



## Short communication

# A porous poly(vinylidene fluoride) gel electrolyte for lithium ion batteries prepared by using salicylic acid as a foaming agent

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## ABSTRACT

A porous gel polymer electrolyte based on poly(vinylidene fluoride) (PVDF) was for the first time prepared via a foaming technology using salicylic acid as a foaming agent. The pores are evenly distributed with an average diameter of about 400 nm. The results from TG/DTA, XRD and FT-IR show that there are no vesicant residues after the PVDF film was heat-treated at 200 °C to get the porous structure. When the film is gelled with liquid electrolyte, the ion conductivity can be up to  $4.8 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature and the activation energy for ionic transfer is  $10.2 \text{ kJ mol}^{-1}$ . LiCoO<sub>2</sub> cathode also presents good cycling performance. These primary results show great promise for this simple method to prepare porous gel polymer electrolytes for practical application in lithium ion batteries.

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## 1. Introduction

Many troubles have been caused by the poor safety of lithium ion batteries (LIBs) using liquid electrolytes such as fire, burn and explosion [1]. An available method to solve the safety and reliability problem is to use gelled polymer electrolytes (GPEs) as the substitute of the liquid electrolytes due to its much lower vapor pressure and combustibility [2]. Many works have been done on GPEs since the idea of ionic conductive polymer gels and membranes for lithium cells was proposed in 1975 [3]. Until now, GPEs based on polyacrylonitrile (PAN) [4], poly(ethylene oxide) (PEO) [5], poly(methyl methacrylate) (PMMA) [6,7] and poly(vinylidene fluoride) (PVDF) [8] have been widely studied. PVDF is chosen as the matrix of GPE because of the good mechanical performance and high dielectric constant ( $\epsilon = 8.4$ ) which are favorable to the transference of lithium ions. However, the solubility of PVDF in carbonates is not high. Preparing porous PVDF membrane is an available way to get GPEs as the pores can accommodate a large amount of liquid electrolytes [9–11]. In 1995, Bellcore Co. Ltd. declared to make porous GPEs via phase inversion method [12]. Since then many ways have been investigated in this field such as solution-casting method

[13], backstop reinforcing method [14], electrospun method [15] and non-solvent induced phase separation (NIPS) process [16,17]. However, the above methods encounter some kind of difficulties such as complicated process and/or high cost. As a result, to our knowledge none of them is commercially available for large-scale production.

Here we for the first time found a simple method via a foaming technology by using salicylic acid as the foaming agent, which has a moderate decomposition temperature, to make porous PVDF gel electrolyte film. Primary results show that the electrochemical performance of the prepared gel electrolyte and this process are of great promise for application in lithium ion batteries.

## 2. Experimental

PVDF (SAFT 761, Germany), salicylic acid (Guoyao. Co. Ltd., China) and *N*-1-methyl-2-pyrrolidone (NMP, Wulian Chem. Co. Ltd., China) were used as received. LiPF<sub>6</sub> solution ( $1 \text{ mol l}^{-1}$ ) in ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC) (1:1:1, v/v/v) was supplied by Guotai Huarong Co. Ltd., and was used without further treatment as the liquid electrolyte.

PVDF (10 g) and salicylic acid (1 g) were dissolved in the solvent NMP (100 ml). The solution was coated on a piece of glass. After the solvent NMP was vaporized at 80 °C, a thin film of PVDF homogeneously mixed with the foaming agent, salicylic acid, was obtained. The film was then heated at an elevated temperature to be porous

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due to the foaming effect of salicylic acid to produce pores. Liquid electrolyte (230 wt.%) was added into the porous polymer film to get PVDF-based porous GPEs.

Differential thermal analysis and thermogravimetry (DTA and TG: PerkinElmer Thermogravimetric Analyzer, TGA7) was employed to evaluate the foaming temperature. The surface morphology was observed with a scanning electron microscope (SEM, Philips XL 300). X-ray diffraction patterns were recorded by an X-ray diffractometer (Bruker D8 Advanced Spectrometer) with monochromatized Cu K $\alpha$  radiation. FT-IR measurement was carried out on a BRUKER VECTOR-22 spectrometer.

The prepared GPEs were sandwiched between two symmetrical stainless steel electrodes and sealed in a model cell, and their electrochemical impedance spectra were measured using an EG&G M273 Potentiostat/galvanostat in conjunction with M5210 Lock-in amplifier electrochemical analysis system in the frequency range 0.01 Hz–100 kHz and the excitation voltage applied to the model cells was 10 mV. The ionic conductivity of GPE was calculated from the Eq. (1):

$$\sigma = \frac{d}{R_b \cdot S} \quad (1)$$

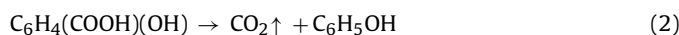
where  $\sigma$  is the ionic conductivity,  $R_b$  the bulk resistance that was determined by the impedance spectroscopy,  $d$  the thickness of the GPEs, and  $S$  the area of the symmetrical electrode.

The charge–discharge curves were measured on a Land battery tester (Land Co. Ltd., China) by a coin-type model cell. The cathode was prepared by coating the mixture of LiCoO<sub>2</sub> (Ruixiang Co. Ltd., China), carbon black and PVDF (weight ratio = 87:5:8) on a piece of aluminum foil. Lithium foil was employed as the reference and counter electrode. The cells were then assembled by sandwiching the PVDF membrane between the Li foil and the cathode. After adding 230 wt.% (based on the weight of the polymer membrane) 1 mol l<sup>-1</sup> LiPF<sub>6</sub> solution of EC/DMC/DEC, the PVDF host was moisturized by the liquid electrolyte to form GPE.

### 3. Results and discussion

#### 3.1. The foaming reaction and the characteristics of the porous PVDF membrane

As a foaming agent, the bubbling temperature and the reaction residues must be considered. If the temperature was below the softening point of PVDF, the foams could not easily escape from the inner matrix. On the contrary, if the temperature was too higher, the pores left by the foaming process would be occupied by the melt polymer host. Fig. 1 shows the DTA curve of salicylic acid, suggesting that it is an ideal foaming agent for PVDF to form porous film. Its melting point is 158 °C. When further heated up to about 183 °C, the thermal decomposition reaction will happen as follows:



The produced C<sub>6</sub>H<sub>5</sub>OH is easily to evaporate below 200 °C and the residue will be very little at last. This is of considerable importance to the application as a gel polymer electrolyte.

Fig. 2 shows TG curves of the PVDF/salicylic acid films after heated at 200 and 80 °C for 0.5 h, respectively. The PVDF/salicylic acid film heated at 80 °C for 0.5 h presents a large mass change, indicating that the foaming agent still exists in the film. When the film was heated at 200 °C for 0.5 h, the mass change is almost negligible, which indicates that there is little foaming agent left.

Fig. 3 shows the SEM micrographs of the PVDF films with or without the foaming agent after heated at 200 °C for 0.5 h. In the case of the film containing salicylic acid, the obtained pores are evenly distributed throughout the whole area, and the diameter

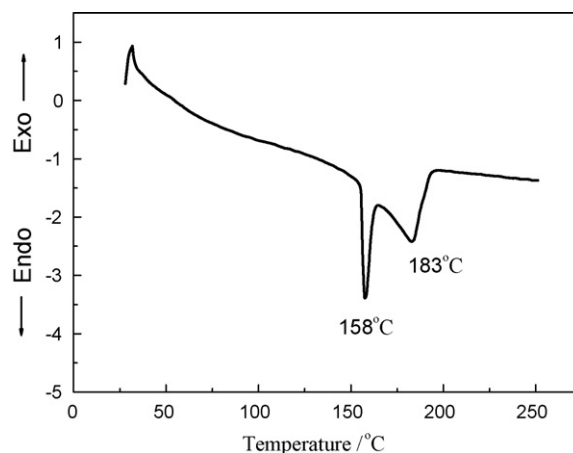


Fig. 1. DTA curve of salicylic acid.

of those pores is about 400 nm. On the other hand, the pores in pure PVDF film are larger in diameter, about 1  $\mu\text{m}$ , and the number of the pores is much less than the former as shown in Fig. 3(d). The existence of the pores in the latter film is due to the evaporation of the solvent NMP, which normally will produce some pores though the amount is small. This comparison shows clearly that the foaming agent is favorable to promote the formation of submicron pores during the foaming process at 200 °C and the pores are not interconnecting.

Fig. 4 shows the FT-IR spectra of the pure PVDF film, pure salicylic acid and PVDF/salicylic acid film heated at 200 °C for 0.5 h. In Fig. 4(a), the peak at 1190 cm<sup>-1</sup> indicates the symmetry stretching band of –CF<sub>2</sub> group, the peak at 1400 cm<sup>-1</sup> corresponds to the deformation vibration band of –CH<sub>2</sub>–, and the peak at 881 cm<sup>-1</sup> is the typical band for the amorphous phase of PVDF [18]. There are two peaks at 1072 and 762 cm<sup>-1</sup> ascribing to the bands of crystal phases of PVDF. In Fig. 4(c), the two peaks become weak, indicating that the amount of the crystal phase was reduced when the pores were generated after the heat-treatment. Compared Fig. 4(c) with Fig. 4(b), the C=O stretching vibration peak at 1659 cm<sup>-1</sup> and the carboxyl absorbing band in the range of 3000–2500 cm<sup>-1</sup> disappear, suggesting that salicylic acid has been decomposed. At the same time, the C–H out-of-plane bending vibration band (at 892 cm<sup>-1</sup>), the C–H in-plane bending vibration band (at 1022 cm<sup>-1</sup>) and the skeletal vibration bands (in the range of 1600–1450 cm<sup>-1</sup>) of aryl disappear, which suggests clearly that the phenol generated

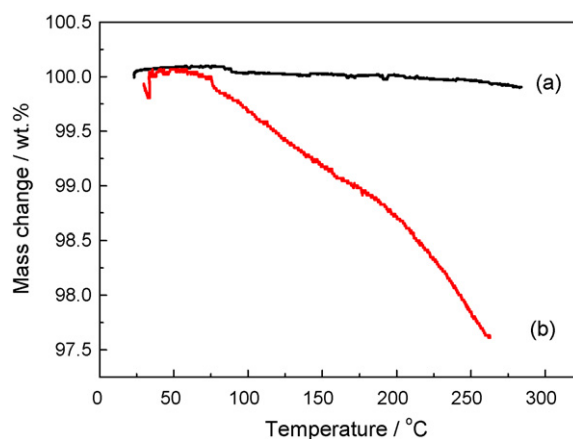


Fig. 2. TG curves of the PVDF/salicylic acid films after heating at (a) 200 °C and (b) 80 °C for 0.5 h, respectively.

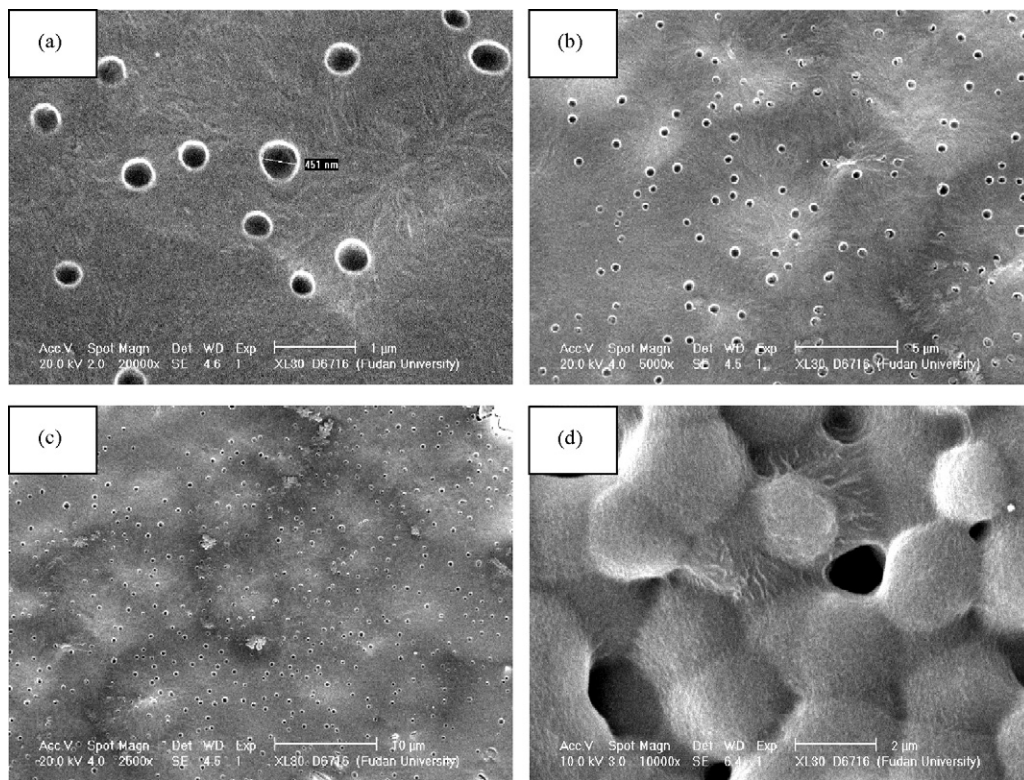


Fig. 3. SEM micrographs of (a), (b) and (c) PVDF/salicylic acid film heated at 200 °C and (d) pure PVDF film.

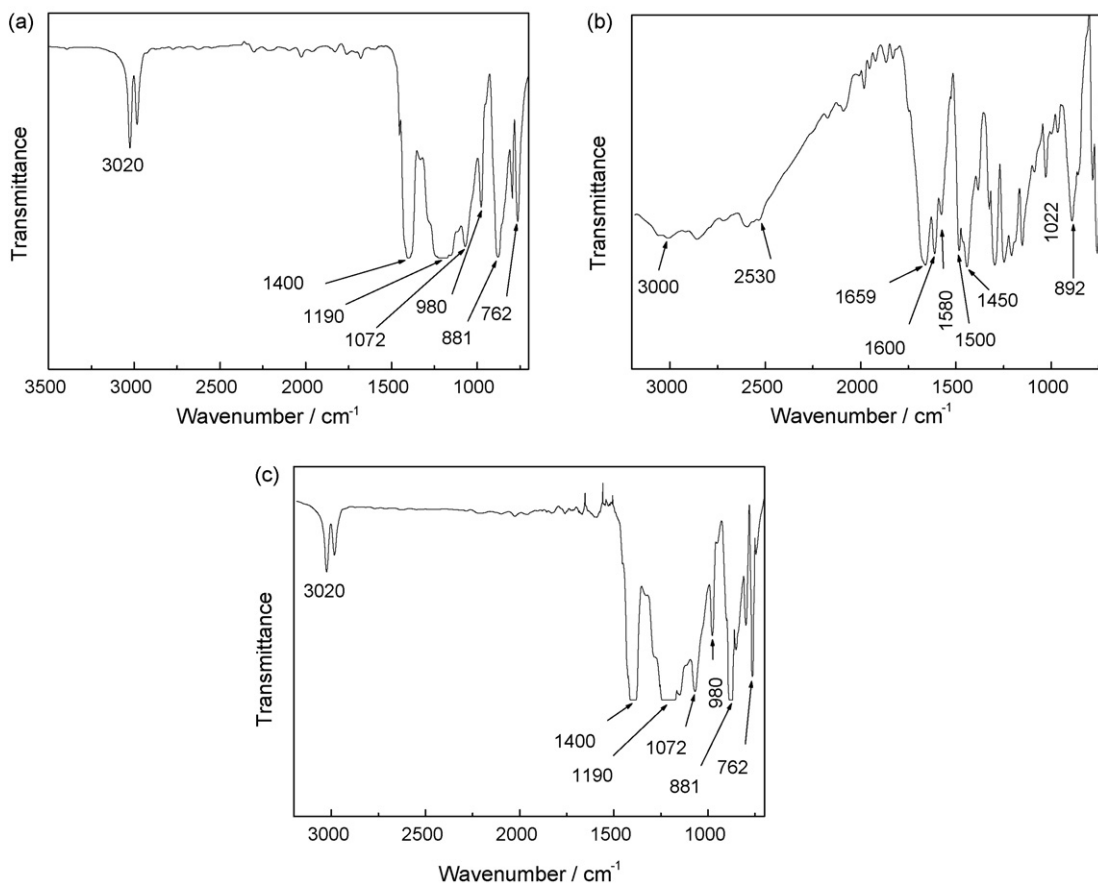
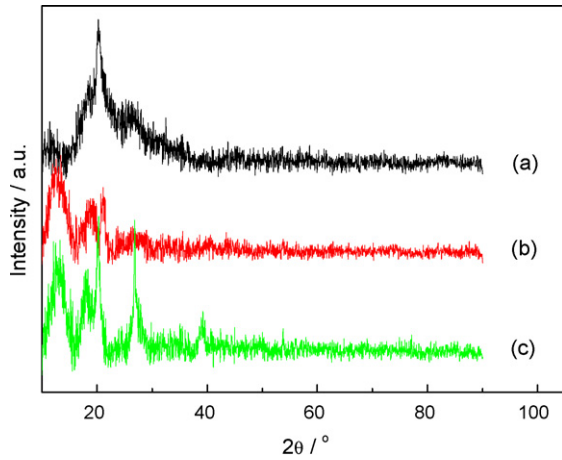


Fig. 4. FT-IR spectra of (a) PVDF, (b) salicylic acid and (c) PVDF/salicylic acid film heated at 200 °C for 0.5 h.



**Fig. 5.** XRD patterns of (a) the pure PVDF film, (b) the PVDF/salicylic acid film after heated at 200 °C for 0.5 h and (c) the PVDF/salicylic acid film without heat-treatment.

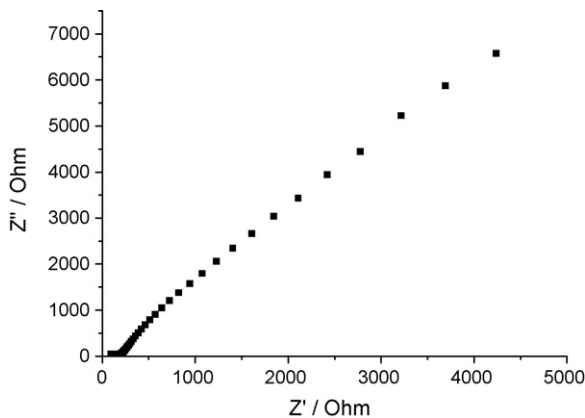
by the decomposition of salicylic acid has also been removed after the foaming process at 200 °C.

Fig. 5 shows the XRD patterns of the pure PVDF film, the PVDF/salicylic acid film without heat-treatment and (c) the PVDF/salicylic acid film after heated at 200 °C for 0.5 h. After heat-treatment or the foaming process, the characteristic crystal peak of PVDF at about 20° becomes weak. In addition, the XRD pattern of salicylic acid at about 27° disappears, which is consistent with the above results of FT-IR spectra.

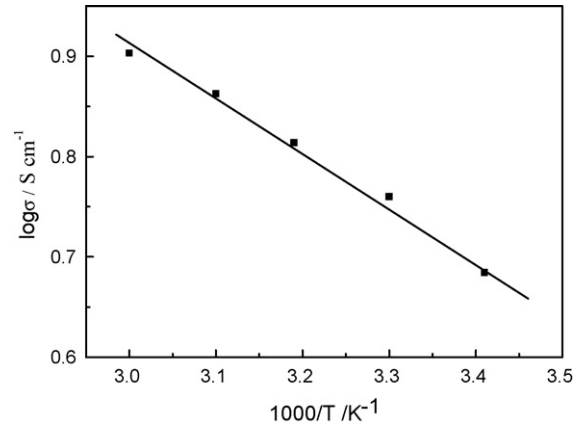
### 3.2. Electrochemical characteristics of the PVDF microporous GPEs

As mentioned above, the pores in the PVDF membrane are not interconnecting. When the liquid electrolyte was added into the membrane, the membrane matrix was gelled by solvents to form GPE. Fig. 6 shows the electrochemical impedance spectroscopy of the porous PVDF GPE. Ionic conductivity  $\sigma$  was calculated based on Eq. (1) to be  $4.8 \times 10^{-3} \text{ S cm}^{-1}$ , which can completely meet the demands for practical application in lithium ion batteries. The main reason is that the number of submicrometer pores is very much, which can absorb a lot of liquid electrolyte.

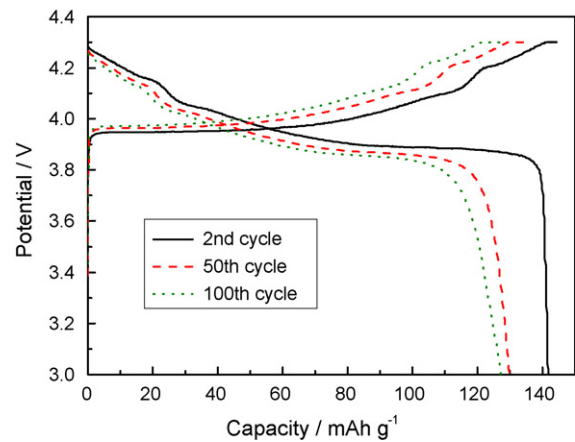
The relationship between the ionic conductivity of the GPE vs.  $1000/T$  is presented in Fig. 7. It indicates that the ionic conductivity



**Fig. 6.** The EIS of the model cell with the configuration of steel|porous PVDF GPE|steel.



**Fig. 7.** Relationship between ionic conductivity of the GPE and temperature.



**Fig. 8.** Charge/discharge curves of the LiCoO<sub>2</sub> cathode using the GPE as the electrolyte and separator at room temperature at different cycles.

follows the Arrhenius formula, which is shown in Eq. (3).

$$\sigma = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where  $A$  is the pre-exponential factor and  $E_a$  the activation energy of ion transference in the GPE. The activation energy of ion transference in the GPE was calculated to be  $10.2 \text{ kJ mol}^{-1}$ , which is consistent with most reported gelled polymer electrolytes [16–18].

Charge–discharge curves of the LiCoO<sub>2</sub> cathode using the gelled polymer electrolyte as the electrolyte and separator at room temperature at different cycles are shown in Fig. 8. It is seen that the capacity fading of LiCoO<sub>2</sub> cathode is slow, only 10% capacity loss after 100 cycles. This implies that the cycling performance is satisfactory, suggesting great promise for practical application.

### 4. Conclusion

A porous gel polymer electrolyte based on PVDF was for the first time successfully prepared via the assistance of salicylic acid as a foaming agent. The porous PVDF membrane can store a large amount of liquid electrolyte in the pores, leading to high ionic conductivity. LiCoO<sub>2</sub> cathode presents good cycling behavior when this GPE is used as the electrolyte and separator. The above primary results indicate a great promise of this method to prepare porous PVDF gel polymer electrolyte for practical applications since this foaming process is very simple.

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