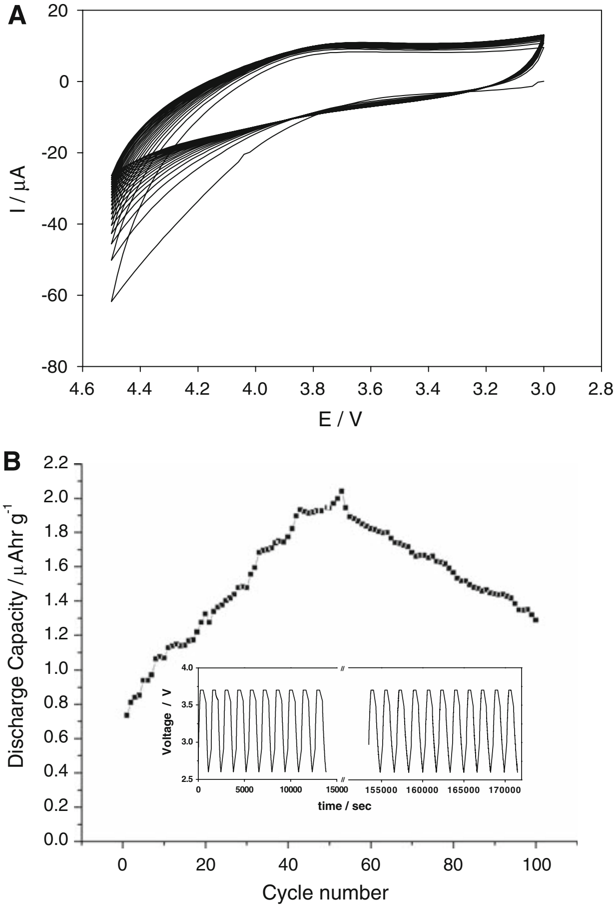

**Fig. 5** **A** CVs recorded during the multiple cycles for $LiNi_{0.5}Co_{0.5}O_2$/PEO:$LiClO_4$:PAA/PMAA/$Li_{0.3}$ cell, and **B** Discharge capacities of the full cell over the potential range from 3.7 to 2.5 V. Temperature was 30 °C

$LiNi_{0.5}Co_{0.5}O_2$ cells were examined by the charge/discharge cycling test. Figure 5B shows the variation of the discharge capacity when the cell was charged at 0.25 µA cm$^{-2}$ and 3.7 V, held at this charge for 5 min, and then discharged at 0.25 µA cm$^{-2}$ and 2.5 V. The cell was operated using a cathode for which the weight of $LiNi_{0.5}Co_{0.5}O_2$ coated on the Al foil was 0.1 g and the current density was 0.25 µA cm$^{-2}$ (10 µA g$^{-1}$, 5 C), where the initial capacity of the cell was 0.736 µAhr g$^{-1}$. The energy density of the Li/SPE/$LiNi_{0.5}Co_{0.5}O_2$ system under the optimized condition was comparable to the previously reported value [27]. The capacity increased from 0.736 µAhr g$^{-1}$ in the first cycle to 2.041 µAhr g$^{-1}$ after 53 cycles. Thereafter, it decreased gradually on cycling, with a value of 1.288 µAhr g$^{-1}$ being obtained at the end of 100 cycles. The reduced capacity might be related to the degradation of the interfacial contact between the electrolyte and the conducting material, which is attributed to the volumetric change caused by the expansion and shrinkage of the active materials. This could lead to an increase in the charge transfer resistance. Additionally, due to the formation of passive films of Li during charge/discharge cycles, the activation of Li was decreased as the cycle test was repeated. The present electrolyte system would be expected to show improved performance when using graphite instead of Li foil, such as $LiNi_{0.5}Co_{0.5}O_2$/SPE/graphite.

## 4 Conclusions

The ionic conductivity of the solid polymer electrolyte increased when $Al_2O_3$ andan organic acid were added to PEO. In addition, the characteristics were improved in the case where PAA rather than an organic acid was added to CSPE. It was confirmed that PAA would be acceptable for Li polymer batteries. In particular, the best enhancement of the ion conductivity was obtained by adding PAA/PMAA/$Li_{0.3}$ to PEO. The ionic conductivity of the PEO film, to which PAA/PMAA/$Li_{0.3}$ were added was of the order of ~ $10^{-4}$ S cm$^{-1}$ at 20 °C. The cycling test indicates that this composition could be used as a polymer electrolyte for lithium polymer batteries.

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