



Research paper

Investigation on polyethylene supported poly(butyl methacrylate-acrylonitrile-styrene) terpolymer based gel electrolyte reinforced by doping nano-SiO₂ for high voltage lithium ion battery



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ABSTRACT

In this paper, we design a novel gel polymer electrolyte (GPE), based on polyethylene (PE) supported poly (butyl methacrylate-acrylonitrile-styrene) (P(BMA-AN-St)) terpolymer reinforced by doping 10 wt.% nano-SiO₂, to be possible application in high voltage lithium ion battery. The physical characterization indicates that P(BMA-AN-St)/SiO₂/PE membrane has multi-layered and cross-linked network structure with the pore diameter of about 1 μm, leading to the highest electrolyte uptake ability of 257% compared with the value of 118% for PE support. Electrochemical performance exhibits that the corresponding GPE presents highest ionic conductivity of $1.9 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature and the improved oxidative stability from 4.2 V (PE support saturated with liquid electrolyte) to 5.2 V (vs. Li/Li⁺). Thus, the high voltage cathode LiNi_{0.5}Mn_{1.5}O₄ using nano-SiO₂ doped GPE presents excellent cyclic stability and rate performance, which retains 93.0% of its initial discharge capacity after 150 cycles at 0.2C rate and keeps 95.0% discharge capacity at 2C rate of that at 0.1C rate, while PE support saturated with liquid electrolyte has 87.9% capacity retention after 150 cycles and with the rate capacity value of 86.8% at the same rate test condition.

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1. Introduction

Lithium ion batteries (LIBs) has been widely used in various power and energy storage devices, due to its advantages of high energy density and operational voltage, long cyclic life, no memory effect and amity environment compared with traditional lead-acid battery [1–5]. Especially, two major challenges of environmental pollution and scarce fossil oil resources brought by the rapid development of automobile industry, force the human being to develop the electric vehicles (EV) by using LIBs as independent power sources. However, short driving distance and security problem of the current LIBs become the two obstacles for the further development of EV [6–8].

Among the strategies, the shortage of driving distance can be solved by promoting the energy density of the LIBs. Developing

higher specific capacities of electrodes or enhancing the working voltage of the LIBs accompanied by using high voltage cathode, such as 5V LiNi_{0.5}Mn_{1.5}O₄, will significantly contribute to the energy density enhancement of the battery. Unfortunately, it is not easy to accomplish in commercial carbonated liquid electrolyte, because the working voltage enhancement is accompanied with the decomposition of liquid electrolyte [9,10].

Since the liquid electrolyte plays the determined role in lithium ion transfer process although it shows the physical properties of low flash point and low ignition temperature, the source for the unsafe LIBs should be ascribed to use the organic liquid electrolyte because the proper temperature will trigger its decomposition [11,12]. However, raised temperature during cycling is inevitable, which is accompanied by intercalation/deintercalation process, especially the inside temperature is shortly enhanced undergoing the bigger current density. The quickly accumulated heat triggers the chain reactions such as the decomposition of the organic liquid electrolyte. Worse still, if the temperature cannot be controlled effectively, combustion or even explosion of the battery will happen naturally. Currently, there

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are two methods to improve the safety of LIB in EV field. One is adding additives into the liquid electrolyte, for example, flame retardant additive, and overcharge protect additive. This effect is obtained by decreasing the specified capacity and coulombic efficiency of electrode materials. The other method is coating copolymer onto both sides of commercial separator to reduce the activity of liquid electrolyte by restricting the liquid component into the copolymer matrix to form the gel polymer electrolyte (GPE) [13–15]. In the early days, many papers are committed to report the GPEs based on polymers matrices that are formed by the same monomers, such as the PEO [16,17], PAN [18–20], PMMA [21–23], PVdF [24]. Those GPEs show some defects in performance, such as low ionic conductivity, mechanical strength, or electrochemical stability [25–27]. To reinforce this effect for the second method, proper content of nano-particles, such as TiO₂, MgO, Al₂O₃, and SiO₂, is added together with the polymer to improve the thermal conductivity inside the battery [28–32], which is still far away for application in commercial LIBs.

To overcome the disadvantages brought by single polymer based GPE, poly(vinylidene fluoride)-hexafluoropropene (PVdF-HFP) as the traditional copolymer, has been successfully used in commercial polymer LIBs, but its disadvantage of high crystallinity along with declining the ionic conductivity of GPE cannot be overcome at present [33]. As alternative, serials poly(methyl acrylate) (PMA) copolymers that has high liquid electrolyte uptake and ionic conductivity are developed in our groups [34–43]. In our previous investigation, self-supported poly(butyl methacrylate-styrene) (P(BMA-St)) binary copolymer, especially adding 10 wt.% nano-SiO₂ to form P(BMA-St)/SiO₂ based GPE, exhibits its improved electrochemical performance compared with single PBMA based GPE [44].

Inspired by copolymerizing with different functional monomers drastically improves the comprehensive performance of single GPE, AN monomer is added to form terpolymer poly(butyl methacrylate-acrylonitrile-styrene) (P(BMA-AN-St)) at the first time, in which combines the advantages of better compatibility with liquid electrolyte of PBMA, the pleasant electrochemical stability of PAN, and the high mechanical strength of PSt.

To further enhance the performance of P(BMA-AN-St) based GPE, 10 wt.% nano-SiO₂ is doped into this typical terpolymer matrix originally. Polyethylene (PE) is used as support with the aim to assure the mechanical strength of developed GPE. The physical and electrochemical performances of GPEs without and with 10 wt.% nano-SiO₂ are investigated systematically in this paper. To explore the practical effect of the developed GPE in high voltage environment, 5V LiNi_{0.5}Mn_{1.5}O₄ is selected as high voltage cathode. The test results show that the improvement in the electrochemical performance by using nano-SiO₂ contained gel polymer electrolyte is significant.

2. Experimental

2.1. Preparation

Commercial BMA (>99.5 wt.%), AN (>98.0 wt.%) and St (>98 wt.%) as monomers, sodium dodecyl sulfate (>59 wt.%) as emulsifier, sodium persulfate (Na₂S₂O₈, >98.0 wt.%) as initiator, aluminum sulfate (Al₂(SO₄)₃, >99.0 wt.%) as demulsifier, were used to prepare the terpolymer P(BMA-AN-St) by emulsion polymerization. The monomers of BMA, AN, and St with the mass ratio of 1:2:1 were mixed, and then dissolved in deionized water with 1.5 wt.% emulsifier to form the homogeneous solution under N₂ atmosphere at 60 °C for 30 min. Subsequently, slowly adding 0.15 wt.% initiator and stirring at 800 rpm persistently for 6 h. The resulting pure white emulsion was poured into 3 wt.% Al₂(SO₄)₃ solution to yield the precipitate. After washing by deionized water

and ethyl alcohol repeatedly, the P(BMA-AN-St) terpolymer in the form of white powder was dried in vacuum at 60 °C for 24 h.

The prepared terpolymer was dissolved in N,N-dimethylformamide (DMF, >99.5 wt.%) at a concentration of 7 wt.%, then stirred at 80 °C for 1 h. To prepare the nano-particle doped terpolymer membrane, 10 wt.% (mass ratio) nano-SiO₂ (Aladdin, 99.5%, average particle size 30 nm) of terpolymer was also added into DMF solution by ultrasonic dispersion. After complete dissolution, the viscous slurry was coated onto both sides of the commercial polyethylene (PE) support. The membranes were immersed into the deionized water for 2 h to induce the phase transition. By the exchange of DMF as solvent and water as non-solvent, the porous polymer membranes were gained. Finally, the polymer membranes without and with 10 wt.% nano-SiO₂ were obtained by drying in vacuum at 60 °C for 24 h.

To prepare the corresponding GPEs without and with 10 wt.% nano-SiO₂, the polymer membranes were cut into 18 mm in diameter and immersed into a liquid electrolyte of 1 M LiPF₆ solution using ethylene carbonate (EC)/dimethyl carbonate (DMC) as solvent (EC/DMC=1/1 (v/v), battery grade, Dongguan Kaixin Materials Technology Co. Ltd, China) for 1 h in an argon-filled glove box (Mbraun Unilab MB20, Germany).

2.2. Characterization

The functional groups of the monomers and synthesized terpolymer were characterized by Fourier transform infrared spectra (FTIR, Nicolet6700, USA) in the range of 500–4000 cm⁻¹. The morphology of the membranes was examined by scanning electron microscope (SEM, Jeol, JSM-6510, Japan). The thermal stability of the terpolymer membranes was carried out on thermogravimetric analyzer (Netzschsta 409 PC/PG, Germany). Mechanical strength was measured by Gotech GT-TS-2000 system with the samples area of 2 cm × 10 cm. The porosity of membranes was calculated by Equation (1):

$$P(\%) = \frac{W_w - W_d}{\rho_b \times V_m} \times 100\% \quad (1)$$

where W_w and W_d were the mass of n-butanol soaked membrane and dry membrane, respectively, ρ_b was the density of n-butanol and V_m was the volume of the dry membrane.

The electrolyte uptake ability of the membranes was obtained according to Equation (2):

$$A(\%) = \frac{W_2 - W_1}{W_1} \times 100\% \quad (2)$$

where $A(\%)$ was the electrolyte uptake percentage, W_1 was the mass of the dry membrane, and W_2 was the mass of the membrane after soaking in liquid electrolyte for a certain time.

The ionic conductivities of the developed GPEs at different temperatures were measured by AC impedance method on the structure of SS(stainless steel)/GPE/SS block cell through electrochemical instrument (Metrohm Autolab, Pgstat302N, Netherlands) over the frequency range from 100 kHz to 1 Hz with the amplitude of 10 mV at open circuit voltage. The ionic conductivity (σ) was calculated from the bulk electrolyte resistance (R) by Equation (3):

$$\sigma = \frac{l}{RS} \quad (3)$$

where l was the thickness of the GPE, S was the contact area between GPE and SS disc.

The activation energy (E_a) for lithium ion transportation was obtained from the slope of the fitted solid line $\lg \sigma \sim 1000/T$ based on the Arrhenius equation (4):

$$\sigma = \sigma_0 \exp[-E_a/(RT)] \quad (4)$$

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