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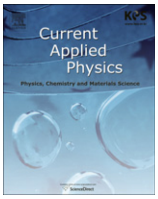

Lithium metal polymer cells assembled with gel polymer electrolytes containing ionic liquid

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ABSTRACT

Gel polymer electrolytes containing a mixture of organic solvent and ionic liquid were prepared and their electrochemical properties were investigated. The gel polymer electrolytes exhibited good electrochemical stability and stable interfacial properties toward lithium metal. Using these gel polymer electrolytes, lithium metal polymer cells composed of a lithium anode and a $LiFePO_4$ cathode were assembled, and their cycling performances were evaluated. The cells showed good cycling performance comparable to that of a cell assembled with gel polymer electrolyte containing only organic liquid electrolyte. The Li/$LiFePO_4$ cells assembled with a gel polymer electrolyte containing ionic liquid are expected to be one of the promising candidates for high energy density lithium batteries with improved safety.

1. Introduction

The rechargeable lithium polymer battery using lithium metal as its anode is the most attractive candidate for the high energy density power sources in portable electronic devices and electric vehicles [1]. This is because lithium metal offers the largest specific capacity as a negative electrode. In this cell, the use of a gel polymer electrolyte enables fabrication of thin batteries with design flexibility [2–4]. However, safety issues surrounding these batteries must be addressed before they can be widely utilized since highly flammable organic solvents are major causes of fire and explosion in short circuit or abuse conditions. In the quest for a non-flammable electrolyte system, ionic liquids (ILs), otherwise known as room temperature molten salts, have been extensively studied and recognized as one of the safest electrolytes for use in lithium batteries [5–10]. They have attractive properties such as a negligible vapor pressure, low flammability, wide electrochemical stability, high ionic conductivity and high thermal stability. Various inorganic materials such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and $LiFePO_4$ have been developed and applied as the cathode material in rechargeable lithium batteries. Among them, lithium iron phosphate ($LiFePO_4$) is of particular interest as an active cathode material because of its high specific capacity, low raw material cost, environmental friendliness and safety [11,12]. With the goal of developing high energy density lithium batteries with improved safety, we assembled lithium metal polymer cells composed of a lithium anode, an IL-containing gel polymer electrolyte, and a $LiFePO_4$ cathode, and their cycling performances were evaluated.

2. Materials and methods

2.1. Preparation of gel polymer electrolytes and electrodes

A porous polymer membrane based on poly(vinylidenefluoride-*co*-hexafluoropropylene) (P(VdF-*co*-HFP)) was prepared according to the procedure previously reported [9]. A gel polymer electrolyte (GPE) was prepared by immersing the membrane in a mixture of organic liquid electrolyte and an ionic liquid. The porous P(VdF-*co*-HFP) membrane could be easily gelled by the mixed electrolyte solution, and the content of electrolyte solution in the GPE ranged from 69 to 72 wt%. The mixed electrolyte was composed of 1 M lithium bis(trifluoromethanelsulfonyl) imide(LiTFSI) in ethylene carbonate(EC)/propylene carbonate(PC)(1:1 by volume) and 1-ethyl-3-methylimidazolium bis(trifluoromethanelsulfonyl)imide (EMITFSI). The content of the IL in the mixed electrolytes ranged from 0 to 30 wt%.

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The cathode was prepared by coating *N*-methyl pyrrolidone (NMP)-based slurry of carbon-coated $LiFePO_4$, PVdF, and super-P carbon (92:4:4) onto an aluminum foil. The thickness of the cathode was about 65 μm and its active mass loading corresponded to a capacity of about 1.8 m Ah cm^{-2}. The anode consisted of a lithium foil of 100 μm that was pressed onto a copper current collector. The lithium metal polymer cell was assembled by sandwiching the GPE between the lithium anode and the $LiFePO_4$ cathode. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. All cell-assembly was carried out in a dry box filled with argon gas.

2.2. Measurements

Linear sweep voltammetry was performed to investigate the electrochemical stability of the GPE on a stainless steel working electrode, with counter and reference electrodes of lithium metal, at a scanning rate of 1.0 mV s^{-1}. The self-extinguishing time (SET) was measured to quantify the flammability of the electrolyte as described in previous literature [9,13]. In order to investigate the interfacial behavior of the Li/GPE/Li cell, AC impedance measurements were performed using an impedance analyzer over the frequency range of 0.1 Hz–100 kHz with an amplitude of 10 mV. Charge and discharge cycling tests of the cells were conducted at a constant current density of 0.36 mA cm^{-2} (0.2 C rate) over a voltage range of 2.5–4.0 V with battery testing equipment.

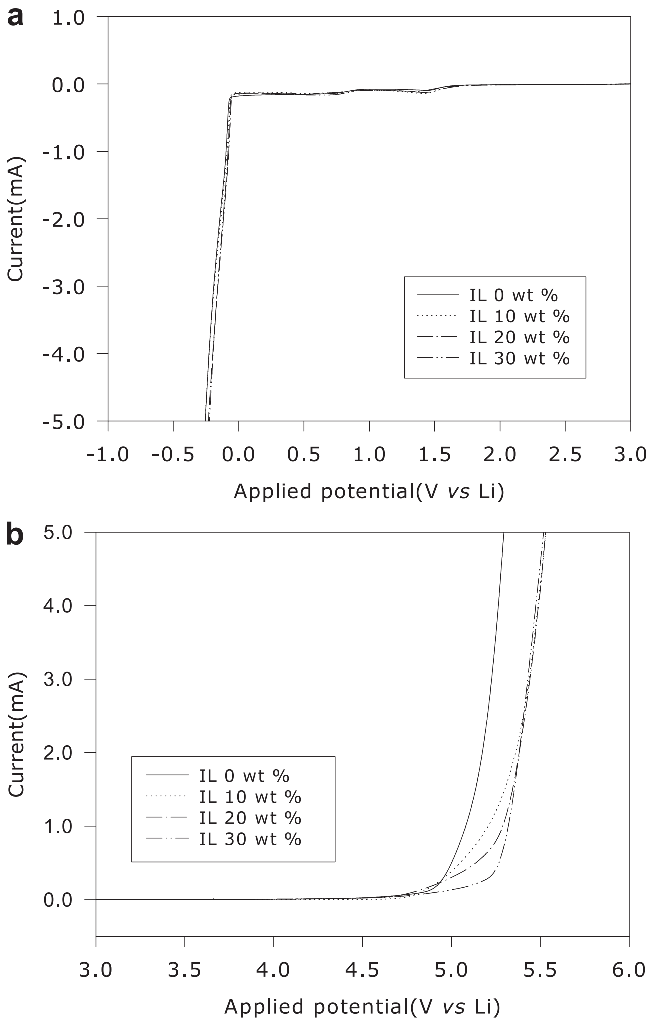

Fig. 1. Linear sweep voltammograms of gel polymer electrolytes prepared with a mixture of organic liquid electrolyte and ionic liquid: (a) cathodic scan, and (b) anodic scan.

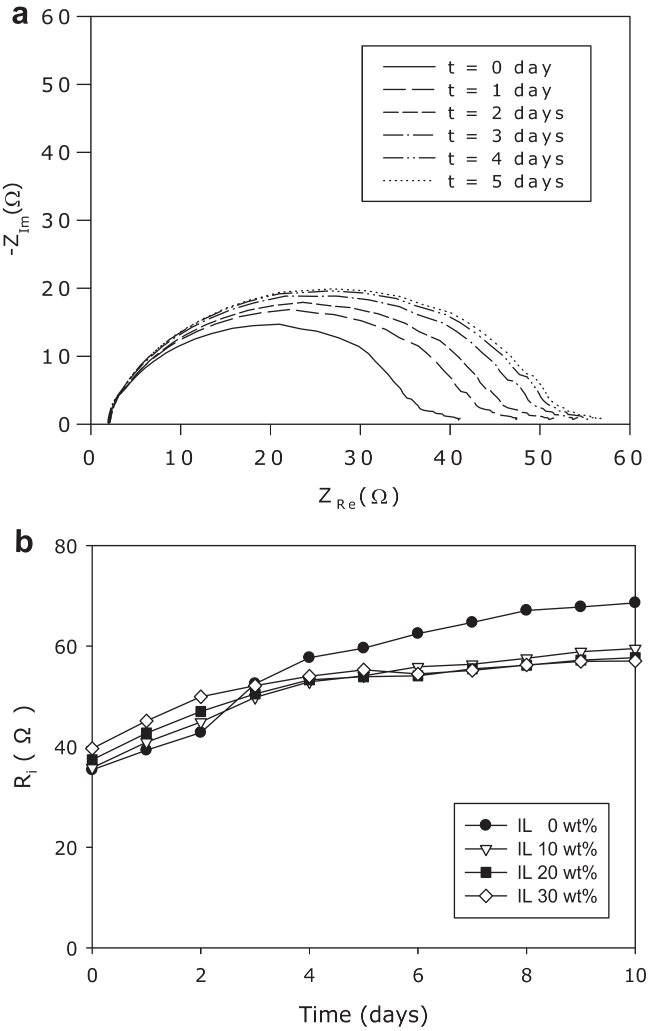

Fig. 2. (a) AC impedance spectra of a Li/GPE/Li cell after storage time at 25 °C, with a GPE containing 30 wt% IL, and (b) the variation in R_i as a function of storage time.

3. Results and discussion

Linear sweep voltammetry curves of the GPEs are shown in Fig. 1(a) and (b), which are obtained from cathodic and anodic scans, respectively. As can be seen in Fig. 1(a), the cathodic decomposition of the electrolyte is difficult to see before lithium deposition is observed around 0 V *vs* Li/Li^+. A small and broad reduction peak appears in the potential range between 1.0 and 1.6 V may be due to the reductive decomposition of EC, which results in the formation of surface film that prevents further reductive decomposition of the imidazolium cation in the IL. This result is consistent with previous work finding that EC could effectively prevent the decomposition of IL [14]. The oxidative current of the GPE is observed at around 5.0 V *vs* Li/Li^+, which corresponds to the anodic decomposition of the electrolyte. It is clear that the decomposition potential of the GPE increased with increasing IL content, suggesting that the addition of IL to the GPE can increase the anodic stability of the electrolyte. These results indicate that the GPEs considered in this study have sufficient electrochemical stability to act as the electrolyte material in $Li/LiFePO_4$ cells.

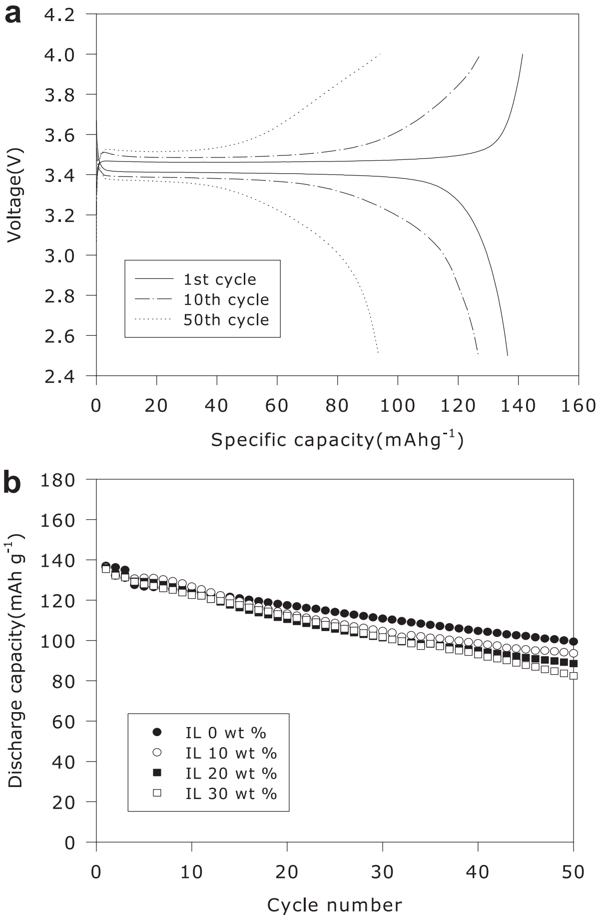

Fig. 3. (a) Charge and discharge curves, and (b) variation in specific discharge capacity with cycle number for the Li/GPE/$LiFePO_4$ cells.

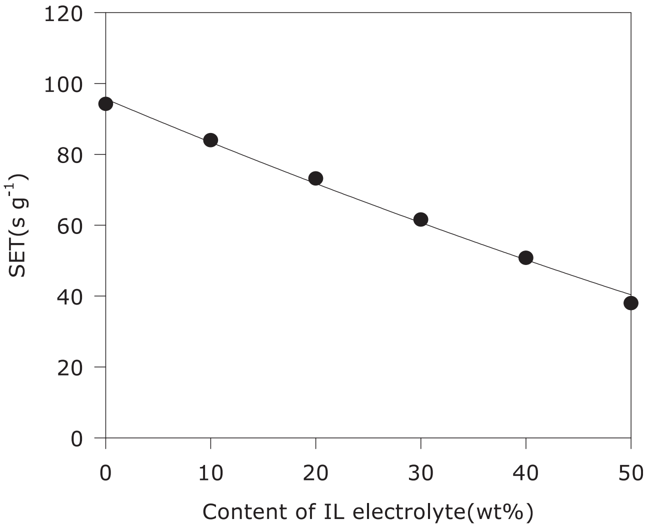

Fig. 4. SET value for a mixture of organic liquid electrolyte and ionic liquid as a function of the content of ionic liquid.

We attempted to investigate the interfacial behavior of a lithium electrode in prolonged contact with a GPE. Fig. 2(a) shows the time evolution of the AC impedance spectra of a Li/GPE/Li cell under open-circuit potential conditions. The spectra are in the form of semicircle with the real axis intercept at high frequency, denoting the bulk electrolyte resistance (R_b), and that at the low frequency denoting the electrode/electrolyte interfacial resistance (R_i). It was found that the electrolyte resistance of the GPE maintained a constant value, irrespective of time. This result suggests that the electrolyte solution was well encapsulated in the closed Li/GPE/Li cell. On the other hand, the interfacial resistance increased initially and eventually stabilized at a constant value, as shown in Fig. 2(b). The initial increase can be attributed to the formation of a passive layer due to the reactivity of the lithium electrode and the GPE. Aprotic solvents such as EC and PC have been well known to form a passivating layer on lithium metal [15,16]. In contrast, the final steady-state value of R_i indicated no further growth of the passive film, which suggests that these GPEs are highly compatible with the metallic lithium anode. It should be noted that the steady-state values of R_i in the GPEs containing IL were lower than that in the GPE without IL. This result may be related to the lower reactivity of viscous IL with metallic lithium.

Cycling performances of lithium metal polymer cells prepared with GPE were evaluated. Fig. 3(a) shows the charge–discharge curves obtained at a constant current density of 0.36 mA cm^{-2}. In this cell, the GPE was prepared by soaking the porous polymer membrane in an electrolyte solution containing 10 wt% IL. The cell had a first discharge capacity of 136.4 mAh g^{-1}, based on the $LiFePO_4$ active cathode material. Both the average discharge voltage and the discharge capacity were found to decrease gradually with increasing cycle number. Fig. 3(b) shows the effect of the IL content on the discharge capacities of the cells as a function of cycle number. The initial discharge capacities were found to be little dependent on the IL content, however, a large capacity decline was observed in the cell containing IL. This capacity decline may be related to the poor interfacial contacts between the cathode material and the electrolyte solution in the GPE during the charge–discharge cycling, which is due to the low mobility of lithium ions within the interface between the $LiFePO_4$ active materials and the electrolyte, arising from the highly viscous nature of IL. Thus, it is thought that the type and composition of IL in the GPE should be optimized to improve the cycle life of the cell.

Finally, in order to investigate the flammable behavior of the IL-based electrolyte used in this study, a flammability test was carried out on the electrolyte solution. Fig. 4 shows the normalized SET values as a function of IL content. From a previous report [13], the flammability of the electrolyte solution is known to be proportional to the SET value. It was clearly observed that the flammability of the electrolyte solution decreased with increasing IL content. Since the pure IL electrolyte is non-flammable, it is plausible that SET values approach to zero as the IL content increases up to 100%. Hence, it is expected that the use of IL-added GPE can improve the safety of the lithium polymer battery. However, the cycling performance was decreased with IL content in the GPE as shown in Fig. 3 (b), it can be concluded that the optimum IL content in consideration of cycle life and safety is about 20 wt% in our system.

4. Conclusions

Gel polymer electrolyte containing non-flammable ionic liquid was prepared and investigated for use in lithium metal polymer batteries. The electrochemical stability of the gel polymer electrolyte was acceptable for use in Li/$LiFePO_4$ cells. The Li/$LiFePO_4$ cell assembled with the gel polymer electrolyte containing IL exhibited reversible charge and discharge cycling, with an initial discharge capacity of 136 mAh g^{-1}. Lithium metal polymer batteries assembled with a gel polymer electrolyte containing IL and $LiFePO_4$ are expected to be potential candidates for high energy density batteries with improved safety.

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