

A study on PVDF-HFP gel polymer electrolyte for lithium-ion batteries

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Abstract. In this paper, poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) gel polymer electrolyte was fabricated via solvent casting method in order to improve the performance of the lithium-ion batteries. By comparing the physical and electrochemical properties of PVDF-HFP gel polymer electrolyte with three different proportions, the optimization of the PVDF-HFP gel polymer electrolyte was obtained: 10wt% PVDF-HFP - 80wt% tetrahydrofuran (THF) / acetone - 10wt% 1mol L⁻¹ lithium perchlorate (LiClO₄) in ethylene carbonate (EC) and diethyl carbonate (DEC). The optimized PVDF-HFP gel polymer electrolyte displayed a high conductivity of 1.06×10⁻³ S cm⁻¹ at room temperature, a high lithium transference number of 0.36 and a good thermal stability within 100°C. Moreover, the discharge specific capacity was 135.1 mAh g⁻¹, and the charge / discharge efficiency was 99.1% at 0.1C rate. Therefore, the fabricated PVDF-HFP gel polymer electrolyte was an effective gel polymer electrolyte to be applied on lithium-ion batteries.

1. Introduction

Lithium-ion batteries have been widely investigated in order to fulfill the ever-increasing demand in portable devices and electric vehicles[1]. According to the physical form of electrolyte in lithium-ion batteries, the electrolyte can be divided into three categories: liquid electrolyte, gel electrolyte and solid electrolyte. Gel polymer electrolyte is an electrolyte formed by polymer network structure filled with liquid electrolyte, and it contains solid phase and liquid phase. In the gel polymer electrolyte, the liquid electrolyte is well retained in the solid polymer matrix, and this structure avoids leakage of the liquid electrolyte. Compared with solid electrolyte and liquid electrolyte, gel polymer electrolyte has many advantages, such as high voltage, high specific capacity, long cycle life, rapid charge and discharge, small size, thin thickness, etc. Therefore, gel polymer electrolyte is the main focus of recent development, because it has high conductivity of the liquid electrolyte and safety of the solid electrolyte[2-3].

The gel polymer electrolyte essentially includes three parts, i. e. polymer matrix, plasticizer and lithium salt. The choice of polymer matrix determines whether the gel polymer electrolyte has excellent properties. In general, the polymer matrix must have the characteristics of good electrochemical performance, excellent thermal stability, low crystallinity, large dielectric constant and strong mechanical property. Various polymers, i. e. polyacrylonitrile (PAN)[4], polyoxyethylene (PEO)[5], polymethylmethacrylate (PMMA)[6], polyvinylidene fluoride (PVDF) and poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)[7], have been developed as polymer matrix for gel



electrolytes. Especially, PVDF with strong electro-withdrawing functional groups (-C-F) shows a high dielectric constant ($\epsilon = 8.4$), which is beneficial for the dissolution of lithium salts to keep a high concentration of charge carriers[8]. Furthermore, since the copolymerization effect of VDF and HFP, PVDF-HFP has a relatively lower crystallinity compared to PVDF[9-10]. Therefore, PVDF-HFP contains more amorphous domains to capable of trapping large amounts of liquid electrolytes. Hence, PVDF-HFP is regarded as the most promising matrix as gel polymer electrolyte material.

The ionic conduction in gel polymer electrolyte is resulted from the diffusion of ions through their free volumes, so it is important that lithium salts be dispersed in polymers at molecular level[11]. The influence of plasticizers on the gel polymer electrolyte has a strong interaction with the specific nature of the plasticizer, such as dielectric constant, viscosity, polymer-plasticizer interaction and ion-plasticizer coordination[12]. Generally, the cyclic carbonate (such as ethylene carbonate or propylene carbonate) has a high dielectric constant, and the chain-like carbonate (such as diethyl carbonate or dimethyl carbonate) has a low viscosity. A mixture plasticizer consists of the cyclic carbonate and the chain carbonate is selected to support the demands of the working temperature and conductivity. As we all know, LiClO_4 has small ionic radius and low dissociation energy, and it can be dissolved in most of the organic solvents[13]. So LiClO_4 is selected as a lithium salt in this study. In this work, PVDF-HFP gel polymer electrolytes with three different proportions were fabricated. We obtained an effective gel polymer electrolyte to be applied on lithium-ion batteries.

2. Experimental

2.1. Materials

PVDF-HFP (kynar LBG, $M_w \sim 500000$) polymer was obtained from Arkema, France. Reagent grade anhydrous LiClO_4 , ethylene carbonate (EC) and diethyl carbonate (DEC) were purchased from Aladdin bio-chem Technology Co., Shanghai, China. The solvent tetrahydrofuran (THF) and acetone were bought from Chengdu Kelong Chemical Reagent Company, China. The LiCoO_2 cathode was purchased from Kejing Star Technology Co., Shenzhen, China.

2.2. Gel polymer electrolyte preparation

PVDF-HFP gel polymer electrolyte was synthesised using a solvent casting method. The solvent casting method is the polymer dissolved in a co-solvent system composed of two or more organic solvents to form gel, then the gel was coated on a glass plate and the volatile solvent was evaporated to obtain gel polymer electrolyte membrane. First, LiClO_4 was dried under vacuum at 100°C for 10 h, and then dissolved in the solution composed of EC and DEC (volume ratio of EC/DEC=1:1) to obtain 1 mol L^{-1} LiClO_4 solution after vigorous stirring at 50°C for 2h. Second, PVDF-HFP polymer was dissolved in solution of THF and acetone (volume ratio of THE/acetone=1:1) under persistent stirring at 50°C for 6h. Third, the LiClO_4 solution was added to PVDF-HFP polymer solution and stirred for another 6h at 50°C to obtain the gel precursor. At last, the gel precursor was casted on a spotless glass plate at room temperature. With the evaporation of THF and acetone solvents, a white gel polymer electrolyte membrane was formed, followed by stripped off from glass substrate and punched into a circle shape with a radius of 9 mm.

2.3. Characterization techniques

Scan electron microscopy (Bruker S3400N) was employed for morphology observation. Thermo gravimetric analysis (TGA) was carried out for thermal stability measurement using a Q50 TGA instrument under N_2 atmosphere from 20 - 500°C with a temperature ramp of $5^\circ\text{C}/\text{min}$. The ionic conductivity was investigated by Electrochemical Impedance Spectroscopy (EIS) method (Parstat 2263 advanced electrochemical system, Princeton Applied Research) in a 2032 coin cell with a GPE sandwiched structure between two stainless (SS) in the frequency range of 0.1 Hz to 10^5 Hz at an alternative signal of 10 mV . The linear sweep voltammetry (LSV) technique was tested on a

Li/GPE/Li cell with the SS as the working electrode and lithium foil as both the reference and counter electrodes. The scanning rate was 5 mV/s over a range of 0-6V.

The chronoamperometry method was carried out to measure the lithium transference numbers, and the step voltage of Li/GPE/Li cells was 0.3V. In short, the initial current I_0 and the steady-state current I_{SS} that spreading through the cell were recorded. Moreover, the initial resistance R_0 and the steady-state resistance R_{SS} were obtained through the impedance spectroscopy monitored by the same cell. Charge-discharge cycling tests of the Li/GPE/LiCoO₂ cell was performed at 0.1C rate within the voltage range of 3.0-4.2V vs. Li/Li⁺ at room temperature.

3. Results and discussion

3.1. Morphology structure

Gel polymer electrolyte membrane not only in its surface has a micro-porous structure, but also its internal is micro-porous structure. This micro-porous structure forms a 3D network structure in gel polymer electrolyte[14]. Table 1 lists the components, pore size and conductivity values of PVDF-HFP gel polymer electrolyte. Figure 1 shows the surface morphology of GPE1, GPE2, GPE3 and the cross-sectional morphology of GPE3. With the increasing of PVDF-HFP ratio and the proportion of solvent decreasing, the concentration of PVDF-HFP become larger and the tendency of polymer swelling to network structure is weaker. So, the pore size of the gel polymer electrolyte membranes is smaller. Nevertheless, the larger pore size means that the network is sparse, and the mechanical strength of gel polymer electrolyte is inoperable. Thus, we think that the pore size is inversely proportional to the mechanical strength [15]. By adjusting the concentration of PVDF-HFP, we can achieve the balance of the mechanical strength and pore size of gel polymer electrolyte.

Table 1. The components, pore size and conductivity values of PVDF-HFP gel polymer electrolytes.

sample	PVDF-HFP	THF/acetone	1mol/L LiClO ₄ -EC/DEC	Pore size (μm)	Conductivity (S cm^{-1})
GPE1	2wt%	90wt%	8wt%	6.88	2.23×10^{-3}
GPE2	5wt%	90wt%	5wt%	3.87	1.27×10^{-3}
GPE3	10wt%	80wt%	10wt%	3.15	1.06×10^{-3}

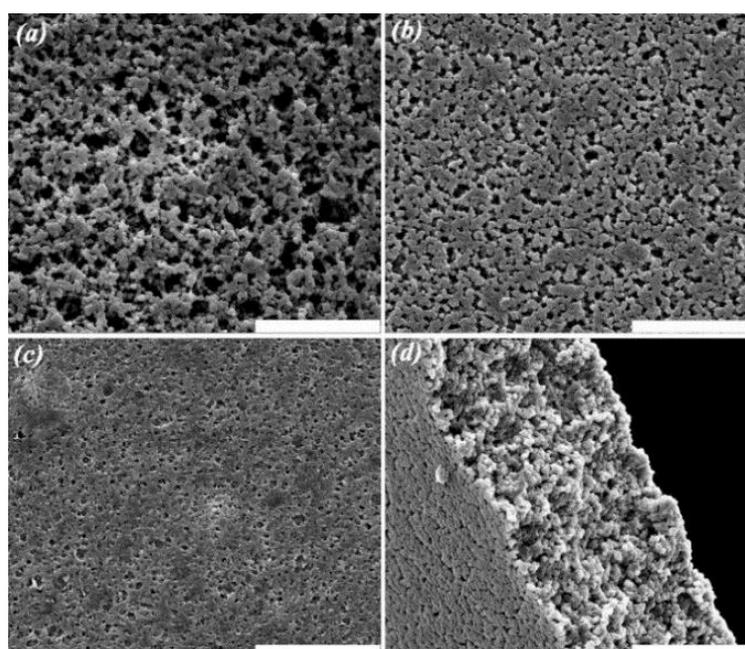


Figure 1. The surface morphology of (a) GPE1, (b) GPE2, (c) GPE3 and (d) the cross-sectional morphology of GPE 3. (Scale=50 μm).

3.2. Ionic conductivity

With the concentration of PVDF-HFP increasing, the impedance increases and the conductivity decreases. Gradual increased curves of the impedance values are revealed in Figure 2a. The conductivity of the gel polymer electrolyte is inversely proportional to the impedance. The conductivity is related to the liquid absorption, and the rate of liquid absorption depends on the gel process. This micro-porous network allows the liquid electrolyte to be embedded in the polymer network to gel the polymer electrolyte. Then, the liquid electrolyte is stored in the pores of the polymer network. The ability of the gel polymer electrolyte to adsorb the liquid electrolyte affects the conductivity. GPE1 has the largest pore size, so the impedance is minimal and the conductivity is maximum. The conductivity of the GPE3 is $1.06 \times 10^{-3} \text{ S cm}^{-1}$, and it also satisfies the demand of gel polymer electrolyte for lithium-ion batteries.

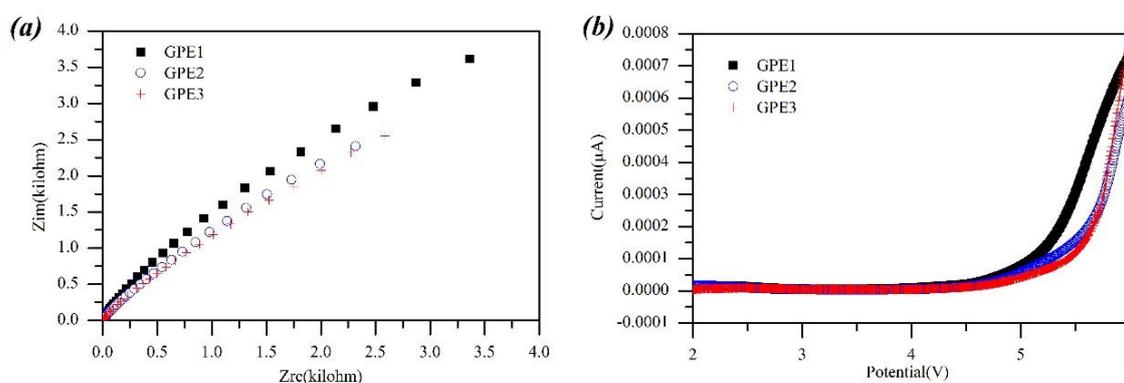


Figure 2. (a) The impedences of GPE1, GPE2, GPE3; (b) the electrochemical stability window values of GPE1, GPE2 and GPE3.

3.3. Electrochemical stability

The curve of current response to the voltage expresses the decomposition voltage of the gel polymer electrolyte, that is, the corresponding electrochemical stability window value. As shown in the Figure 2b, the currents of the GPE1, GPE2 and GPE3 start to increase sharply around 4.5V. That means the oxidation and decomposition voltages of the three kinds of gel polymer electrolytes are about 4.5V. This shows that prepared PVDF-HFP gel polymer electrolyte can be used with LiCoO_2 cathode material for preparing high performance lithium-ion batteries.

3.4. Thermal stability

With the temperature rising, the mass of the gel polymer electrolyte gradually decline shown in Figure 3. There are three significant mass losses between 30°C and 500°C. The gel polymer electrolyte is basically stable within 100 °C. A little mass loss may be due to the evaporation of residual solvents such as THF and acetone; There are 20% reduction in mass at 100-200°C, and it maybe because of PVDF-HFP preliminary decomposition and DEC evaporation[16-17]; It has a 10% mass loss at 300°C, and this situation probably due to the evaporation of EC and LiClO_4 ; The mass of the gel polymer electrolyte begin to decrease significantly at 460°C, and it probably because of the decomposition of the great mass of PVDF-HFP. Usually, the operating range of lithium-ion battery is 40-70 °C. The prepared PVDF-HFP gel polymer electrolytes have good thermal stability within 100°C.

3.5. Lithium transference number

In Table 1, the maximum conductivity ($2.23 \times 10^{-3} \text{ S cm}^{-1}$) is exhibited by the sample GPE1, but the mechanical strength of the GPE1 is too terrible to operate. Considering the conductivity, mechanical strength, electrochemical stability and thermal stability of the three gel polymer electrolytes, the various properties of the GPE3 are excellent. Therefore, we selected GPE3 as the preferred sample. Further, we measured the lithium transference number of the GPE3 and obtained a value of 0.36. The impedences and currents before and after polarization are shown in the Figure 4a. High lithium transference number can reduce the polarization of the lithium-ion battery during charging and discharging. Generally, the lithium transference number of the gel polymer electrolyte is about 0.4, so that the prepared PVDF-HFP gel polymer electrolyte shows excellent battery performance.

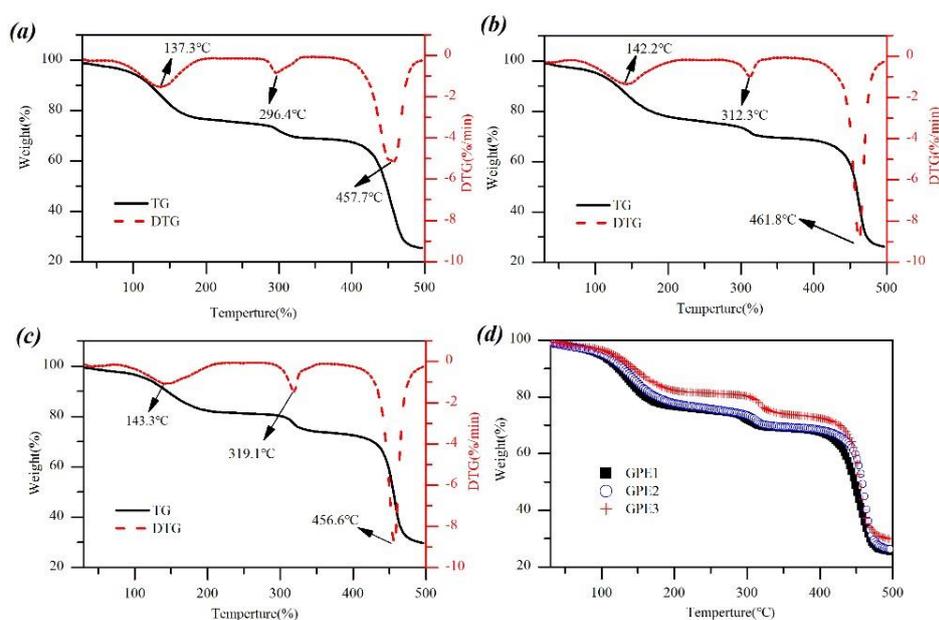


Figure 3. TG and DTG curves of (a) GPE1, (b) GPE2 and (c) GPE3, and (d) TG curves of GPE1, GPE2 and GPE3.

3.6. Cycle stability

The charge and discharge specific capacity and Coulombic efficiency of the GPE3 are revealed in Figure 4b. The actual specific capacity of the LiCoO_2 cathode material is 140 mAh g^{-1} . At 0.1 C rate, the discharge specific capacity of GPE3 up to 135.1 mAh g^{-1} , and the Coulombic efficiency of GPE3 reach to 99.1%. It indicates that the compatibility between prepared PVDF-HFP gel polymer electrolyte and LiCoO_2 cathode material is good.

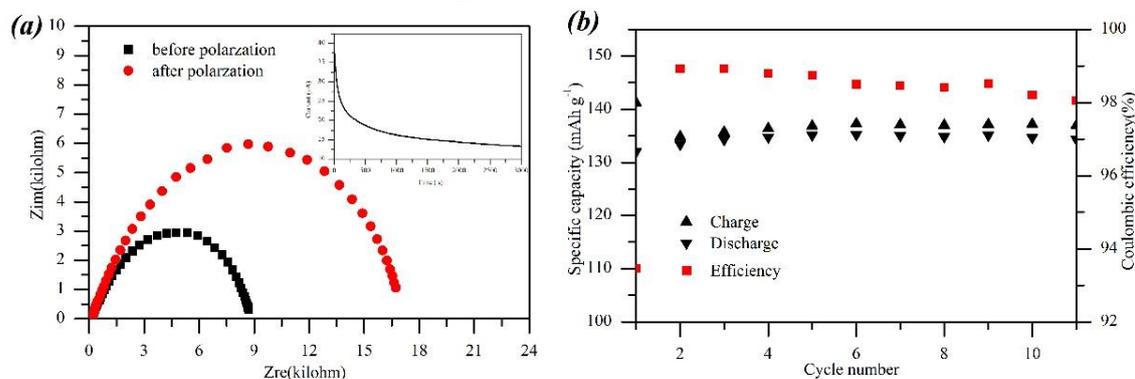


Figure 4. (a) The impedences and currents before and after polarization of GPE3; (b) the charge and

discharge specific capacity and Coulombic efficiency of the GPE3.

4. Conclusions

In summary, the prepared PVDF-HFP gel polymer electrolyte has been demonstrated to be an effective gel polymer electrolyte to be applied on lithium-ion batteries. The optimized PVDF-HFP gel polymer electrolyte expressed a high conductivity of $1.06 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, the electrochemical window value of 4.5 V, a high lithium transference number of 0.36, a good thermal stability within 100°C, the discharge specific capacity of 135.1 mAh g⁻¹ and the charge / discharge efficiency of 99.1% at 0.1C rate. Our work supplies a basic PVDF-HFP gel polymer electrolyte. Later, we can optimize and improve the performance of this PVDF-HFP gel polymer electrolyte by adding nano-fillers, such as SiO₂, TiO₂, Al₂O₃, etc.

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