



Preparation, characterization and properties of poly(propylene carbonate)/poly(methyl methacrylate)-coated polyethylene gel polymer electrolyte for lithium-ion batteries

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ABSTRACT

A poly(propylene carbonate) (PPC)/poly(methyl methacrylate) (PMMA) polymer precursor was developed via solution polymerization with different mass ratios of methyl methacrylate (MMA) and PPC. Then, PPC/PMMA-coated Celgard PE membranes were prepared by the dip-coating method with this polymer precursor and activated to fabricate gel polymer electrolytes (GPEs). The structure and performance of the samples were characterized with FTIR, DSC, SEM, water contact angle analysis and electrochemical performance tests, such as electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV) and galvanostatic charge-discharge measurements. The effect of the ratio of MMA to PPC on the performance of the as-prepared PPC/PMMA-coated Celgard PE GPEs was considered. Benefiting from the composite structure, the GPE produced from the Celgard PE coating polymer with a PPC to MMA ratio of 8:2 (by weight) had the highest ionic conductivity and showed superior electrolyte wettability with 347% electrolyte uptake. Additionally, the as-prepared GPEs displayed good compatibility with the anodes and cathodes of lithium-ion batteries (LIBs), and their oxidation potentials were stable to 5.0 V (vs Li/Li⁺). The LiFePO₄ battery using this PPC/PMMA-coated Celgard PE GPE exhibited an excellent initial discharge capacity of 154 mAh g⁻¹, cyclic stability and rate capability.

1. Introduction

Since the launch of the first all-electric sports car (Tesla Roadster) by Tesla in 2008, lithium-ion batteries (LIBs), which served as the main energy storage device, have attracted increasing attention [1–2]. LIBs have been considered one of the most promising green power sources for hybrid electric vehicles (HEVs) and electric vehicles (EVs) due to their long cycle life, high power density and pollution-free characteristics [3–8]. However, the safety problems of commercial LIBs that use liquid electrolyte restrict the wide use of lithium-ion batteries in vehicular applications [9–10]. Commercial LIBs use aliphatic carbonic acid esters as the main component of the liquid electrolyte, which is highly hazardous, flammable, and explosive [11–13]. Moreover, misuse, short circuiting or local overheating cause LIBs to easily catch fire, leading to explosion [14–15]. As an effort to increase the safety performance, gel polymer electrolytes (GPEs) have been developed as separators on account of their high conductivity (compared with solid electrolyte) and high safety (compared with liquid electrolyte) [16–17]. However, after

activation in an electrolyte solution, some GPEs lose their mechanical strength, which unfortunately cannot satisfy requirements for flexibility, safety and design of high-power LIBs [18–19].

In particular, self-supported GPEs have been regarded as the most potential GPEs for LIBs because of their excellent mechanical strength and appropriate ionic conductivity [20]. In self-supported GPEs, copolymers formed with different functional monomers are required for improving the comprehensive performance of GPEs. Among the copolymers, poly(methyl methacrylate-acrylonitrile-butyl acrylate) [P(MMA-AN-BA)] [16], poly(acrylonitrile-co-methyl methacrylate) [P(AN-co-MMA)] [21], poly(ethylene oxide)-co-poly(propylene oxide) [P(EO-co-PO)] [22], and poly(methyl methacrylate-co-butyl acrylate) [P(MMA-co-BA)] [23,24] have been the most extensively applied to self-supported GPEs for high-performance LIBs.

In our previous study, we obtained a polybutadiene rubber-interpenetrating, cross-linking poly(propylene carbonate) (PCC) GPE using the solution casting and thermal pressing methods [25]. In particular, PPC has been widely used as a promising polymer electrolyte due to its

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good ability for trapping and storing liquid electrolyte and providing paths for lithium ion transport through its ether linkages [11,26,27]. On the other hand, butadiene rubber (BR) with a cross-linking polymeric framework as a supporter has been introduced to PPC to increase the mechanical strength; however, the low electrolyte uptake due to its nonpolar groups limits its application. Obviously, the interpenetrating, cross-linking polymeric framework is built through the cross-linking of C=C in the BR main chain. Polymethyl methacrylate (PMMA) is a popular and well-sourced traditional polymer electrolyte material for LIBs [28–31]. In addition, PMMA has a unique molecular structure, as its monomer contains C=C and ester groups. The ester groups can provide the polymer with good affinity for electrolytes and good compatibility with electrodes [32,33]. To overcome the safety problems of LIBs, in this paper, we combine the performance advantages of different polymeric materials and a composite structure to synthesize a PPC/PMMA-coated Celgard PE membrane. The influences of the mass ratio of PPC to MMA monomer on the structure of the membrane and the electrochemical performance of the PPC/PMMA-coated Celgard PE GPE used in 4.0 V LiFePO₄/Li cells are investigated by FTIR, SEM, DSC and AC impedance spectroscopy, etc.

2. Experimental

2.1. Materials

PPC (MW = 120,000, Henan Tianguan Co., Ltd.) was dried under vacuum at 80 °C for 24 h prior to use. MMA (A.R., Baishi Chemical Industry Co., Ltd.) was distilled under vacuum to remove the aggregation inhibitor. A 1.0 mol dm⁻³ LiPF₆ solution in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) was purchased from Shenzhen CAPCHEM Technology Co., Ltd.

2.2. Preparation

Different weight ratios of PPC to MMA (5:5, 6:4, 7:3, 8:2, 9:1) were dissolved in acetone with 10 wt% BPO (related to weight of MMA) and vigorously stirred under N₂ flow at 80 °C for 6 h. Then, a microporous PE separator was soaked in the above homogeneous solutions for 2 h and then heated at 45 °C for 12 h to cure the impregnated polymer. Finally, flexible and semi-transparent PPC/PMMA-coated Celgard PE membranes with thicknesses of approximately 40 μm were obtained, which were soaked in an electrolyte solution of 1.0 mol dm⁻³ LiPF₆ dissolved in EC/DMC (1:1 by volume) for 1 h to form the PPC/PMMA-coated Celgard PE GPEs.

2.3. Characterization

Fourier transform infrared (FTIR) spectra of the various as-prepared membranes were recorded with a Nicolet Magna II 550 spectrometer in the wavenumber range of 500–3500 cm⁻¹. The surface and cross-sectional morphologies of the relevant membranes were examined using a high-resolution field-emission scanning electron microscope (SEM, JEOL JSM-6380LA). The wettability was measured with a water droplet on a separator and recorded by a contact angle analyzer (JC2000C1, POWEREACH).

The electrolyte uptake was calculated by Eq. (1):

$$\text{Electrolyte uptake(\%)} = \frac{W - W_0}{W_0} \times 100\% \quad (1)$$

where W_0 and W represent the weights of the membranes before and after soaking them in a liquid electrolyte (1.0 mol dm⁻³ LiPF₆ in EC/DMC (1:1 by volume)) for 1 h. Differential scanning calorimetry (DSC) measurements were performed on a calorimeter (NETZSCH DSC-200PC Instrument) at 10 °C min⁻¹ under nitrogen atmosphere. The crystallinity (X_c) was calculated using Eq. (2), and the melting enthalpy ($\Delta H_m^{\text{sample}}$) was obtained from the DSC curves:

$$X_c = \frac{\Delta H_m^{\text{sample}}}{\Delta H^*} \times 100\% \quad (2)$$

where ΔH^* is the crystalline melting enthalpy of perfectly crystalline PE (288 J g⁻¹).

2.4. Electrochemical measurements

The ionic conductivities (σ) of the relevant GPEs were measured by EIS measurements using a Zahner IM6ex electrochemical analyzer. The EIS measurements were performed on GPEs sandwiched between two polished gold electrodes (diameter $\Phi = 16.0$ mm), which act as blocking electrodes, over a frequency range of 0.1 Hz to 1 MHz with an amplitude of 5 mV. The ionic conductivity can be calculated by Eq. (3):

$$\sigma = \frac{d}{R_b \cdot S} \quad (3)$$

where d (cm) and S (cm²) are the thickness and area of the relevant GPEs, respectively, and R_b (Ω) is the bulk resistance estimated from the impedance spectrum at the high frequency intercept of the Nyquist plot on the real axis. The electrochemical stabilities of the GPEs were determined by linear sweep voltammetry (LSV) with stainless steel (SS) as the working electrode and lithium metal as the reference electrode/counter electrode (SS/GPE/Li) at a scan rate of 5 mV s⁻¹ over a potential range of 2.0–6.0 V vs Li/Li⁺.

Galvanostatic charge–discharge measurements and rate performance tests under different current densities in Li/GPE/LiFePO₄ 2025 coin-type half-battery cells were carried out using a battery testing system (BTS XWJ, Neware Tech. Co., Ltd., China) between 2.5 and 4.0 V. The cells consisted of the cathode as the working electrode and Li foil as the counter and reference electrode. The cathode was prepared by coating a slurry consisting of 80% LiFePO₄, 10% conductive carbon and 10% PVDF binder dissolved in *N*-methyl pyrrolidinone (NMP) on copper foil and was then dried under vacuum at 80 °C for 24 h. All the battery assembly processes were carried out in an argon-filled glove box with oxygen and moisture levels < 1 ppm.

3. Results and discussion

3.1. FTIR

Fig. 1 shows the FTIR spectra of MMA, PPC, the PE separator and the PPC/PMMA-coated Celgard PE membrane. It can be seen from the spectrum of the MMA monomer that the characteristic absorption peaks are located at 1745 cm⁻¹ and 1643 cm⁻¹, corresponding to the

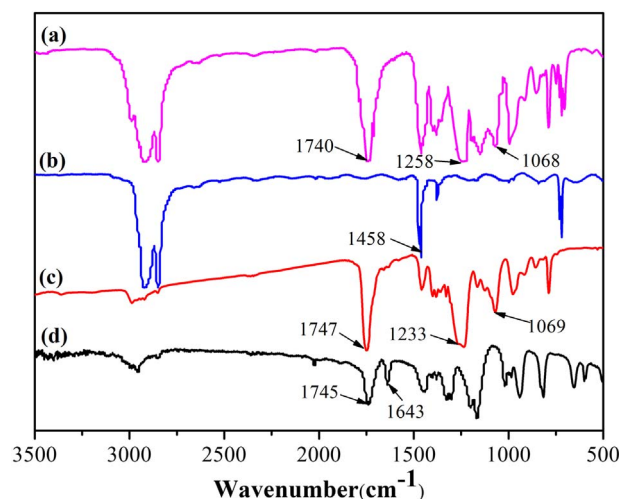


Fig. 1. FTIR spectra of (a) the PPC/PMMA-coated Celgard PE membrane, (b) the PE separator, (c) PPC and (d) MMA.

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