Gel polymer electrolytes based on nanofibrous polyacrylonitrile–acrylate for lithium batteries

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ABSTRACT

Nanofibrous membranes for gel polymer electrolytes (GPEs) were prepared by electrospinning a mixture of polyacrylonitrile (PAN) and trimethylolpropane triacrylate (TMPTA) at weight ratios of 1/0.5 and 1/1. TMPTA is used to achieve crosslinking of fibers thereby improving mechanical strength. The average fiber diameters increased with increasing TMPTA concentration and the mechanical strength was also improved due to the enhanced crosslinking of fibers. GPEs based on electrospun membranes were prepared by soaking them in a liquid electrolyte of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v). The electrolyte uptake and ionic conductivity of GPEs based on PAN and PAN–acrylate (weight ratio; 1/1 and 1/0.5) were investigated. Ionic conductivity of GPEs based on PAN–acrylate was the highest for PAN/acrylate (1/0.5) due to the proper swelling of fibers and good affinity with liquid electrolyte. Both GPEs based on PAN and PAN–acrylate membranes show good oxidation stability, >5.0 V vs. Li/Li+. Cells with GPEs based on PAN–acrylate (1/0.5) showed remarkable cycle performance with high initial discharge capacity and low capacity fading.

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1. Introduction

The majority of lithium secondary batteries currently use liquid electrolytes, which can easily leak out of the cells and can cause safety problems. Lithium polymer batteries employing gel or solid polymer electrolytes have attracted much attention and various polymer electrolytes have been studied to develop technology of lithium polymer batteries and enhance the electrochemical performance of cells since they possess a great variety of advantages such as excellent safety characteristics, flexibility of shape and high ionic conductivity [1]. Gel polymer electrolytes (GPEs) are usually made from a polymer host, a salt and a solvent or a mixture of solvents. GPEs have good ionic conductivity with relatively good mechanical properties at a wide temperature range due to the inclusion of a higher amount of organic electrolyte in the polymer hosts.

Many polymers can be used in GPEs, such as poly(ethylene oxide) (PEO) [2–6], poly(ethylene glycol) (PEG) [7], poly(vinylidene fluoride) (PVdF) [8–10], poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-HFP)) [11–14], and polyacrylonitrile (PAN) [15–17]. Among these polymer hosts, PAN-based GPEs offer many good characteristics like high ionic conductivity, thermal stability, good morphology for electrolyte uptake and compatibility with lithium electrodes [18]. Also, PAN can minimize the formation of dendrite growth during the charging/discharging process of lithium-ion polymer batteries [16]. However, PAN-based GPEs suffer from poor mechanical strength that is difficult to meet the requirement of practical application of lithium polymer batteries [19,20]. Therefore many efforts have been made to improve PAN-based GPEs. Rajendran et al. [19] reported GPEs based on PAN–PVC prepared by casting technology. They demonstrated that the addition of PVC could improve the mechanical strength of polymer membranes and achieve strong and free-standing thin films. However, the GPEs based on PAN–PVC had a low ionic conductivity. Prasanth et al. [21] reported electrospinning is an efficient method to prepare polymer nanofibrous membrane with fully interconnected pore structure and the membranes show high porosity and electrolyte uptake, and comparable leakage property compared to conventional separator. PAN–PVC fibrous membranes were prepared by

Zhong et al. [22] with electrospinning and such electrospun PAN–PVC GPEs showed both good mechanical stability and electrochemical properties.

Trimethylolpropane triacrylate (TMPTA) was reported for use in the preparation of GPEs with a crosslinking structure, and the cell with TMPTA-based GPEs showed stable cycle performance [23]. In this work, naonfibrous membranes for GPEs were prepared by blending PAN with TMPTA to form crosslinking of fibers thereby improving their mechanical strength. The physical and electrochemical characteristics of the GPEs were studied in detail.

2. Experimental

PAN is commercially purchased from Polyscience Inc. with a number-average molecular weight (M_n) of 150,000 g/mol. It was vacuum dried at 60 °C for 6 h before use. Trimethylolpropane triacrylate (TMPTA, Aldrich) and azobisisobutyronitrile (AIBN, Duksan) were used as the crosslinking agent and initiator, respectively. The solvent N,N-dimethyl formamide (DMF, Aldrich) was used as received. Nanofibrous membranes were prepared by a typical electrospinning method at room temperature [11,12]. PAN and TMPTA with different weight ratios (1.0/0.5 and 1.0/1.0 g/g) were homogeneously dissolved in 10 mL of DMF by mechanical stirring at 60 °C. 0.02 g of AIBN was added to the solution with stirring. The resulting solutions were electrospun at 25 °C and the essential spinning parameters used are: applied voltage 15 kV, distance between the tip of the needle and collecting Plate 20 cm, needle size 1.27 mm and solution feed rate 2.0 mL/h. The electorspun membranes thus obtained were then annealed for radical reaction at 100 °C for 3 h. PAN membranes without TMPTA were also electrospun using a 13 wt% PAN solution in DMF for comparison.

The fiber morphology was observed with scanning electron microscope (SEM, JEOL JSM 5600) and the average fiber diameter (AFD) was estimated from the micrographs taken at high magnification. The tensile strength of PAN and PAN–acrylate membranes were evaluated with universal testing machine (UTM, Instron 3343). The porosity of the membranes was measured by mercury porosimetry (Micromeritics, ASAP 2010).

GPEs were prepared by soaking the electrospun nanofibrous membranes in the electrolyte solution: 1 M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v) (Soulbrain Co., Ltd.) mixture. The electrolyte uptake was calculated according to the following equation:

$$\text{uptake}\,(\%) = \frac{W_t - W_0}{W_0} \times 100,$$

where W_0 is the mass of the dry membrane and W_t is the mass of the membrane after soaking with the electrolyte. Ionic conductivity of GPEs was measured by the AC impedance of the cell with 1M6 frequency analyzer over the temperature range from 0 to 60 °C. The cell was fabricated by sandwiching GPEs between two stainless steel electrodes (SS/GPE/SS) and the impedance measurements were performed at an amplitude of 20 mV over the frequency range from 100 mHz to 2 MHz. The cell was kept at each measuring temperature for 1 h to ensure the thermal equilibration of the sample at temperature before measurement. The ionic conductivity could be calculated based on the following equation:

$$\sigma = \frac{t}{R_b} \cdot A,$$

where σ is the ionic conductivity (S cm^{-1}), R_b is the bulk resistance (Ω), t and A are the thickness (cm) and area (cm^2) of the GPEs, respectively. Electrochemical stability was determined by linear sweep voltammetry (LSV) using Li/GPE/SS cells at a scanning rate of 1 mV s^{-1} over the potential range of 2.5–6 V vs. Li/Li$^+$.

Swagelok cells were fabricated by placing the GPEs between lithium metal anode and carbon coated lithium iron phosphate (LiFePO$_4$) cathode. LiFePO$_4$ was synthesized as previously studied [24] and the cathode was prepared by mixing LiFePO$_4$ powder, conductive carbon and PVdF binder in the weight ratio of 80:10:10 with N-methyl-2-pyrrolidone (NMP). The slurry was cast onto aluminum foil and dried at 80 °C for 24 h in vacuum for further use. The electrochemical tests of the Li/GPE/LiFePO$_4$ cells were performed in an automatic galvanostatic charge–discharge unit, WBCS3000 battery cycler (WonA Tech. Co.), between 2 and 4.2 V at room temperature with a current density of 0.1 C.

3. Results and discussion

The preparation of nanofibrous membranes based on PAN–acrylate is aimed to achieve freestanding GPEs with good mechanical strength by the addition of TMPTA as a crosslinking agent. As expected, the mechanical properties of PAN–acrylate electrospun membranes are improved compared to PAN membranes as given in Table 1. Both tensile strength and modulus are higher for PAN–acrylate membranes.

The morphology of electrospun nanofibrous PAN and PAN–acrylate membranes is shown in Fig. 1(a–c). All membranes showed a three-dimensional network structure with fully interconnected pores made up of fibers. The average fiber diameter is around 435 nm for PAN membranes, and 522 and 620 nm for PAN–acrylate (1/0.5) and PAN–acrylate (1/1), respectively. PAN–acrylate (1/0.5) membranes were observed to have denser morphology with smaller pores than PAN membranes, which is supposed to result from the addition of TMPTA that formed a crosslinking structure. It was found that the fiber diameter was not uniform with increased concentration of TMPTA (Fig. 1(c)), which suggests that an excess of TMPTA in the polymer blend may increase the viscosity of the polymer blend solution with too much crosslinking agent that distort the uniformity of fibers.

To observe the swelling behavior of electrospun membranes, they were soaked in liquid electrolyte of 1 M LiPF$_6$ in EC/DMC (1/1, v/v) for 15 h. Membranes were then washed with ethanol and dried at 80 °C in vacuum for 12 h before taking SEM observation. The SEM images of nanofibrous PAN and PAN–acrylate membranes after being soaked in liquid electrolyte for 15 h are given in Fig. 1(d–f). It is shown that the swelling ability was much improved

Table 1
Properties of electrospun membranes and GPEs based on nanofibrous PAN and PAN–acrylate membranes activated with 1 M LiPF$_6$ in EC/DMC.

Properties	PAN	PAN–acrylate (1/0.5, w/w)	PAN–acrylate (1/1, w/w)
Average fiber diameter (nm)	435	522	620
Tensile strength (MPa)	13.0	14.2	15.4
Modulus (MPa)	454.0	556.1	661.0
Porosity (%)	78.8	72.8	64.1
Thickness (um)	45	40	33
Electrolyte uptake (%)	420	340	280
Ionic conductivity at 25 °C (mS cm^{-1})	3.77	5.22	2.59