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# Porous poly(vinylidene fluoride-co-hexafluoropropylene) polymer membrane with sandwich-like architecture for highly safe lithium ion batteries

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## ABSTRACT

Porous polymer membrane with a sandwich-like architecture has been prepared by coating poly(methyl methacrylate) (PMMA) on poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) porous membranes. Field emission scanning electron microscopy analysis identified that the PMMA/PVDF-HFP porous polymer membrane consists of the stacking of several porous layers with one layer of large pores in the middle of the membrane. This unique sandwich-like structure provides large porosity and good affinity towards a liquid organic electrolyte, leading to a high electrolyte uptake of 342 wt%, excellent electrolyte retention, and enhanced tolerance towards high temperature and fire. The gel polymer electrolyte membrane achieved a high ionic conductivity of  $1.31 \text{ mS cm}^{-1}$  with similar activation energy as the conventional Celgard 2400 separator in liquid electrolyte. The porous polymer electrolyte membrane also has an outstanding thermal and electrochemical stability. When applied in lithium ion batteries with  $\text{LiFePO}_4$  cathode and lithium metal anode, the PMMA/PVDF-HFP electrolyte membrane demonstrated high discharge capacity, enhanced high rate capability, and extended cycle life. The PMMA/PVDF-HFP porous polymer membrane could be employed as an integrated separator and electrolyte for lithium ion batteries with high safety.

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## 1. Introduction

Lithium ion batteries have been intensively investigated in the past few decades. Their high energy density and efficiency makes them promising candidates as the power sources for portable electronics, hybrid electronic vehicles, and electric vehicles [1,2]. Lithium ion batteries can also be used for electrical energy storage from renewable energy sources generated by solar or wind. Nevertheless, lithium ion batteries are still associated with severe safety risks such as fire and explosion hazards owing to the use of flammable separators and liquid organic electrolytes [3].

The concept of solid electrolytes was proposed in order to solve these safety issues. By eliminating flammable organic liquids, the risk of causing fires can be greatly reduced [4–7]. However, solid electrolytes usually contain inorganic  $\text{Li}^+$  conductors as the main skeleton, which cannot provide sufficient ionic conductivity for fast ion transport during battery operation. Solid polymer electrolytes also suffer the same disadvantages. Gel polymer electrolytes,

prepared by adding organic liquid electrolytes to a polymer system, can achieve high ionic conductivity and good safety [8,9]. By replacing the physical combination of separator and liquid electrolyte, gel polymer electrolytes, which are often made to be free-standing, can serve both roles. Porous gel polymer electrolytes showed distinguished characteristics such as high ionic conductivity, good processability, wide electrochemical operating windows, and thermal stabilities, as well as excellent capability to prevent electrolyte leakage [10–13]. Compared to inorganic separators, porous gel polymer electrolytes provide more interactions between the liquid electrolytes and porous polymers by gelling with each other. Gelled skeleton and retained liquid electrolytes inside the porous polymer electrolyte membranes can both contribute to the ionic conductivity and mechanical property [14,15]. Therefore, the electrochemical performance of porous polymer electrolytes is closely related to the porous structure of the polymer membrane matrix [16,17]. However, membranes with too large pore sizes can induce internal short circuits due to the mass transportation of electrode particles, leading to failure of the batteries. Several approaches such as embedding inorganic nanoparticles and the coating of other polymer species have been investigated to reduce the pore size of the polymer membranes [18,19]. Usually a glass substrate is

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used when there is an evaporation process involved during preparation of the membrane. Solution is poured on the glass substrate which acts as a support. It is interesting that the substrate has some influence on the surface morphology. Pu et al. investigated the effect of using substrate on morphologies on both surface sides [20].

The choices for polymer matrices are versatile. For example, poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) have been intensively studied [16,21–23]. PMMA demonstrated the best affinity with liquid electrolytes, resulting in high electrolyte uptake and high ionic conductivity [12]. However, PMMA membranes are usually fragile and difficult to process. After absorption of liquid electrolytes, the integrity of membranes can be easily destroyed. The flammability of PMMA also limits its application as single polymer matrix in gel polymer electrolytes. PVDF-HFP is able to provide sufficient mechanical properties and a relatively high ionic conductivity. The semi-crystal structure of crystal VDF and amorphous HFP makes it suitable to be used in porous gel polymer electrolytes [24]. Several reports have already investigated the blend of PMMA and PVDF-HFP polymer electrolytes [25]. Zhang et al. prepared a novel sandwich-like membrane by coating PVDF layers onto both sides of PMMA membrane, which exhibited enhanced electrochemical performances [26]. Inspired by those outcomes, we prepared a sandwich-like polymer membrane with multi-size porous structure by coating PMMA onto PVDF-HFP porous membrane. The as-prepared polymer membrane showed an outstanding stability towards high temperature and fire. When gelling with a liquid electrolyte, the polymer membrane exhibited high electrolyte uptake and an excellent electrochemical performance in lithium ion batteries. This as-developed porous gel polymer electrolyte could be applied in lithium ion batteries with enhanced performance and safety.

## 2. Experimental

### 2.1. Preparation of PVDF-HFP porous polymer membranes

PVDF-HFP porous polymer membranes were prepared by a breath-figure method [27–29]. First, a homogeneous 10 wt% PVDF-HFP/acetone solution was obtained by dissolving PVDF-HFP into acetone solvent. The solution was then cast onto a flat glass substrate and allowed to dry under a room humidity of 45%. After fully drying, the obtained membrane was carefully peeled off from the flat glass substrate, vacuumed, and stored inside a glovebox.

The as-prepared PVDF-HFP porous polymer membrane has two sides. For convenience, the side that was in direct contact with room humidity was called front side, and the other side in contact with the flat glass substrate was called back side.

### 2.2. Preparation of PMMA/PVDF-HFP porous polymer membranes

Two pieces of the as-prepared PVDF-HFP porous polymer membranes were used as one by putting them together with both front sides facing inside. The connected membranes were immersed in 2.5 wt% PMMA/CHCl<sub>3</sub> solution for 1 h. The membranes were then taken out and cleaned with a tissue to eliminate the surface solution residue. During the drying process, the membranes gradually self-adhered and became one piece of membrane after fully drying. The obtained PMMA/PVDF-HFP porous membrane was then stored in an argon-filled glovebox.

### 2.3. Preparation of gel polymer electrolyte membranes

The polymer electrolyte membranes were prepared by immersing the as-prepared porous membranes in liquid electrolyte solution (1 M LiPF<sub>6</sub> in 1:1 ethylene carbonate (EC): dimethyl carbonate (DMC)) overnight. The excess liquid residue on the membrane surface was carefully wiped off with a tissue.

### 2.4. Characterizations of the as-prepared porous polymer membranes

A field emission scanning electron microscope (FESEM, Zeiss Supra 55 VP) was used to observe the morphology of the as-prepared porous polymer membranes. Thermal stabilities of the polymer membranes were measured by Thermogravimetric analysis using a Mettler Toledo TGA/DSC instrument. Infrared spectroscopy was conducted on a Cary 630 FTIR-ATR spectrometer (Agilent Technologies). All spectra were obtained by using 8 cm<sup>-1</sup> resolution and 32 scans at room temperature.

The amount of liquid electrolyte uptake is calculated using Eq. (1).

$$\eta = \frac{W_t - W_o}{W_o} \times 100\% \quad (1)$$

Where  $\eta$  is the uptake of liquid electrolyte, and  $W_o$  and  $W_t$  are the weight of the membranes before and after absorption of the liquid electrolyte, respectively.

### 2.5. Electrochemical characterisation of polymer electrolyte membranes

To equate the thickness and morphology, two pieces of PVDF-HFP polymer electrolyte membrane were used as one where front side was put inside together with the back side exposed to the outside. The PMMA/PVDF-HFP polymer electrolyte membrane and Celgard 2400 separator were used a single piece, respectively, as electrolyte membrane.

Linear sweep voltammetry measurements were conducted to determine the stability of the polymer electrolyte membranes. The polymer membranes were sandwiched between a lithium anode and stainless steel (SS) electrode. The electrochemical impedances at different temperatures were measured by sandwiching polymer electrolyte membranes between two stainless steel electrodes. The ionic conductivity was calculated using Eq. (2).

$$\sigma = d / (R_b \times S) \quad (2)$$

Where  $\sigma$  is the ionic conductivity,  $d$  is the thickness of the membrane,  $R_b$  is the bulk resistance, and  $S$  is the area of the electrode. All electrochemical characterizations were conducted using a CH Instrument 660D electrochemical workstation.

The electrochemical performances of lithium ion batteries with polymer electrolyte membranes were conducted by assembling CR2032 coin cells with lithium metal as the counter and reference electrode. LiFePO<sub>4</sub> prepared by conventional solid state reaction was used as the working electrode active material. The working electrode was prepared by mixing PVDF (10%), carbon black (10%), and LiFePO<sub>4</sub> (80%) in 1-Methyl-2-pyrrolidinone (NMP). The mixture was then coated onto aluminium foil, dried at 80 °C for 12 h in a vacuum, and punched into disks. All cells were assembled in an argon-filled glovebox with water and oxygen content lower than 0.1 ppm.

## 3. Results and discussion

Fig. 1 shows the FESEM images of the PVDF-HFP and PMMA/PVDF-HFP porous polymer membranes. Fig. 1(a) shows the

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