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Poly(dimethylsiloxane) hybrid gel polymer electrolytes of a porous structure for lithium ion battery

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ABSTRACT

A porous fabric membrane (XSAE) was prepared from the crosslinked hybrid composite of poly(dimethylsiloxane)/polyacrylonitrile/poly(ethylene oxide) (PDMS/PAN/PEO) to simultaneously act as a separator and functionalized gel polymer electrolytes (GPEs). The porous structure enables hybrid membranes (XSAE) to absorb a large amount of electrolyte solution, thereby significantly increases the performance of GPEs. The addition of PDMS induces phase segregation to form a porous morphology and deteriorates the crystallization of PAN. Owing to these effects, the ionic conductivity of the gel hybrid membrane at room temperature more than doubled, and the lithium transport number increased from 0.41 up to 0.58. Compared with a composite membrane without PDMS (XAE), the battery application half-cell capacities of both XAE and XSAE were close to 150 mAh g^{-1} at 0.1C. However, at high *C* rate (3C), the capacities of composite membranes with PDMS (PDMS/PAN/PEO) can reach 114 mAh g^{-1}, significantly higher than that without PDMS (70 mAh g^{-1}). Moreover, the aforementioned properties of the XSAE membrane allow this composite to act as both an ionic conductor and separator.

1. Introduction

Lithium-ion batteries are widely used in mass-produced digital devices and are gaining popularity in the booming electric vehicle market and energy storage systems because of their high energy density and long cycle life [1–5]. Be that as it may, safety issues still prevent full utilization of these batteries due to several as yet unresolved issues of the electrolytes, including the potential to leak, catch fire and become unstable [6,7]. Therefore, safety concerns and better robustness of electrolyte systems have been the focus of much attention, with gel polymer electrolytes (GPEs) emerging as a possible solution for overcoming these critical issues [8–10].

Poly(ethylene oxide) (PEO) is currently the most prominent example of a polymer electrolyte due to its ability to solvate and transport lithium-ions, the main drawback is that its ionic conductivity without liquid electrolyte is low at room temperature [11–13]. Therefore, polymers such as PEO, poly(vinylidene fluoride) (PVdF), polyimide and polyacrylonitrile (PAN), are often combined with electrolyte solution to create GPEs for the large scale application [14–17]. Furthermore, highly saturated polymer gels often cannot have the ability to hold their shape when subjected to even small levels of loaded electrolyte solution. Thus, many studies use to target extending the mechanical strength with a high lithium transference number and other physical properties [18–21]. To overcome these disadvantages, some efforts to use polyimide and inorganic fillers to improve dimensional and thermal stabilities. Cross-linked structure gave the GPEs good mechanical strength and easily to introduce PEO segment to enhance ionic conductivity [22-24]. In our previous work, cross-linked GPEs penetrated with PAN were used as alternative GPEs because of their better electrical and mechanical properties leading to excellent battery performance [21].

PDMS has low glass transition temperature (T_g) and excellent chemical constancy. We have demonstrated that hybrid polymer electrolytes incorporating polysiloxane and PEO segments were fabricated by the cross-linking process to achieve satisfactory process ability and high ionic conductivity [25–28]. Furthermore, it has been reported that PDMS segments tend to segregate the other rest organic moieties due to its low surface energy and poor miscibility [29]. Moreover, there are many studies to prepare polymer electrolytes possessing phase-separated morphologies to enhance their Li$^+$ transport and mechanical properties [30–34].

In this study, PDMS was introduced into cross-linked PAN/PEO GPEs with unique characteristics. The addition of PDMS causes the hybrid GPEs to form a sponge structure derived from the phase segregation which also reduces the crystallinity of PAN. This porous morphology results in a high uptake of liquid electrolytes as well as a high lithium transference number. Under all charge/discharge rates (from 0.1 to 3C), the capacities of the cells

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comprising this hybrid polymer electrolyte containing PDMS were higher than those of the polymer electrolytes without PDMS, particularly under the high discharge rate of 3C (114 mAh g^{-1} vs 70 mAh g^{-1}). In addition, the cross-linked hybrid GPEs interpenetrated by high-modulus PAN comprise a sturdy scaffold to efficiently function as a partition.

2. Experimental

2.1. Preparation of PEO-b-PAN copolymer

The poly(ethylene oxide-b-acrylonitrile) (PEO-b-PAN) copolymer was produced by the redox copolymerization of acrylonitrile monomer (≥ 99%, Sigma-Aldrich) with polyetheramine (JEFFAMINE® ED2003), the polymerization which was carried out by the method of our previously published procedures [21–35]. Polyetheramine was placed in a flask and dissolved in water, and nitrogen gas was introduced into the flask for 30 min. Thereafter, acrylonitrile was added into the flask to obtain a reaction mixture. Ceric ammonium nitrate in 1 M nitric acid was added drop-wise to the reaction mixture, and polymerization was allowed to proceed with stirring for 6 h to obtain a precipitated copolymer. The precipitated copolymer was washed three times with water. Next, the copolymer was dissolved in dimethylformamide (DMF) and precipitated with methanol. Then, the copolymer was dried at room temperature in vacuum for 48 h to obtain the PEO-b-PAN copolymer.

2.2. Preparation of hybrid polymer membrane (XSAE)

The polydimethylsiloxane (PDMS, Shinetsu KF-105) and polyetheramine were vigorously stirred for 24 h in N-methyl-2-pyrrolidone (NMP) solution. Then, different amounts (as outlined below) of PEO-b-PAN copolymers, polyetheramine and PDMS-PEO solution were mixed, after which poly(ethylene glycol) diglycidyl ether (PEGDE) (Kyoeisha Chemical Co., Ltd) was added under intense stirring for 6 h, producing two different systems of four solutions each. The solutions were then transferred to an aluminum plate to slowly remove the solvent at 80 °C; then, they were cured at 100 °C for 24 h and 155 °C for 2 h under vacuum to produce a cross-linked hybrid material. Subsequently, the solutions were stored in an Ar-filled glove box (Vacuum Atmosphere, USA) for further measurement. The thicknesses of these hybrid film specimens were controlled in the range of 130–150 µm. The four prepared samples are identified as XSAE(x–y), where x represents the PDMS–hybrid membrane weight ratio, while y denotes the acrylonitrile–ethylene oxide molar ratio; the sample without PDMS is labeled by XAE.

2.3. Characterization methods

The morphology of the GPE was investigated by field-emission scanning electron microscope (FESEM) (JEOL, JSM-6380LV); further, Fourier transform infrared spectroscopy (FTIR) was utilized to analyze the hybrid membranes from a Nicolet Magna II 550 spectrometer. The 1H NMR spectra of PEO-b-PAN copolymer was recorded on a Bruker AMX600MHz Digital NMR. Thermal gravimetric analyses (TGA) were measured by TGA7, Perkin-Elemer at a heat increment of 20 °C min^{-1} under ambient atmosphere. Differential scanning calorimetry (DSC) measures were run on a TA Instruments Q100 DSC under nitrogen atmosphere. The crystalline structures of the samples were characterized by X-ray diffraction (XRD) using a RIGAKU D/MAX with a step size of 0.01° for Cu-Kα radiation operated at 30 kV and 30 mA.

The amount of liquid electrolyte uptake (η) is calculated by using following equation:

$$\eta = (w_t - w_0)/\ w_t\ \times 100\% \qquad (1)$$

where W_0 and W_t are membrane weights prior and after absorbing the electrolyte solution, respectively. Weights were measured in a glove box.

2.4. Methods of electrochemical performance

The GPEs were analyzed by ac-impedance spectroscopy on an electrochemical instrument (CHI604A, CH Instrument, Inc.) and assembled between two stainless steel electrodes to characterize its ionic conductivity from 30 to 80 °C. Measurement was carried out at 0 V with an ac impedance spectroscopy of 10 mV while the frequency varied from 0.1 Hz to 1 MHz. The ionic conductivity (σ) was calculated according to the bulk electrolyte resistance (R) by using following equation:

$$\sigma = l/RA \qquad (2)$$

where l is the GPEs thickness and A is the contact area between GPEs and steel electrodes. Electrolyte t_{Li^+} values were measured by dc polarization and ac-impedance spectroscopic analysis with a sandwich-type cell Li/GPE/Li, combining the obtained parameters calculates the t_{Li^+} values [36].

Battery performance tests of the membranes were conducted by fabricating a 2032 coin-type cell with $LiFePO_4$ cathode and lithium metal anode. The cathodes were made by pouring a NMP-based slurry onto aluminum foil containing 80 wt% $LiFePO_4$ powder (Aleees, Taiwan),10 wt% polyvinylidene fluoride (PVDF), and10 wt% Super P. The electrodes were dried at 120 °C for 48 h under vacuum and were roll-pressed to ensure better particulate contact and foil adhesion. The cell assembly took place in a dry, Ar-filled glove box (the moisture content is < 5 ppm), and charge–discharge battery testing was conducted in the range of 2.5–4.0 V at 25 °C on a Battery Automatic Test System (Acu Tech Systems, BAT-750B).

3. Results and discussion

When applied in lithium batteries, GPEs should exhibit not only high ionic conductivity, electrochemical stability and good mechanical strength, but also chemical and thermal stability. To achieve these requirements, PDMS was introduced into cross-linked PAN/PEO as a good candidate for novel GPE systems. The PEO-b-PAN copolymer with amino group formation reacts in non-stoichiometric terms, with Ce(IV) as the initiator, which was synthesized in our previous work [21,35]. A series of cross-linked PDMS with PAN/PEO interpenetrated networks were prepared by curing PEO-b-PAN and polyetheramine with PEGDE and epoxied-PDMS in different compositions. The polyetheramine is pre-reacted with epoxied-PDMS to increase reactivity; the resulting polymer films were clear and supple, the schematic network structure of which is illustrated in Fig. 1. The IR spectra of PEO-b-PAN and the XSAE membrane are shown in the Supporting information. The PDMS shows strong bands at 800 and 861 cm^{-1}, which corresponds to Si-$(CH_3)_2$ symmetrical and asymmetrical rocking vibrations, respectively. The PEO-b-PAN shows that peaks at 2242 and 1094 cm^{-1} can be attributed to the -Cing vibrations, respectively. The PEO-b-PAN shows that peaks at 2242 and 1094 cmture of which is illustrated in e clea PDMS and PEO-b-PAN indicates that the XSAE membrane was successfully prepared.

The thermal stability property is paramount for polymer electrolyte application in lithium ion batteries. The weight-loss behaviors of the cross-linked polymers, given in Fig. 2, were