Phase-separated polymer electrolyte based on poly(vinyl chloride)/poly(ethyl methacrylate) blend

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Abstract

The characteristics of polymer electrolytes based on a poly(vinyl chloride) (PVC)/poly(ethyl methacrylate) (PEMA) blend are reported. The PVC/PEMA based polymer electrolyte consists of an electrolyte-rich phase that acts as a conducting channel and a polymer-rich phase that provides mechanical strength. The dual phase was simply developed by a single-step coating process. The mechanical strength of the PVC/PEMA based polymer electrolyte was found to be much higher than that of a previously reported PVC/PMMA-based polymer electrolyte (poly(methyl methacrylate), PMMA) at the same PVC content, and even comparable with that of the PVC-based polymer electrolyte. The blended polymer electrolytes showed ionic conductivity of higher than 10^{-3} S cm^{-1} and electrochemical stability up to at least 4.3 V. A prototype battery, which consists of a LiCoO$_2$ cathode, a MCMB anode, and PVC/PEMA-based polymer electrolyte, gives 92% of the initial capacity at 100 cycles upon repeated charge–discharge at the 1 C rate.
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1. Introduction

In recent years, there has been an increasing need for rechargeable batteries of high specific energy for portable electronic equipment. Among them, lithium-polymer batteries are now being widely investigated and developed. This is because these batteries can be produced in a variety of forms, thus permitting portable batteries of the required shape to be produced readily, and enabling customization of portable-powered electronic equipment to be produced [1–3]. Conventional poly(ethylene oxide)-based polymer electrolytes are the most commonly studied. The electrolytes exhibit a conductivity which ranges from 10^{-8} to 10^{-5} S cm^{-1} at room temperature. This excludes practical application at ambient temperature [4].

Gel polymer electrolytes, in which liquid electrolyte is immobilized in a polymer matrix, can exhibit ionic conductivity in excess of 10^{-3} S cm^{-1} at room temperature. Their mechanical properties are not sufficient, however, to produce thin films, because the impregnation of a liquid electrolyte into a polymer results in softening of the polymer.

The problem of poor mechanical strength can be circumvented by blending a host polymer, which mainly accommodates liquid electrolyte, with a polymer, such as poly(vinyl chloride) (PVC). The latter which manifests itself in a phase-separated morphology, because of its poor solubility in the liquid electrolyte, to provide a rather rigid framework in the polymer electrolyte films. Since electrolytes based on a polymer blend are free from any additional supporting layer and any chemical cross-linking reaction, they are highly promising for large-scale production in terms of both simplicity and cost.

Proof of the blend concept was demonstrated with a PVC/poly(methyl methacrylate) (PMMA) polymer electrolyte by Rhoo et al. [5], and the characteristics of a lithium-ion polymer battery that employed a PVC/PMMA polymer electrolyte was reported by Kim et al. [6]. From these studies, it was found that the mechanical strength of PVC/PMMA blend electrolytes, which is imparted by the PVC-rich phase, increased with increasing PVC content. Increase of PVC content also leads, however, to decrease of ionic conductivity and to poor adhesion which causes to increase of interfacial resistance during repeated charge–discharge. Investigations of the influence of plasticizer in optimizing polymer electrolyte design [7] and on the

dependence of ionic conductivity on salt concentration [8] were also reported for a PVC/PMMA polymer electrolyte.

In this work, we have prepared a new phase-separated polymer electrolyte based on a blend of PVC and poly(ethyl methacrylate) (PEMA). The primary objective is to develop a phase-separated polymer electrolyte that shows better mechanical strength than that reported for a PVC/PMMA blend polymer electrolyte at the same PVC content, and also provides acceptable adhesion to electrode. The electrochemical characteristics of the PVC/PEMA blend polymer electrolyte are also evaluated. In order to check the suitability of the polymer electrolyte for lithium-ion polymer batteries, we have prepared $LiCoO_2$|graphite cell and investigated its cycleability. Comparisons with PVC and PVC/PMMA blend polymer electrolytes are also made to elucidate the function and the merit of the incorporated PEMA.

2. Experimental

2.1. Preparation of polymer electrolyte

PVC, PMMA, and PEMA were purchased from Aldrich and used after drying under vacuum at 60 °C for 1 day. Typical preparation of the polymer electrolyte film includes the following steps. The solution for film casting was prepared by dissolving appropriate amounts of PVC, PEMA and liquid electrolyte (1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate and propylene carbonate) in anhydrous tetrahydrofuran (THF). The weight ratio of the liquid electrolyte and the polymer was set at 3:1. The solution was agitated for 1 day at 80 °C. The resulting homogeneous mixture was cast on a releasing layer. After evaporating the THF, the resulting films were peeled from the releasing film. The thickness of the electrolyte film was controlled in the range 50–60 μm.

2.2. Characterization of polymer electrolyte

The morphologies of the polymer electrolytes were investigated by scanning electron microscopy (Hitach 2400s). The liquid electrolyte in the specimen was removed by freeze–drying without any change in the morphology of the specimen. Elastic modulus and elongation at break of the polymer electrolytes were measured by using a universal tensile meter (UTM, Lloyd, LR 10k) according to ASTM 882. The tensile rate was controlled at 1 cm/min.

2.3. Electrical measurements for polymer electrolyte

The specimen for ionic conductivity measurement was prepared by sandwiching the polymer electrolyte between two nickel electrodes. The impedance of the specimen was measured over the frequency range 10 Hz to 10 MHz using a IM6 impedance analyzer. The ionic conductivity was obtained from the bulk resistance found in the complex

impedance diagram. The electrochemical stability of the polymer electrolyte was determined by means of linear sweep voltammetry. Nickel and lithium were used as the working and a counter electrodes, respectively.

2.4. Cell fabrication and performance

$LiCoO_2$ |polymer electrolyte| graphite cells were fabricated by sandwiching the polymer electrolyte between a graphite anode (3.3 cm × 5.5 cm) and a $LiCoO_2$ cathode (3 cm × 5 cm). The stack was sealed in an aluminium-
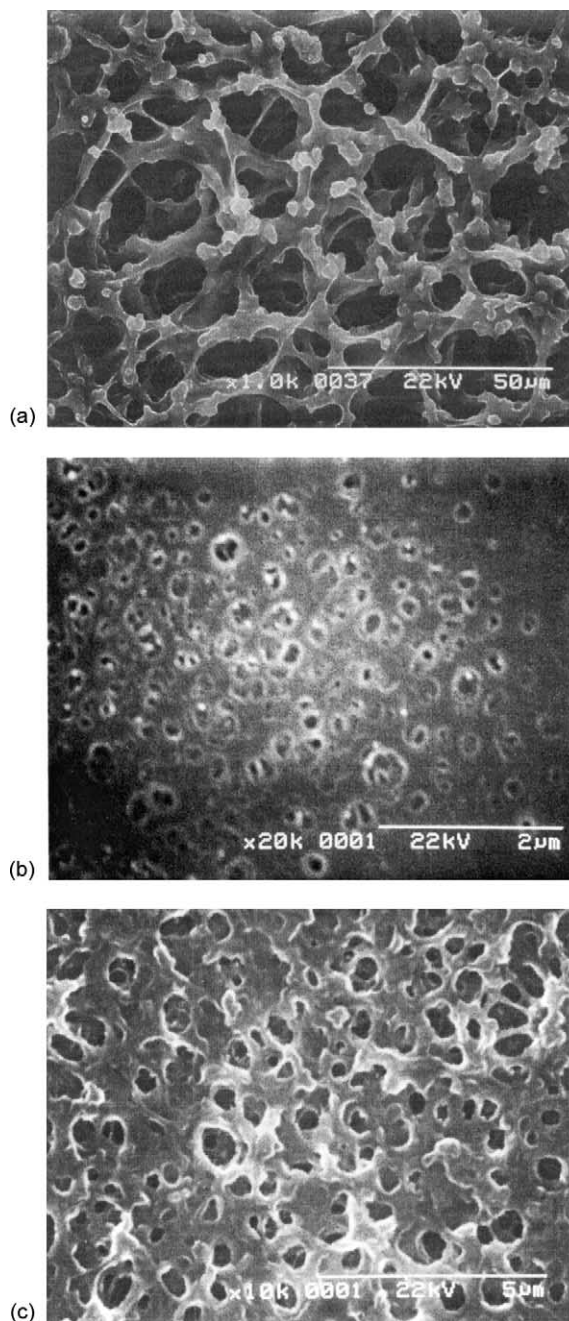

Fig. 1. Electron micrographs of polymer electrolytes based on: (a) PVC, (b) PVC/PMMA = 1/1 and (c) PVC/PEMA = 1/1.

coated plastic pack under vacuum. The cycling behavior and rate capability were investigated by means of a MACCOR battery cycler.

3. Results and discussions

3.1. Morphological characteristics of PVC/PEMA blend polymer electrolyte

Scanning election micrographs of (SEM) of polymer electrolyte films based on the PVC, PVC/PMMA = 1/1

blend, and PVC/PEMA = 1/1 blend are shown in Fig. 1. The pores in the micrographs indicate the occurrence of phase-separation in the polymer electrolytes. Since the liquid electrolyte is removed from the polymer electrolyte film by freeze–drying before SEM measurement, the pores are the sites where liquid electrolyte has been absorbed. The three-dimensional polymer network corresponds to the PVC-rich phase, which has been previously confirmed by [5] from the strong Cl peak in the EDAX spectra of this phase. The pore size is found to increase in the order: PVC < PVC/PEMA < PVC/PMMA. The difference in the pore size is related with the difference in the driving
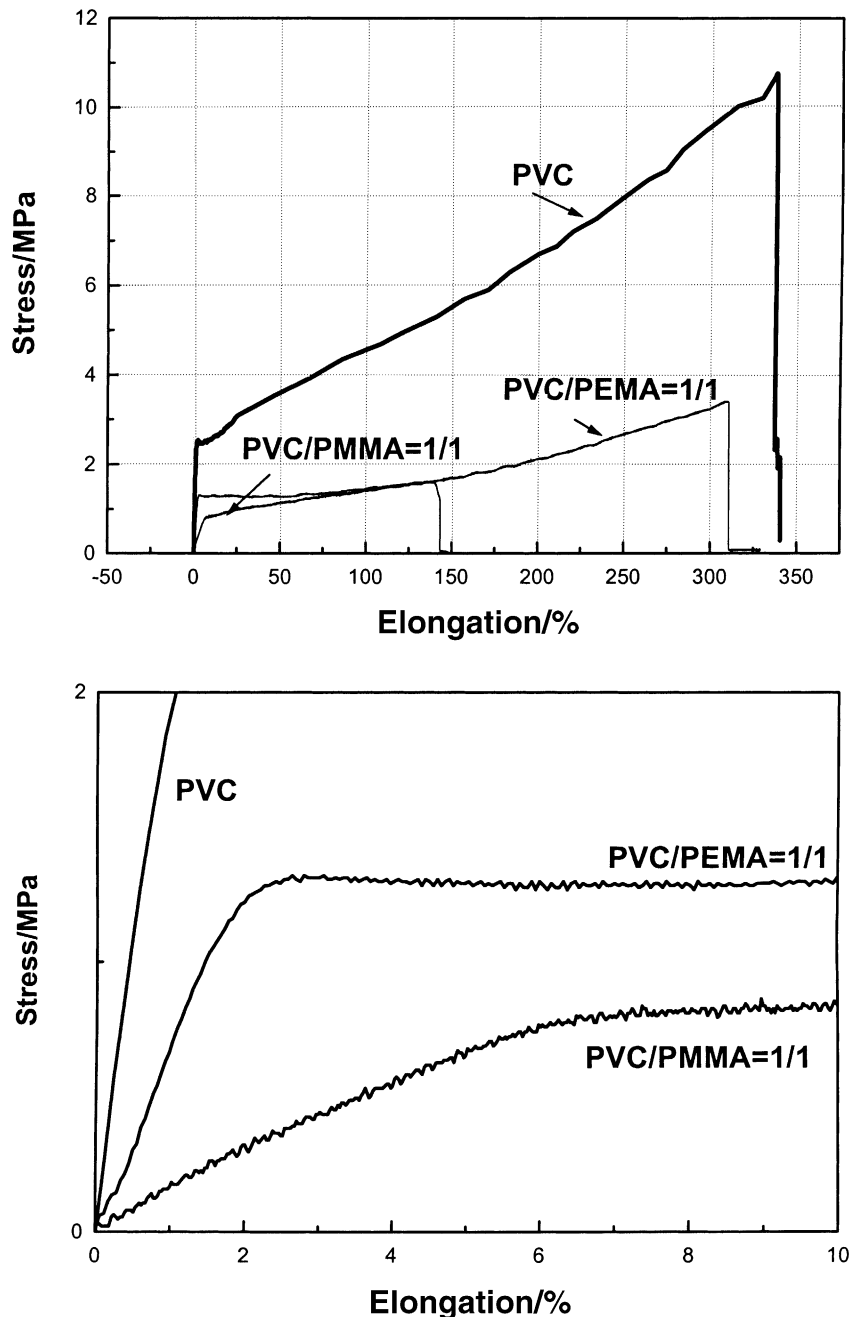

Fig. 2. Stress–strain curves of polymer electrolytes based on PVC, PVC/PEMA = 1/1, and PVC/PMMA = 1/1.
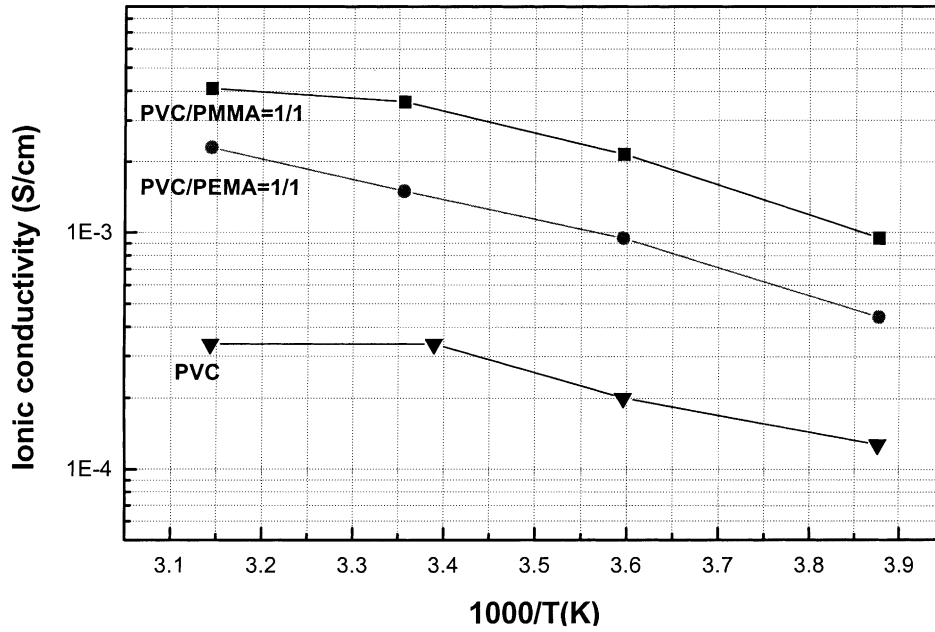
Fig. 3. Ionic conductivities of polymer electrolytes based on PVC, PVC/PMMA = 1/1 and PVC/PEMA = 1/1.

force for phase separation [5]. The phase separation in the PVC containing polymer electrolyte originates from the immiscibility of PVC with the liquid electrolyte. The morphology of the phase separation is determined when

the PVC-rich phase is coagulated and immobilized. For the PVC-based polymer electrolyte, PVC is coagulated at the early stage of phase separation before a large electrolyte-rich phase is developed. The incorporation of a polymer
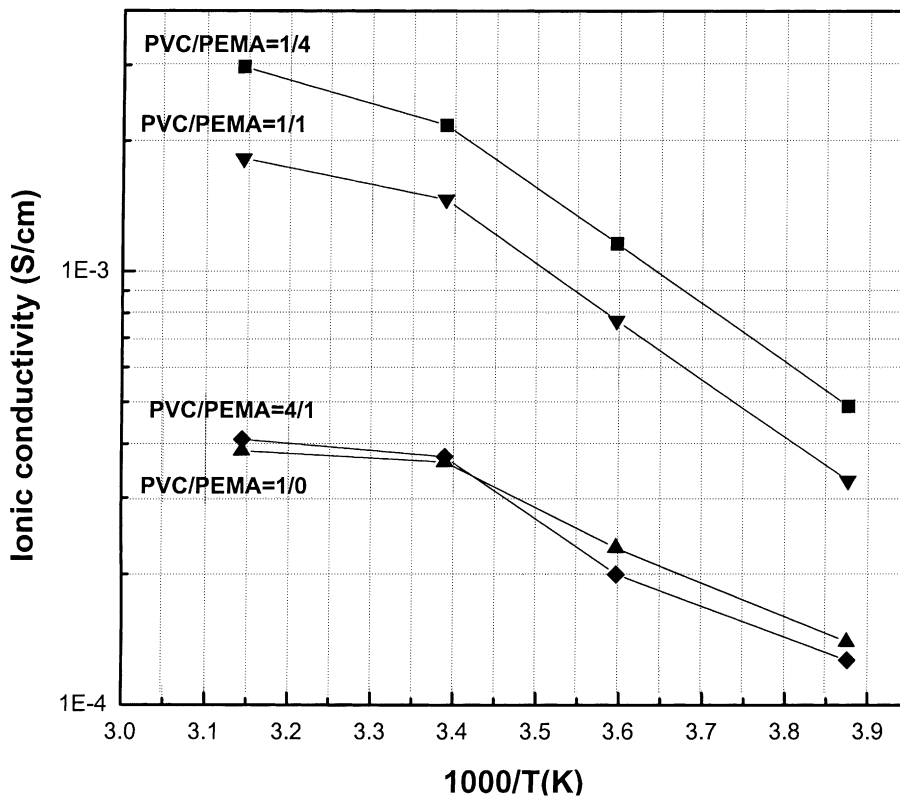

Fig. 4. Ionic conductivities of polymer electrolytes based on PVC/PEMA blends at various ratios.

such as PMMA and PEMA, which has a compatibility with both the PVC and the liquid electrolyte, lowers the driving force for phase separation. This leads to slower coagulation of the PVC and thus to better development of the electrolyte-rich phase. The difference in the size of the electrolyte-rich phase between the PVC/PEMA and PVC/PMMA based polymer electrolytes is believed to be due to a difference in compatibility with the liquid electrolyte. PMMA is completely soluble in 1 M $LiPF_6$-EC/PC = 1/1, whereas, PEMA swells the liquid electrolyte with a swelling ratio of 4.6 at room temperature. The higher compatibility with liquid electrolyte for PMMA leads to the slower coagulation and, as a result, to a larger electrolyte-rich phase.

3.2. Mechanical strength of the PVC/PEMA blend polymer electrolyte

The stress–strain curve that reflects the mechanical properties of the PVC/PEMA-based polymer electrolyte is shown in Fig. 2. For comparison, the stress–strain curves for the PVC based polymer electrolyte and the PVC/PEMA-based polymer electrolyte are also displayed in Fig. 2. The PVC/PEMA-blend polymer electrolyte has a much higher elastic modulus and higher elongation than the PVC/PMMA-blend polymer electrolyte, which fulfills a major objective of the present study. This is a result of the solidly developed polymer network in the PVC/PEMA polymer electrolyte, as seen in Fig. 1. The poor mechanical strength of the PVC/PMMA-based polymer electrolyte is attributed to softening of the PVC-rich phase by the liquid electrolyte. The elastic modulus and elongation at break of the PVC/PEMA-blend polymer electrolyte are even found to be comparable with those of the PVC based polymer electrolyte. This indicates that the PVC-rich phase in the PVC/PEMA blend polymer electrolyte is not significantly softened by the liquid electrolyte.

3.3. Electrochemical characteristics of PVC/PEMA-blend polymer electrolyte

The ionic conductivity of the PVC/PEMA-blend polymer electrolyte is given in Fig. 3. Comparisons with the PVC/PMMA-blend polymer electrolyte and the PVC-based polymer electrolyte at the same electrolyte content are also provided in Fig. 3. The ionic conductivity of the PVC/PEMA-blend polymer is somewhat lower than that of the PVC/PMMA-blend polymer electrolyte, whereas, it is much higher than that of the PVC-based polymer electrolyte. Since the PVC-rich phase blocks ionic transport [5,6], ionic transfer should be more facile for a higher volume fraction of the electrolyte-rich phase.

The effect of blend ratio of PVC/PEMA on ionic conductivity is shown in Fig. 4. The poor ionic conductivity at high PVC content is caused mainly by the low electrolyte content. Due to the poor compatibility between PVC and the

liquid electrolyte, the liquid electrolyte spontaneously oozes, which results in a low electrolyte content in the matrix. By contrast, leakage of liquid electrolyte is not observed at low PVC content. These observations are typically shown
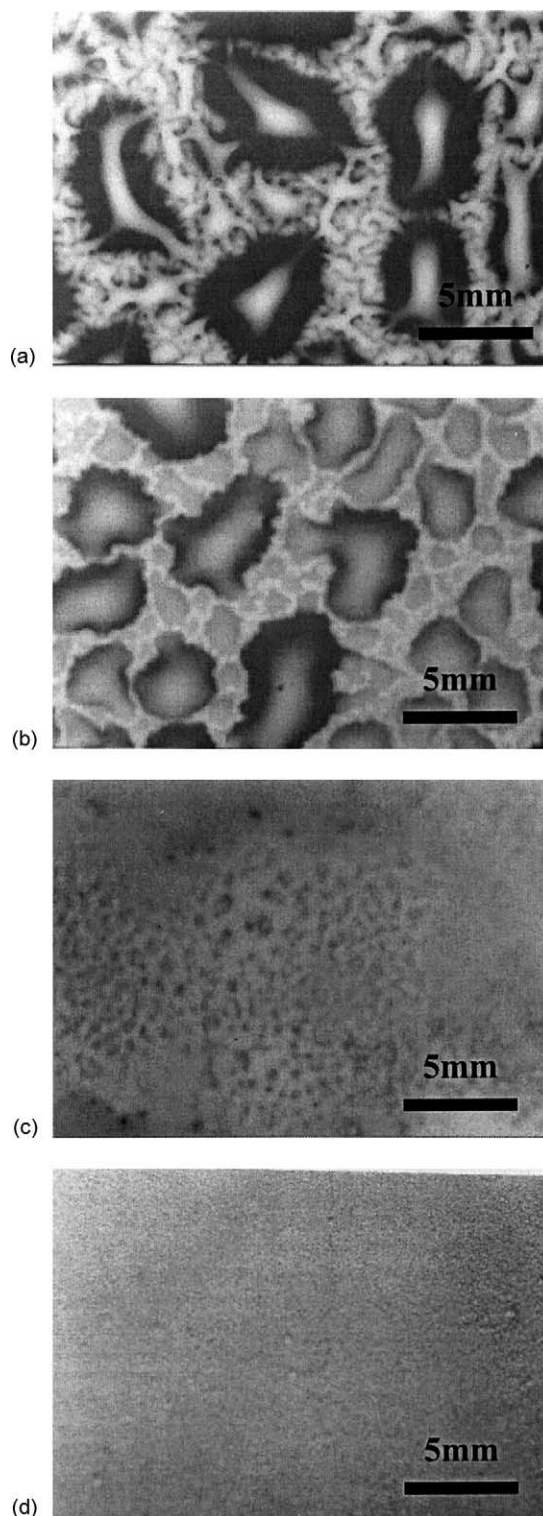

Fig. 5. Optical microscopic images of polymer electrolytes based on PVC/PEMA blends at various ratios, PVC/PEMA: (a) 1/0; (b) 4/1; (c) 1/1; and (d) 1/4.
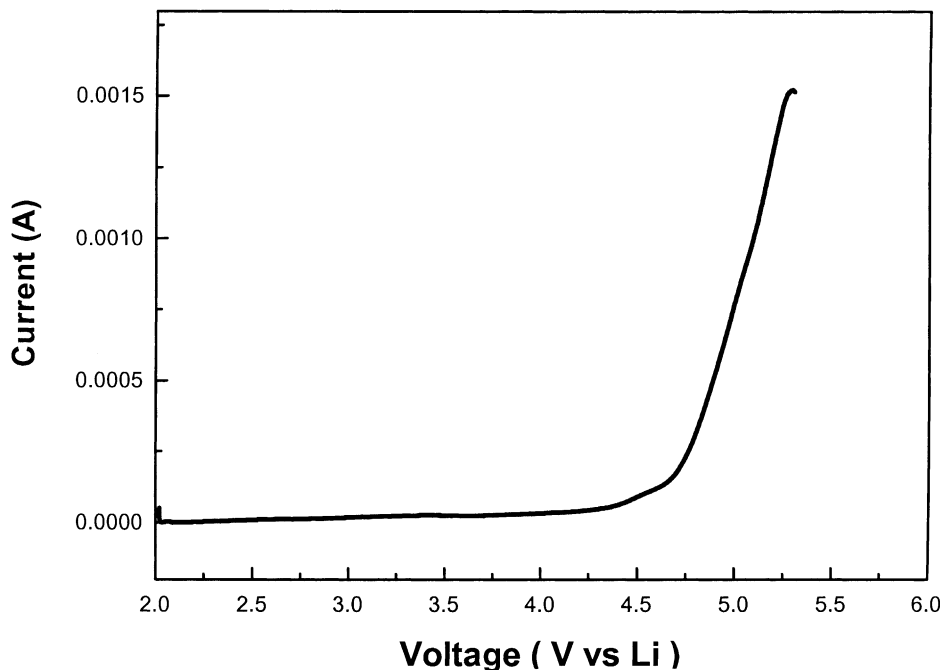
Fig. 6. Linear sweep voltammetry response for polymer electrolyte based on PVC/PEMA = 1/1.

by optical microscopic images of the PVC/PEMA based polymer electrolytes with various blend ratios after storage for 1 day (Fig. 5).

The electrochemical stability of the PVC/PEMA blend polymer electrolyte was also evaluated. As shown in Fig. 6, the blend polymer electrolyte is stable up to 4.3 V, which is sufficiently high for the lithium oxide cathodes $LiCoO_2$ and $Li_2Mn_2O_4$. Based on the above results, it is concluded that the PVC/PEMA-based electrolyte can be successfully used for lithium-ion polymer batteries in terms of ionic conductivity and electrochemical stability.

3.4. Compatibility of PVC/PEMA based polymer electrolyte with lithium metal

Besides high ionic conductivity, electrochemical stability, and good mechanical strength, low passivation at the lithium interface are also required for practical application of the polymer electrolyte in lithium batteries. The stability of the Li|polymer electrolyte interface was examined by means of impedance spectroscopy. Accordingly, evaluation of the interface characteristics was carried out by monitoring the time evolution of the ac impedance of the symmetric cell (Li |polymer electrolytes| Li) at room temperature. The complex impedance responses of three Li |polymer electrolyte| Li cells prepared with the PVC, PVC/PMMA = 1/1, and PVC/PEMA = 1/1 based polymer electrolytes are presented in Figs. 7 and 8. The diameter of the semicircle found in Fig. 7 corresponds to the interfacial resistance, which is caused by the formation

of the passivation layer on the Li electrode by reaction between the electrolyte. The middle frequency semicircle progressively expands after storage at room temperature. This expansion indicates an increase in the interfacial resistance and may quite likely be associated with a continuous growth of the passivation layer, which is the product of the corrosion reaction of Li in the electrolyte medium [9]. The PVC-based polymer electrolyte has a much higher interfacial resistance than the PVC/PMMA- and the PVC/PEMA-based polymer electrolytes. This suggests that the formation of the passivation layer is suppressed by the incorporation of PMMA or PEMA into the PVC matrix.

The time evolution of the interfacial resistance for the PVC, the PVC/PMMA, the PVC/PEMA based polymer electrolytes. The interfacial resistance is significantly increased for the PVC-based polymer electrolyte, but the PVC/PMMA- and the PVC/PEMA-based polymer electrolytes experience a revealed rather slow increase. It is considered that this behavior is related with the prevention of the electrolyte leakage by PEMA or PMMA. When the PVC-based electrolyte is stored at room temperature, the exudate is found on the surface of the polymer electrolyte. Due to the poor compatibility between the PVC and the liquid electrolyte, the liquid electrolyte oozes to the surface during the storage. By contrast, PVC/PEMA does not show exudates, as shown in the previous section. Due to the prevention of leakage of liquid electrolyte by PEMA, the formation and the growth of the passivation layer, which contains the products of the reactions between lithium and the solvent, salt and impurities, are reduced.
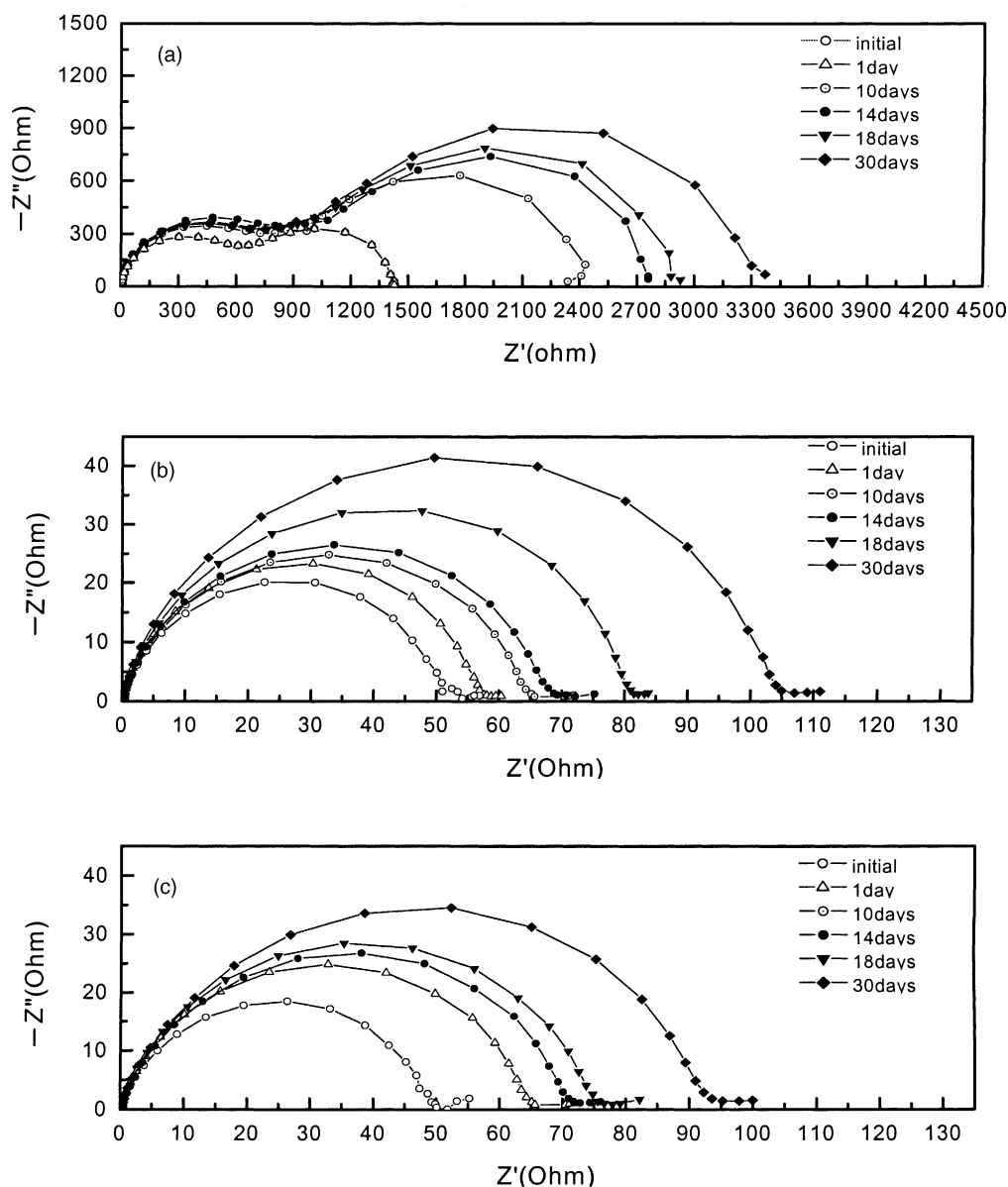
Fig. 7. Time evolution of complex impedance diagram for symmetric Li-ion cell employing polymer electrolytes based on: (a) PVC, (b) PVC/PMMA = 1/1, and (c) PVC/PEMA = 1/1.

3.5. Performance of lithium-ion polymer battery based on PVC/PEMA-blend polymer electrolyte

In order to evaluate the electrochemical performance of a lithium-ion cell using PVC/PEMA-based polymer electrolyte, a LiCoO$_2$|polymer electrolyte–MCMB cell. The assembled cells are subjected to a pre-conditioning cycle with a cut-off voltage of 4.2 V for the upper limit and 3.0 V for the lower limit at a 0.1 C current before repeated charge and discharge at a higher rate. The active electrode area and the theoretical capacity of the cell are approximately 30 cm^2 and 93 mAh, respectively. The discharge capacity as a function of cycle number at a 1 C rate charge and discharge is given in Fig. 9. The use of a PVC/PEMA-blend polymer electrolyte allows good cycling characteristics to

be reached. At 100 cycles, 92% of the initial discharge capacity is retained without any sign of cell failure. It should be noted that the cycling tests have been performed without applying external pressure to the cell. The PVC/PEMA-based polymer electrolyte can be adapted to encapsulate an electrolyte solution at PVC/PMMA = 5/5, as demonstrated in Fig. 4. This will further assist the adherence of the electrodes to the polymer electrolyte. This result is convincing evidence of the good capacity retention of a lithium-ion polymer cell which employs a phase-separated polymer electrolyte, even without applying any external pressure to the cell. From the above results, it is expected that a PVC/PEMA-blend polymer electrolyte is a promising electrolyte material for rechargeable lithium batteries.
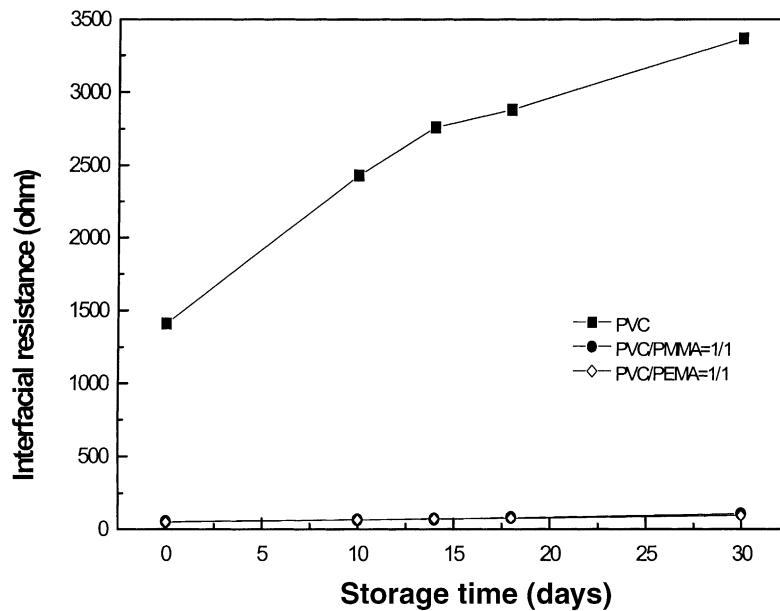
Fig. 8. Plot of interfacial resistance of the symmetric Li-ion cell as function of storage time for PVC-, PVC/PMMA- and PVC/PEMA-based polymer electrolytes.
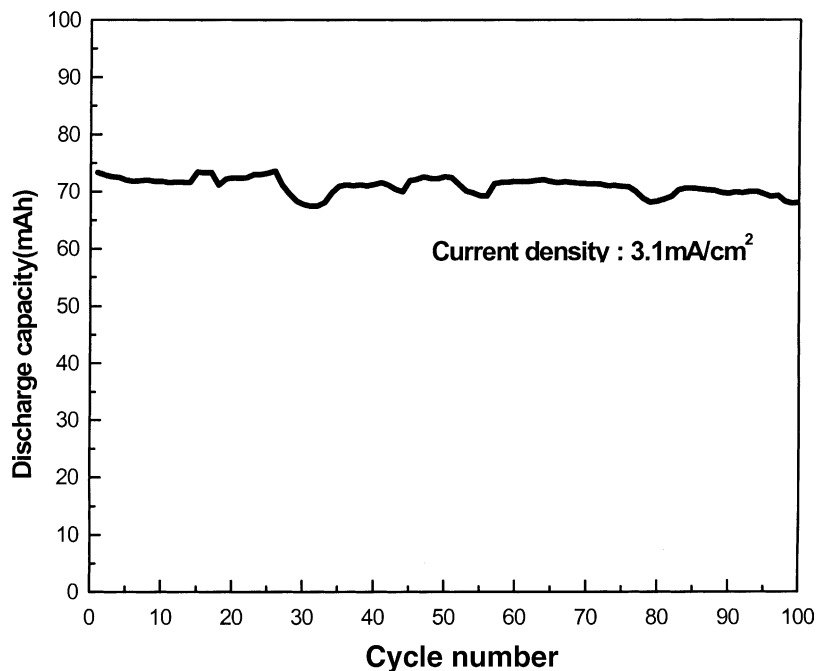

Fig. 9. Discharge capacity of Li-ion cell employing polymer electrolyte based on PVC/PEMA = 1/1 as function of cycle-life (discharge–charge rate = 1 C).

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