



## Short communication

# Studies on polymer nanofibre membranes with optimized core–shell structure as outstanding performance skeleton materials in gel polymer electrolytes



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## HIGHLIGHTS

- The skeleton materials with optimized core–shell fibre structure were prepared.
- The well-sourced polymers and facile processing techniques were involved.
- The GPE had excellent electrochemical properties and cycle performance.
- The GPE showed good stability and compatibility with lithium electrode.
- High applicable value of the GPE in lithium-ion batteries was presented.

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## ABSTRACT

The polyporous polymer nanofibre membranes with optimized core (polyacrylonitrile, PAN)-shell (polymethylmethacrylate, PMMA) structure are prepared by coaxial electrospinning, and then converted to gel polymer electrolytes (GPEs) after the activation process of stacked nanofibre membranes in liquid electrolyte. Based on the proper collocation of polymer materials, the desirable microstructure of polymer membranes as well as the affinity between fibre shell and the electrode/electrolyte result in a high saturated electrolyte uptake and conservation rate. The electrochemical testing results of the GPEs indicate high ionic conductivities, good electrochemical stability and appropriate lithium-ion transference numbers, which are realized through choosing optimal core–shell flow rate ratio. Furthermore, the interface impedance performance of the GPEs shows good stability and compatibility with lithium electrode, which is beneficial for long-term storage and use of the lithium-ion battery. The Li/GPE/LiCoO<sub>2</sub> cells with GPEs based on the electrospun membranes with optimized core–shell structure present excellent cycle performance compared to the cell involved with GPEs based on PAN and commercial Celgard 2500. Thus, the polymer membranes consisting of nanofibres with well-designed core–shell structure can be used as a new type of skeleton material in GPEs used in lithium-ion batteries.

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## 1. Introduction

Polymer electrolytes possess relatively high ionic conductivity, as well as the unique characteristic of light weight, excellent corrosion resistance and easy shaping, have been used in chemical power sources in recent years. Many polymers, such as polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyethylene

oxide (PEO) and polymethylmethacrylate (PMMA), etc., have been widely studied and developed as candidate materials for polymer electrolytes [1–6]. Polymer lithium-ion batteries work basically the same way as liquid lithium-ion batteries. But compared to liquid lithium-ion batteries, the energy density of polymer lithium-ion batteries is higher, and the problem of leakage of electrolyte can be avoided, followed by the enhancement of battery capacity. Polymer electrolytes can be made considerable thin and large in area to ensure fully contacts with the electrodes, facilitating development of electronic items in the direction of miniaturization, light weight and films [7]. For pragmatic reasons, polymer

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electrolytes must meet the following prerequisites: 1) ionic conductivity above  $10^{-3}$  S/cm at room temperature; 2) high lithium-ion transference number; 3) electrochemical stability window is larger than 4.2 V; 4) good mechanical properties and thermal stability [8].

For now, ionic conductivity of solid polymer electrolytes is far lower than liquid electrolytes at room temperature, which limits their practical application. The different techniques, such as blending, copolymerization as well as crosslinking have been employed to fabricate polymer electrolytes with improved ionic transport properties and low crystallinity [9,10]. In addition, polymer with polyporous structure can absorb a large amount of liquid electrolytes to form gel polymer electrolytes (GPEs), so that their ionic conductivity can be close to that of liquid electrolyte. Therefore, GPEs have been widely used in the commercial polymer lithium-ion battery at present [11]. Some typical methods for the preparation of porous polymer materials include: the Bellcore process, thermally induced phase separation, thermally assisted evaporative separation, immerse precipitation, and self-assembly method [12–14]. With these methods, large amounts of organic solvents are required which can cause environmental pollution, the residue solvents can bring about negative effects on the performance. Besides, these methods are difficult to control the structure and uniformity of micropores in polymer materials. Development of electrospinning in recent years provides an effective method to prepare membranes consisting of ultrafine polymer fibres, with diameters being in the sub-micrometre down to the nanometre range [15–17]. Polymer membranes with the porosity of 30%~90% can be easily prepared by controlling electrospinning parameters. The polyporous structure can provide a large specific surface area and abundant channel for lithium ions to transfer, and improve the electrode/electrolyte interface as well as the compatibility and stability between polymer materials and liquid electrolytes. Thus, high discharge current performance and cycle performance of the obtained lithium-ion batteries can be expected.

PAN and PMMA are two cheap and well-sourced traditional electrolyte materials. PAN possesses good mechanical strength, heat resistance, chemical stability and good flame retardancy. Because some chemical actions exist between nitrile groups and lithium ions, PAN-based GPEs were reported to show bad compatibility with lithium electrodes, and the passivation on the interface can be serious [18,19]. PMMA based GPEs satisfy the needs of basic electrochemical performance, especially they have good compatibility with lithium electrode, and low interface impedance, however, the poor mechanical strength also limits their application. Blending, solvent-casting, and in situ polymerization have been attempted to form free-standing PMMA membranes with a high content of liquid electrolytes, however, it is difficult to obtain excellent electrochemical performance due to the imperfect microstructure [20]. Besides, PMMA is fragile and displays poor film-forming property during the electrospinning, continuous and uniform PMMA nanofibres are more difficult to prepare compared to PAN. In order to combine the performance advantages of different polymeric materials and polyporous structure, the polymer membranes consisting of nanofibres with core (PAN)-shell (PMMA) structure were prepared by using coaxial electrospinning in this paper. GPEs can be produced after the activation process of stacked polymer membranes in liquid electrolytes. The optimized microstructure of nanofibres and membranes was obtained by adjusting core-shell flow rate ratio, which brought the good electrochemical properties and compatibility with lithium electrode. The polymer nanofibre membranes with optimized core-shell structure can act as high performance of new skeleton material in GPEs.

## 2. Experimental section

### 2.1. Materials

PAN (average molecular weight of  $10^5$  g mol<sup>-1</sup>, Jilin Petrochemical Co., China.), PMMA (average molecular weight of  $1.2 \times 10^5$  g mol<sup>-1</sup>, Aldrich Chemical Co., USA.) and *N,N'*-dimethylformamide (DMF, analytical reagents, Beijing Chemicals Co., China) were used to prepare the PAN and PMMA spinning solution, respectively. 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>)/ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1, vol. %) (Battery grade, MERCK) was used as the liquid electrolyte solution.

### 2.2. Sample preparation

#### 2.2.1. Preparation of polyporous polymer membranes

The polyporous polymer membranes consisting of nanofibres with core (PAN)-shell (PMMA) structure were prepared by coaxial electrospinning at room temperature and a humidity of 30%. A laboratory-produced coaxial dual-spinneret was used. A positive high voltage of 18 kV was applied to an 18-cm gap between the spinneret and a flat plate collector covered with aluminium foil. During the electrospinning process, the core-shell flow rate ratio was controlled at 0.3/0.6, 0.4/0.7, 0.8/1.0 (ml h<sup>-1</sup>) by using a dual syringe pump (JZB-1800D, Jian Yuan Medical Technology Co. Ltd., China), respectively. Flow rate of shell solution was faster than that of the core solution, which could more conducive to form into continuous nanofibres with core-shell structure. The whole electrospinning process take for about 6 h. Then nanofibre membranes were vacuum-dried at 60 °C for 12 h to remove residual solvent. For comparison, electrospun PAN membranes were also prepared under the similar condition.

#### 2.2.2. Preparation of gel polymer electrolytes (GPEs)

Polyporous polymer membranes were punched into several small discs with a diameter of 22 mm. Small discs were stacked together to form the skeleton structure of GPEs, then precursors were vacuum-dried at 50 °C for 6 h and transferred into an argon filled glove box (moisture level < 10 ppm). GPEs were prepared by immersing precursors in 1 M LiPF<sub>6</sub>/EC: DMC (1:1, vol. %) for about 24 h at room temperature, the saturated GPEs were used after removal of excess liquid electrolyte with a filter paper for the measurement of electrochemical properties.

### 2.3. Characterization

The surface morphology of electrospun membranes was examined using scanning electron microscopy (SEM, Hitachi S-4700, Japan). The core-shell structure of single nanofibre was examined using transmission electron microscopy (TEM, Hitachi H800, Japan). *N*-butanol uptake method was employed to calculate the porosity of electrospun membranes [21].

Saturated electrolyte uptake of stacked electrospun membranes was measured after the immersion process. GPEs was placed in an argon filled glove box without sealing, and weighed every 24 h for 15 days. All the electrochemical properties were measured on Autolab PGSTAT 302N (Metrohm) at room temperature. The ionic conductivity was determined by AC impedance spectroscopy in the range of 0.1 Hz–100 KHz using the cell inserted GPEs into two parallel stainless steel (SS) discs. The electrochemical stability window was examined using the method of linear sweep voltammetry in the cell Li/GPE/SS at a scan rate of 1 mV s<sup>-1</sup>, potential voltage ranging from 1 V to 7 V. The lithium-ion transference number was measured using the method of chronoamperometry (CA) in the cell Li/GPE/Li with a polarization voltage of 5 mV. The

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