

Electrochemical characteristics of polymer electrolytes based on P(VdF-co-HFP)/PMMA ionomer blend for PLIB

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Abstract

The polymer electrolytes composed of the blend of poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-co-HFP)], and poly(methyl methacrylate-co-lithium methacrylate) [P(MMA-co-LiMA)] ionomer, and the mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC), and LiPF_6 salts were prepared. The introduction of the ionomer into P(VdF-co-HFP) was found to enhance the compatibility of the polymer matrix with the liquid electrolyte. This increase of compatibility could lead to the increase in the uptake amount of the liquid electrolyte into the porous matrix and the ionic conductivities at ambient and sub-ambient temperature were, thus, enhanced. The charge–discharge efficiency of the carbon/polymer electrolytes/ LiCoO_2 cell was also significantly improved by introducing the ionomer into the P(VdF-co-HFP) matrix for the polymer electrolyte. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ionomer; Compatibility; Uptake of liquid electrolyte; Porous polymer matrix

1. Introduction

Plastisized polymer electrolytes in which liquid electrolyte is incorporated into a matrix polymer have been proved to be most promising for the electrolyte of the lithium batteries using the polymer electrolytes owing to their high ionic conductivities [1,2]. Various kinds of polymers have been considered as a matrix for plasticized polymer electrolytes and the PVdF-based polymer electrolyte has received special attention by many researchers in recent years due to its high ionic conductivity and good mechanical strength [3–8]. Gozdz et al. reported a new preparation method for a polymer electrolyte system based on a copolymer of vinylidene fluoride and hexafluoropropylene [P(VdF-co-HFP)] [4]. The plasticization of P(VdF-co-HFP) copolymers, subsequent removal of the plasticizer from the polymer matrix and immersion in a liquid electrolyte solution is of critical importance in this process. Thus, it would be very important to enhance the uptake amount of liquid electrolyte and to sustain the absorbed liquid electrolyte within the matrix polymer during the storage or charge/discharge cycles.

These considerations motivated us to modify the P(VdF-co-HFP) matrix by introducing the ion-containing polymer which can contribute to enhancing the interaction between

the matrix polymer and liquid electrolyte. In this work, we have prepared new polymer electrolytes based on the blend of P(VdF-co-HFP) and P(MMA-co-LiMA) ionomer by using the above process, and investigated their electrochemical characteristics.

2. Experimental

2.1. Preparation of polymer electrolyte

Poly(methyl methacrylate-co-methacrylic acid) [P(MMA-co-MAA)] was prepared by solution copolymerization of methyl methacrylate (MMA) and methacrylic acid (MAA). The poly(methyl methacrylate-co-Li methacrylate) [P(MMA-co-LiMA)] ionomers were made by neutralizing the P(MMA-co-MAA) with the stoichiometric amount of lithium hydroxide (LiOH). The ion content of the P(MMA-co-LiMA) ionomers was controlled by regulating the feed composition and was determined from the titration method. The appropriate amount of P(VdF-co-HFP) (Kynar FLEX 2801, Elf Atochem), P(MMA-co-LiMA) ionomer, dibutyl phthalate (DBP) (Aldrich), and silanized fumed silica (TS-530, CAB-O-SIL) were completely dissolved in acetone. These viscous solutions were then coated on the glass substrates. DBP was extracted from the cast film with a diethyl ether to form a porous matrix polymer. The porous

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films were then immersed in a liquid electrolyte (1 M LiPF₆ in EC/DMC (1/1, w/w) mixture) for a proper time.

2.2. Preparation of unit cell

The positive and negative electrodes were firstly laminated with the aluminum and copper grids, respectively. The polymer film containing DBP was then placed between the positive and negative electrode laminates and the layers made in the duplex type were thermally fused. DBP was then extracted from the unit cell with diethyl ether and the cell was later activated in the liquid electrolyte (1 M LiPF₆ in EC/DMC (1/1, w/w) mixture). The cell was then cut, tabbed and packaged in an aluminized polyethylene bag.

3. Results and discussion

3.1. Uptake of liquid electrolyte into the blended porous polymer matrix

Fig. 1 shows the uptake amount of the liquid electrolyte (1 M LiPF₆ in EC/DMC (1/1, w/w)) into the various porous polymer matrices based on the blend of P(VdF-co-HFP)/P(MMA-co-LiMA) with the uptake time. The uptake of the liquid electrolyte is found to increase with the increase of the uptake time and also the ion content of the ionomer. This is caused by the fact that the ion groups in the ionomer enhance the compatibility between the matrix polymer and EC [9,10], which can be evidenced by the DSC thermograms of the mixture of P(VdF-co-HFP) and organic solvents as shown in Fig. 2(A). Because DMC (dielectric constant, $\epsilon = 3$) is quite compatible with P(VdF-co-HFP) ($\epsilon = 6-8$), the crystalline structure of DMC is almost dis-

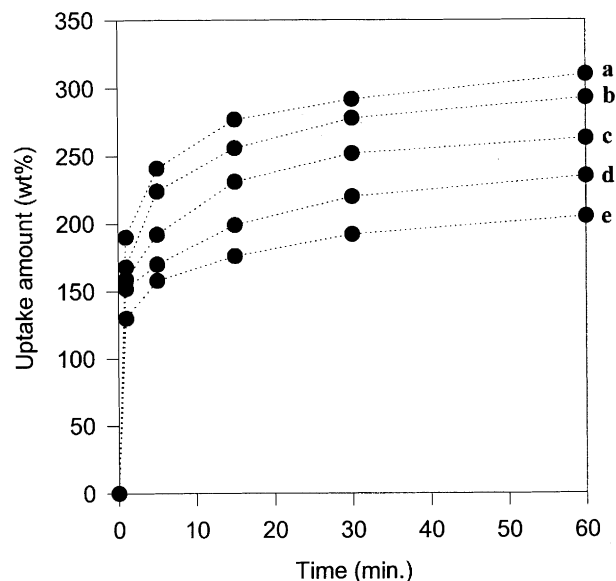


Fig. 1. Uptake amount of liquid electrolyte into the porous polymer matrix (40 wt.% silica, 150 wt.% DBP of matrix polymer, liquid electrolyte, 1 M LiPF₆ in EC/DMC (1/1, w/w): a, 11.7 mol% ionomer blend; b, 8.0 mol% ionomer blend; c, 4.5 mol% ionomer blend; d, 2.3 mol% ionomer blend; e, P(VdF-co-HFP).

rupted in P(VdF-co-HFP) matrix as shown in Fig. 2(A) (d). However, EC ($\epsilon = 95$) seems to be not so compatible with P(VdF-co-HFP) as shown in Fig. 2(A) (e), which can be expected from their large difference in polarity. Fig. 2(A) (h) shows that the crystalline structure of EC is still retained with addition of EC into the mixture of P(VdF-co-HFP), DMC, salt, and silica. Fig. 2(B) shows the effect of the ion group in the ionomer on the crystalline structure of the blended polymer electrolytes. The melting temperature and the heat of fusion of the co-crystal that is assumed to

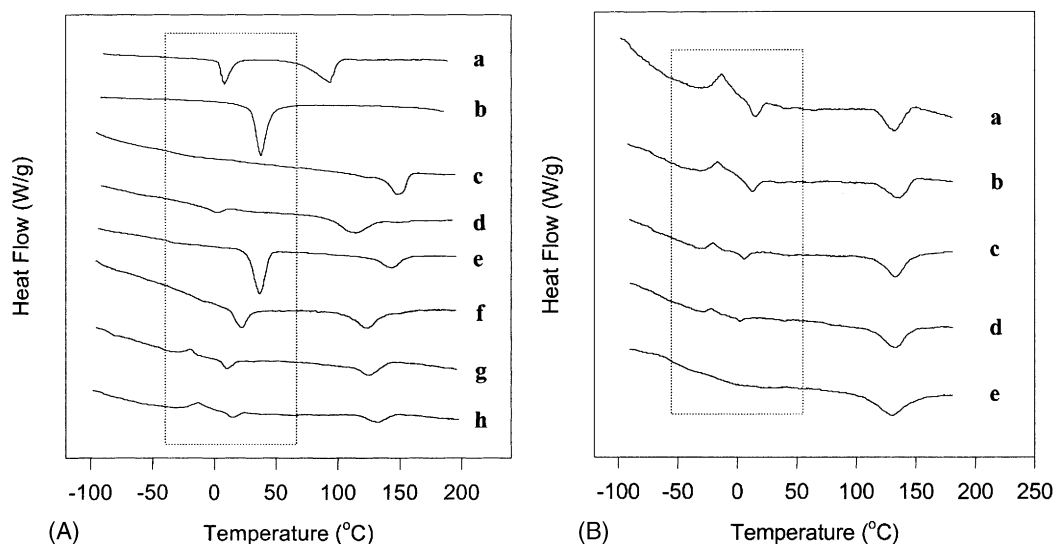


Fig. 2. DSC thermograms of the mixture: (A) DSC thermograms of the P(VdF-co-HFP)/organic solvent mixtures: a, DMC; b, EC; c, P(VdF-co-HFP); d, P(VdF-co-HFP)/DMC; e, P(VdF-co-HFP)/EC; f, P(VdF-co-HFP)/EC/DMC; g, P(VdF-co-HFP)/EC/DMC/LiPF₆; h, P(VdF-co-HFP)/Silica/EC/DMC/LiPF₆; (B) DSC thermograms of the polymer electrolytes based on P(VdF-co-HFP)/PMMA ionomer blend (8/2, w/w) as a function of ion content of the ionomer: a, P(VdF-co-HFP); b, 2.3 mol% ionomer blend; c, 4.5 mol% ionomer blend; d, 8.0 mol% ionomer blend; e, 11.7 mol% ionomer blend.

generate from the mixed liquid electrolyte in the polymer electrolyte decreased with the increase of the ion content of the ionomer, which supports the compatibility enhancement of the polymer electrolytes by addition of P(MMA-co-LiMA) into the P(VdF-co-HFP) matrix.

3.2. Effect of ion groups in the ionomer on the ionic conductivities of the polymer electrolytes

Fig. 3 shows the ionic conductivities of the polymer electrolytes based on the porous matrix polymer of the P(VdF-co-HFP)/P(MMA-co-LiMA) blend as a function of the ion content in the ionomer at various temperatures. It is found that the ionic conductivities of the polymer electrolytes increase as the ion content of the ionomer increases. This increase of the ionic conductivities seems to be associated with the fact that the amount of liquid electrolyte absorbed into the porous matrix polymer increases with the increase in the ion content of the ionomer as was already shown in Fig. 1. The increase in the absorbed amount of the liquid electrolyte into the porous matrix would make the ion conduction path less tortuous. In addition, the glass transition temperature of the liquid electrolyte-rich-phase was shown to decrease with the increase in the amount of the liquid electrolyte, which could also contribute to the enhancement of the ionic conductivities. The low-temperature ionic conductivity could be significantly enhanced by introducing the ion-containing polymer into the matrix polymer for polymer electrolytes.

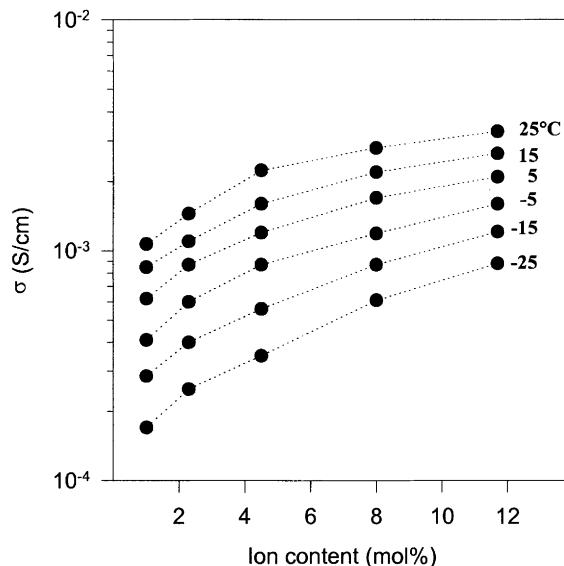
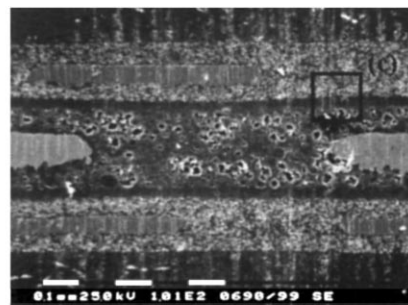
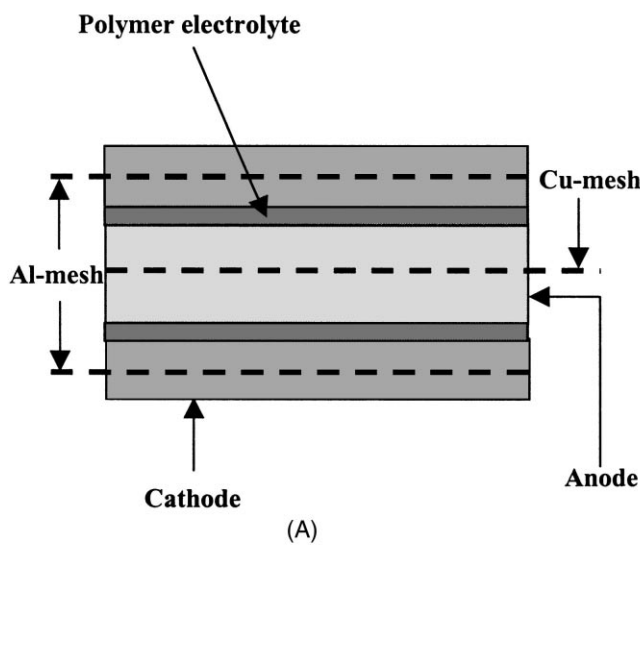


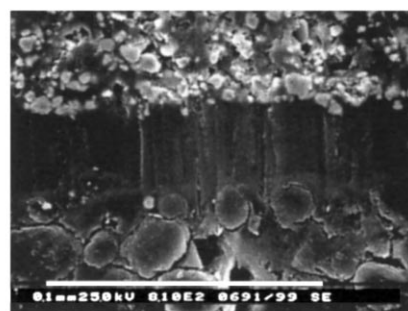
Fig. 3. Ionic conductivities of the polymer electrolytes as a function of ion content of the ionomer in the matrix polymer at various temperatures (P(VdF-co-HFP)/PMMA, ionomer = 8/2 (w/w), uptake time: 60 min, liquid electrolytes: 1 M LiPF₆ in EC/DMC (1/1, w/w)).

3.3. Charge–discharge characteristics of the unit cell using the polymer electrolyte based on the porous matrix polymer

Fig. 4(A) shows the construction of the unit cell (duplex type: cathode/polymer electrolyte/anode/polymer electrolyte/cathode) for charge–discharge test. Carbon was used



(B)



(C)

Fig. 4. Carbon/polymer electrolyte/LiCoO₂ unit cell: (A) construction of unit cell (duplex type); (B) scanning electron micro-graph of the cross-sectional area of the unit cell (11.7 mol% ionomer blend); (C) enlarged region of the scanning electron micro-graph (B).

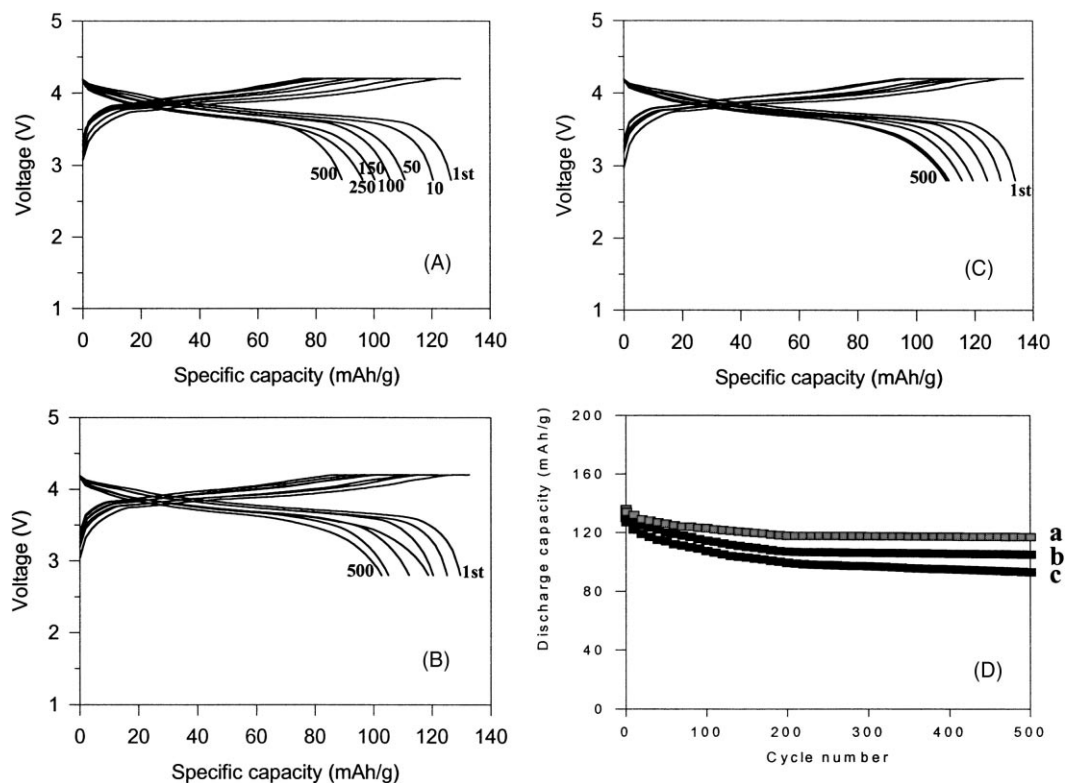


Fig. 5. Charge–discharge curves for carbon/polymer electrolyte/LiCoO₂ cell at the current density of 2.25 mA cm⁻² (C/3 rate, 2 cm × 2 cm): (A) unit cell using the P(VdF-co-HFP)-based polymer electrolyte; (B) unit cell using the 4.5 mol% ionomer blended polymer electrolytes; (C) unit cell using the 11.7 mol% ionomer blended polymer electrolytes; (D) specific discharge capacities of the carbon/polymer electrolyte/LiCoO₂ cell as a function of cycle number: a, unit cell using the 11.7 mol% ionomer blended polymer electrolytes; b, unit cell using the 4.5 mol% ionomer blended polymer electrolytes; c, unit cell using the P(VdF-co-HFP)-based polymer electrolyte.

for negative electrode and LiCoO₂ was used for positive electrode. Fig. 4(B) is the scanning electron micro-graph of the cross-sectional area of the prepared unit cell using the polymer electrolyte based on the ionomer with the 11.7 mol% ion content and Fig. 4(C) is the enlarged image of the indicated region of Fig. 4(B). It is observed that the polymer electrolyte and the electrodes are well inter-fused at the interfaces. Fig. 5(A)–(C) shows the voltage profiles for the charge–discharge of the unit cell based on different polymer electrolytes. Cycling test of the unit cell (cell size: 2 cm × 2 cm) was carried out galvanostatically between 2.8 and 4.2 V with the current density of 2.25 mA cm⁻² (C/3 rate for charge and discharge). The specific discharge capacities of the unit cell are plotted as a function of cycle number in Fig. 5(D). For the unit cell prepared with the P(VdF-co-HFP)-based polymer electrolyte (Fig. 5(A) and Fig. 5(D) (c)), the initial discharge capacity is 127 mAh/g and it falls to 107 mAh/g at 100 cycles, 98 mAh/g at 250 cycles, and 93 mAh/g at 500 cycles. At 500 cycles, the discharge capacity is 73% of the initial value. This may be associated with the leakage of the liquid electrolyte from the polymer matrix which is caused by the poor compatibility between the P(VdF-co-HFP) and EC. However, with introduction of the ionomer in the matrix of the polymer electrolyte, the capacity fade could be reduced and show more

stable cycle behavior. In the case of the blended polymer electrolyte containing the ionomer of which ion content is 11.7 mol% (Fig. 5(C) and Fig. 5(D) (a)), the initial discharge capacity is 134 mAh/g and it becomes 87% of the initial value at 500 cycles, which indicates the very significant improvement in cycling performance of the unit cell prepared by introduction of the P(MMA-co-LiMA) ionomer into the P(VdF-co-HFP) matrix polymer.

4. Conclusion

The introduction of the P(MMA-co-LiMA) ionomer into P(VdF-co-HFP) matrix was found to enhance the compatibility of the polymer matrix with the liquid electrolyte. This enhanced compatibility could lead to the increase in the uptake amount of the liquid electrolyte into the porous matrix and consequently the ionic conductivities at ambient and sub-ambient temperature could be significantly enhanced. The cycle performance of the carbon/polymer electrolytes/LiCoO₂ unit cell was also improved with the increase of the ion content of the ionomer in the matrix polymer. Suppression of the leakage of the organic solvent from the polymer electrolyte seems to be the principal reason for the long-term stability in the charge/discharge behavior.

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