

Preparation and Characterization of P(AN-MMA)/GO Composite Microporous Polymer Electrolyte for Li-ion Batteries

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Abstract. This paper reports the synthesis and performance of microporous polymer electrolyte (MPE) based on P(AN-MMA)/GO Li-ion batteries. The MPE based on P(AN-MMA)/GO has an interconnected uniform porous morphology with an average diameter of 500nm. The MPE based on P(AN-MMA)/GO with the GO content of 3% shows ionic conductivity of 4.12×10^{-3} S/cm. The MPE is stable at the higher potential more than 5.5V (versus Li⁺/Li). The discharge capacity of LiFePO₄ in the cell Li/GPE/LiFePO₄ is 139mAh/g at the charge-discharge rate of 0.1C. The prepared MPEs are promising materials for Li-ion batteries.

Keywords: P(AN-MMA), GO, Polymer electrolyte, Li-ion battery

1. Introduction

Microporous polymer electrolyte (MPE) with its microporous structure to absorb and fix liquid organic solvents as electrolyte has been attracting continuous attention [1]. MPE has higher ionic conductivity than solid polymer electrolyte and higher stability than liquid electrolyte, providing a solution to safety problems [2]. Many polymers have been reported to be used as MPEs, such as poly(vinylidene fluoride) (PVDF) [3] and polyvinyl chloride (PVC) [4]. The copolymer such as poly(vinylidene fluoride-hexafluoropylene) (P(VDF-HFP)) [5] and poly(acrylonitrile-methyl methacrylate) (P(AN-MMA)) [6,7] perform well as the electrolyte materials. The ionic conductivity of the polymer electrolyte can be enhanced by doping with inorganic oxides, such as SiO₂ [8], CeO₂ [9] and ZrO₂ [10]. Graphite oxide (GO) has a layered structure and contains a much number of groups [11]. GO can form intercalated or exfoliated structures in the polymer matrix to create nanocomposites [12]. The P(AN-MMA) was selected to study due to its low cost. In order to improve the ionic conductivity of the MPE, we doped GO in the P(AN-MMA) and studied the performance of the composite membrane and its MPE for Li-ion battery use. The thermal stability of the membrane, the electrochemical stability of the MPE, and the cyclic performance of the battery were improved.

2. Experimental

2.1. Materials Preparation

Commercial AN (>99.5 wt.%) and MMA (>99.5 wt.%) (2:1 in mass) were mixed with sodium dodecyl sulphate emulsifier in deionized water. A certain concentration of GO (1wt.%, 2wt.%, 3wt.%, 4wt.% and 5wt.%) was dispersed in the mixture by ultrasonic. Ammonium persulfate was used as an initiator. The polymerization was continued for 2h with stirring at 60°C. The product was dried in a vacuum oven at 60°C for 24 h. The composites samples were named as G-1, G-2, G-3, G-4, G-5. P(AN-MMA) without GO was also prepared for comparison, and named as G-0. The copolymer composites were dispersed in N,N-dimethylformamide by ultrasonic method. The resulting viscous slurry was cast with a blade onto a

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glass plate, inducing phase inversion. The resulting membrane dried under vacuum at 60°C for 12h. The porous membrane was immersed in 1M LiPF₆ (EC/DMC/DEC) (1:1:1 in volume) for 2h.

2.2. Characterization

The morphology was characterized by scanning electron microscopy (SEM, HITACHI S-4800). The crystallinity was characterized by X-ray diffraction (XRD, D/max-III B-40 KV, Japan, Cu-K α radiation, $\lambda=1.5406 \text{ \AA}$, 5°~60°). Thermogravimetric analysis (TGA, Netzsch TG209F3) was carried out to survey the thermal stability. The electrolyte uptake of MPEs was calculated by: $Q=(W-W_0)/W_0 \times 100\%$. The W_0 and W were the mass of the dry and wet membranes. The electrochemical measurements were carried out on an electrochemical instrument (CHI660, Shanghai). The ionic conductivity was measured by the AC impedance method using stainless steel (SS) electrode. The compatibility was determined by the linear sweep voltammetry with the cell Li/MPE/Li. The cell of Li/MPE/LiFePO₄ was set up and charge-discharge test was carried out using Land Battery Test System (Wuhan Land Electronic Co. Ltd.).

3. Results and Discussion

3.1. Material Characterizations

Fig.1 presents the SEM images of G-0 and G-3 membranes. It can be seen from Fig.1(a, b) that there are non-uniform pores on the surface of the G-0 membranes. After doping GO in the amount of 3wt.%, the pore morphology exhibits great difference. There are some large layered pores on the surface of the membrane, as shown in Fig.1(c). The formation of layered pores due to the intercalation behaviour of long-chain copolymer in GO. And the uniform nanoporous structures on the composite films are shown in Fig.1(d). The pores are separated and spherical with the diameter less than 500nm. It is suggested that the pore structure of the P(AN-MMA) membrane can be improved by the doping suitable amount of the GO.

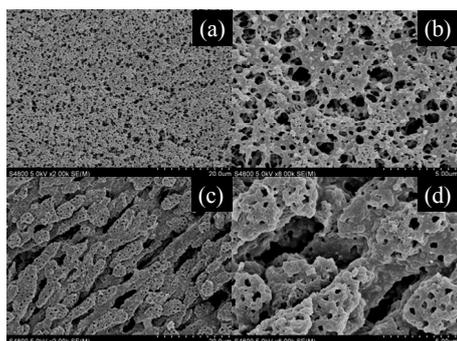


Fig. 1: SEM surface images of P(AN-MMA)/GO composite membranes: (a, b) G-0 and (c, d) G-3.

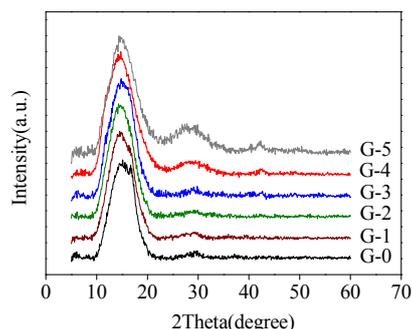


Fig. 2: XRD curves of P(AN-MMA)/GO composite porous membranes.

Fig.2 shows the XRD patterns of P(AN-MMA)/GO composite membranes. In the case of G-0 the spectrum shows an intense peak at 17.7° and a weak peak at 29.6°, which are the characteristics peak of PAN crystallite. Compared with diffraction peak of G-0, a peak shift to the lower 2 θ side, lowering and widening of the diffraction intensity of the peak is observed, when GO is composited with P(AN-MMA). The stack of GO and P(AN-MMA) diffraction peaks results in the peak shift. The degree of crystallinity is decreased with increasing content of GO. Therefore, the lower crystallinity of the polymer electrolyte is expected to contribute high ionic conductivity to the MPE based on P(AN-MMA)/GO composites.

The thermal stability of the P(AN-MMA)/GO composites were analyzed by TGA in N₂ atmosphere. The peak temperature indicates the highest working temperature for the polymer electrolyte. As shown in Fig.3(A), all the samples have about 80% weight loss above 360°C in the TG curves. It can be seen from Fig.3(B) that the decomposition temperatures of the P(AN-MMA)/GO composites are 380, 385, 388, 393 and 397°C, respectively, which are all higher than that of pure P(AN-MMA) of 363°C. This reflected that added GO can improve the thermal stability of the polymer electrolyte due to the interaction of the polymer matrix with the GO.

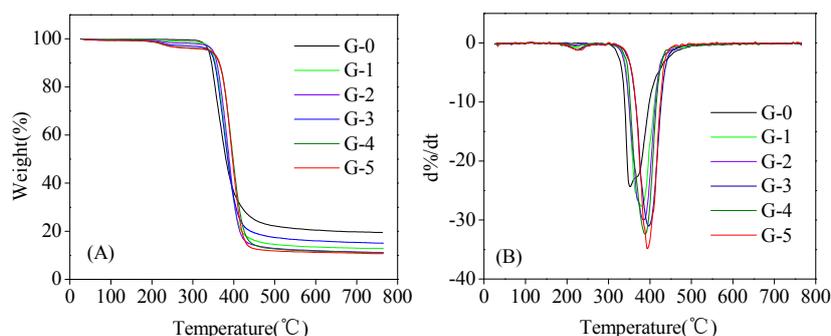


Fig. 3: TG-DTA curves of P(AN-MMA)/GO composites from room temperature to 800°C at a heating rate of 10°C/min. (A) the TG curves; (B) the DTA curves.

3.2. Electrochemical Characterizations

The electrolyte uptakes and ionic conductivities of the MPEs based on P(AN-MMA)/GO are shown in Fig.4. It can be seen from Fig.4 (a) that the electrolyte uptake of the G-0 is the lowest. The electrolyte uptake of G-1 is 372.7% and increases to 431.9% when the concentration of GO is 3%. As the content of GO increases further, the electrolyte uptake decrease slowly. The electrolyte uptake of the MPEs is related to its porous structure and affinity to electrolyte. The GO as a layered frame helps to form larger three-dimensional porous structures, which result in the improvement of the electrolyte uptake ability. The uniform nanoporous structures of composite membranes provide stronger affinity to electrolyte. However, when the addition amount of GO was over 3%, the GO indicate agglomerate state. This might reduce the electrolyte uptake. It can be noted from Fig.4(b) that the ionic conductivity of the G-3 is $4.12 \times 10^{-3} \text{ S/cm}$, which is larger than other MPEs. The variation trend is nearly the same as their electrolyte uptake. This may be ascribed to porous connectivity of MPEs. The agglomerate action of GO may break the interconnection of the pores in the MPE, which may lower ionic conductivity.

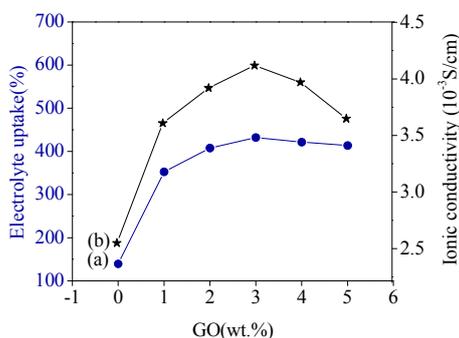


Fig. 4: Variation of electrolyte uptake (a) and ionic conductivity (b) of MPEs based on P(AN-MMA)/GO composites with different contents of GO.

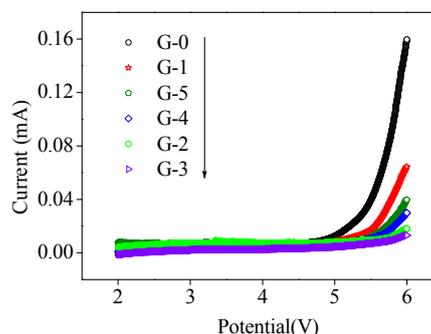


Fig. 5: Linear voltammograms of composite polymer electrolyte membranes.

Fig.5 presents the linear voltammograms obtained for the cell Li/MPE/Li with G-0, G-1, G-2, G-3, G-4 and G-5. It can be seen from Fig.5 that the MPE with P(AN-MMA) decomposes at about 5.0V. Obviously, the MPEs based on the P(AN-MMA)/GO composite exhibit an anodic stability $\geq 5.5\text{V}$, which are greater than that of P(AN-MMA). This can be ascribed to the excellent affinity of the membrane to the electrolyte that is partially dissolved in the pore of composite membrane. The MPE based on P(AN-MMA)/GO has better electrochemical stability than the MPE based on P(AN-MMA), suggesting that the synergistic effect of GO and P(AN-MMA) in the composites membrane.

The cell Li/MPE/Li was set up and AC impedance spectroscopy was used to monitor the change in impedance with time. The initial impedance behavior of MPE based on G-0 and G-3 at ambient temperature are shown in Fig.6. Both of the samples display similar curvature but the diameter of the semicircle different. The initial interfacial resistance is 339 and 408Ω for the MPE based on G-0 and G-3, respectively. The evolution of the interfacial resistance with storage time is shown in the inset of Fig.6. It can be seen that the MPE based on G-3 has the less change in interfacial resistance compared with G-0. This indicates that the

MPE based on G-3 has better compatibility with Li electrode than G-0. The resistance of the MPEs based on G-0 and G-3 increases within two weeks but keeps almost unchanged after two weeks. This suggests that it takes two weeks for the formation and stabilization of MPE on Li. This confirms that the G-3 can function as an efficient ion transport media between the electrodes.

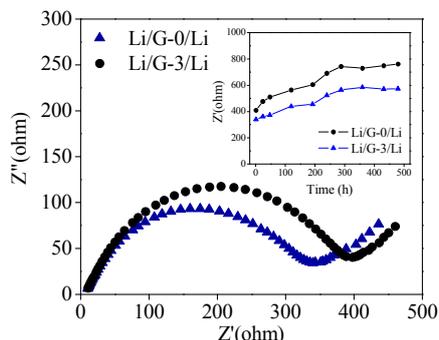


Fig. 6: Impedance spectra of cell Li/MPE/Li at open circuit potential with G-0 and G-3; Inset: the variation of interfacial resistance of cell Li/MPE/Li with storage time.

3.3. Battery Performance

Li/MPE/LiFePO₄ cell is assembled. The electrochemical performance of the cell is evaluated by galvanostatic cycling under constant current of 0.1C between 2.7 and 4.3V. Fig. 7 shows the first charge-discharge profile of the Li/G-3/LiFePO₄ cell. The cell delivers initial discharge capacity of 139mAh/g, which is 82.4% of the theoretical capacity of LiFePO₄. The G-3 shows the highest porosity and contains the largest amount of electrolyte, and hence more liquid electrolyte can diffuse from the polymer electrolyte to the cathode, which leads to higher utilization of the active material. The ionic conductivity of the MPE may also affect the discharge property. This improved performance is attributed to the higher amorphous content, and electrolyte uptake and ionic conductivity of G-3.

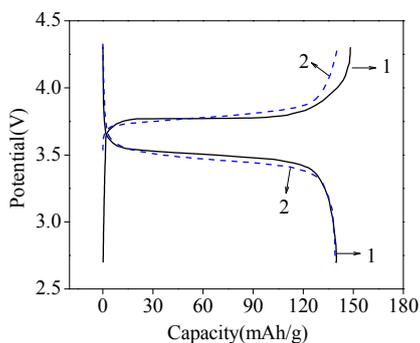


Fig. 7: Initial charge-discharge properties of Li/MPE/LiFeO₄ cell with polymer electrolytes based on G-3, at room temperature, (0.1C rate, 2.7-4.3V).

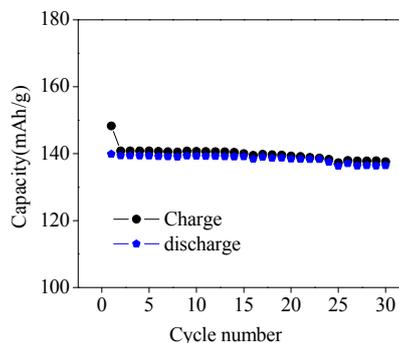


Fig. 8: Cycle properties of Li/MPE/LiFeO₄ cell with polymer electrolytes based on G-3, at room temperature, (0.1C rate, 2.7-4.3V).

Fig.8 presents the cyclic stability of the Li/MPE/LiFePO₄ cell with G-3 up to 30 cycles at 0.1 C rate between 2.7 and 4.3V. It can be seen from Fig. 8 that the discharge capacity is slightly decreasing with numerous of cycling. After 30 cycles the cell with G-3 retains a discharge capacity of 136mAh/g, which is 97.8% of its initial discharge capacity. These results indicate the excellent efficiency of the G-3 polymer membrane to conduct the ions between electrodes during cycling processes, and have good compatibility with electrodes.

4. Conclusions

The MPEs based on P(AN-MMA)/GO composites were prepared. With doping of 3% GO in the P(AN-MMA), the thermal stability of the P(AN-MMA) is improved to 388°C, the ionic conductivity of MPE is improved to $4.12 \times 10^{-3} \text{S/cm}$, the decomposition voltage of the MPE is greater than 5.5V, the electrochemical compatibility and battery performance is also improved. The high ionic conductivity can be

ascribed to the low crystallinity and uniform interconnected porous structure of the membrane. The MPE based on P(AN-MMA)/GO is suitable for the application in safe, reliable and long lasting Li-ion batteries. This MPE has great economic value due to the low cost of materials of AN, MMA and GO.

5. Acknowledgments

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6. References

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