



Effect of polyacrylonitrile on triethylene glycol diacetate-2-propenoic acid butyl ester gel polymer electrolytes with interpenetrating crosslinked network for flexible lithium ion batteries



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HIGHLIGHTS

- Flexible GPE(TEGDA-BA/PAN) with interpenetrating crosslinked network is fabricated.
- The GPE exhibits excellent mechanical bendability and stable Li⁺ diffusion channel.
- The resulting GPEs have high ionic conductivity up to $5.9 \times 10^{-3} \text{ S cm}^{-1}$.
- The addition of PAN effectively improves compatibility between GPE and Li metal.
- Cycle stability of LiFePO₄/GPE|Li₄Ti₅O₁₂ full cells is demonstrated.

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ABSTRACT

A new flexible gel polymer electrolytes (GPE) with interpenetrating cross-linked network is fabricated by blending long-chain polyacrylonitrile (PAN) polymer matrix and short-chain triethylene glycol diacetate-2-propenoic acid butyl ester (TEGDA-BA) framework, with the purpose of enhancing the mechanical stability of the GPE frameworks via synergistic effects of the linear polymers and crosslinked monomers. The as fabricated frameworks enable the liquid electrolytes to be firmly entrapped in the polymeric matrices, which significantly improves the mechanical bendability and interface stability of the resultant GPE. The GPE with 5 wt% PAN exhibits high ionic conductivity up to $5.9 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C with a stable electrochemical window observed (>5.0 V vs. Li/Li⁺). The Li|GPE|LiFePO₄ half cells demonstrate remarkably stable capacity retention and rate ability during cycling tests. As expected, the LiFePO₄/GPE|Li₄Ti₅O₁₂ full cells also exhibit discharge capacity of 125.2 mAh g⁻¹ coupled with high columbic efficiency greater than 98% after 100 cycles. The excellent mechanical flexibility and charge/discharge performance suggest that the GPE holds great application potential in flexible LIBs.

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1. Introduction

High-performance rechargeable flexible lithium-ion batteries (LIBs) with long cycle life, high specific power and energy density are attractive candidates for portable electronic devices, electric vehicles and bendable electronic products [1–3]. The flexible polymer electrolytes of high safety, mechanical flexibility and electrochemical performance are the key components for constructing flexible LIBs [4]. However, common liquid electrolytes

may raise crucial crisis, such as fires and explosion, due to the existence of highly flammable organic solvents (usually carbonates such as ethyl carbonate and dimethyl carbonate), which could cause safety problems [5]. Compared to dried solid polymer electrolytes [6,7], gel polymer electrolytes (GPE) [8–10], formed by immersing large amount of liquid organic electrolytes into polymer frameworks, have received increasing attention in the flexible LIBs due to their high ionic conductivities on the order of $10^{-3} \text{ S cm}^{-1}$ at ambient temperature. Various polymer matrices, such as polyethylene oxide (PEO) [11,12], polyacrylonitrile (PAN) [13,14], polyvinylidene fluoride (PVDF) [15–17], poly(vinylidene fluoride-hexafluoro propylene) (PVDF-HFP) [18,19], polymethylmethacrylate (PMMA) [20,21], polyimide (PI) [22,23],

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poly(urethane) (PU) [24,25] and etc., have been widely developed as candidate materials for the preparation of polymer electrolytes. Especially, PAN have been developed and attracted as the main component for applications not only in electric double layer capacitors [26,27], but also in LIBs [28,29]. GPE can be prepared by solvent-casting techniques [30,31], thermally induced phase separation [32,33], electrospinning technology [34,35] and *in situ* polymerization [36,37]. Among the aforementioned methods, *in situ* polymerization can provide an effective approach to achieve the targeting electrolytes and batteries in one step, which effectively improves production efficiency. To fabricate crosslinked GPE, precursor solutions composing of liquid electrolytes, initiators and monomers with low molecular weight are treated by methods such as thermal initiation [38,39], UV-crosslinking [40,41] and γ -ray irradiation [42] to achieve free radical polymerization. In the GPE system, host polymers provide dimensional stability, and liquid electrolytes trapped in the polymer framework contribute to the ionic conduction. However, the high reactivity with lithium metals, insufficient mechanical strength and persistent structure of GPE are critical deficiencies for preventing their use in practical LIBs [43]. Significant efforts have been made to enhance physical and electrochemical performance, such as grafting [44], blending [45], copolymerizing [46] and incorporating inorganic fillers [47,48] into polymer matrices. In comparison, interpenetrating crosslinked networks by blending different polymeric matrices are capable of providing enhanced mechanical flexibility and compatibility for the electrodes, which is essential for improving safety operation in the charge/discharge cycling processes [28,49].

According to our previous studies [50], GPE with three-dimensional network structures that composed triethylene glycol diacetate (TEGDA)-2-propenoic acid butyl ester (BA) copolymers and liquid electrolytes, has been fabricated via *in situ* polymerization. The high ionic conductivities and enhanced electrochemical properties can be ascribed to the fact that liquid electrolytes have been well dispersed in the polymer networks, which makes the major contribution to the migration of Li ions. However, the mechanical strength of GPE is seriously deteriorated because of the presence of liquid electrolytes. Thus, this GPE presents gelatinous jelly at macroscopic level with unsatisfied mechanical properties, and exhibits poor dimensional stability. Hence, these undesirable features would lead to mechanical damage in further cell assembly. The TEGDA-BA is lack of mechanical robustness to be self-supported. Thus, a Celgard 2400 separator is a requirement to absorb the gel precursor solution for improving the cell safety.

To address the incompatible issue between mechanical properties and ionic conductivities, a new flexible GPE with interpenetrating cross-linked networks was synthesized by blending PAN polymer matrix with TEGDA-BA framework. The highly robust free-standing film demonstrates significant improvements in the flexibility and dimensional stability, which is mainly attributed to the synergistic effect of the crosslinked short-chain monomers (TEGDA-BA) and linear long-chain polymer (PAN). Owing to the co-presence of TEGDA-BA and PAN polymer matrices, the GPE exhibits considerable enhancement in the film formability, bendability and interface stability. Up to date, very limited literature has reported the studies on the bendable GPE reinforced with an interpenetrating cross-linked network via *in situ* polymerization at high-concentration liquid electrolytes (94 wt%). Electrochemical performances of the resultant GPE with different contents of PAN has been investigated using Li|GPE|LiFePO₄ half cells and LiFePO₄|GPE|Li₄Ti₅O₁₂ full cells separately. The well-established interpenetrating cross-linked framework provides stable Li⁺ diffusion channels, which significantly increase the cycle stability of the cells. As is essential for practical application, the influence on charge/discharge performance of full cells is discussed.

2. Experimental

2.1. Materials

TEGDA (C₁₂H₁₈O₆), BA (C₇H₁₁O₂), 2, 2'-Azobis-(2, 4-dimethylvaleronitrile) (ABVN, C₁₄H₂₄N₄) and 1 M LiPF₆/ethylene carbonate (EC): dimethyl carbonate (DMC): ethylmethylcarbonate (EMC) (1:1:1, in volume) were obtained from Shenzhen Capchem Technology Co., Ltd. and used as received without further purification. PAN (Mw = 150,000) was purchased from Alfa Aesar. The cathode material LiFePO₄ was purchased from Aleees. The anode material Li₄Ti₅O₁₂ was prepared according to the literature [51].

2.2. Preparation of gel polymer electrolytes

For the preparation of GPE, PAN was firstly suspended in 1 M LiPF₆/(EC + DMC + EMC) under magnetic stirring for 24 h, and then TEGDA, BA and ABVN were dissolved in the above suspension and further stirred for 0.5 h to form precursor solution. The composition ratio of the precursor solution was liquid electrolytes/comonomer = 94/6 w/w, wherein concentration of TEGDA and BA (monomer mixtures) was in a weight ratio of 4:2, ABVN (thermal initiator) was 1 wt% of the monomer mixtures. The concentration of PAN in the prepared GPE varied from 0 to 7.5 wt%. Then, the precursor solution was cast onto a Teflon plate, followed by being sealed in a closed glass dish. Finally, the GPE were formed by heating the above mixture at 80 °C (30 min) for *in situ* thermal polymerization. All the procedures were carried out in the glove box under argon atmosphere (H₂O < 1 ppm).

2.3. Characterization of the gel polymer electrolytes

The surface morphology was characterized by high field-emission scanning electron microscopy (FE-SEM, JSM-6330). The Brunauer–Emmett–Teller (BET) surface area was determined from the nitrogen adsorption–desorption isotherms using Quantachrome Autosorb-IQ2 analyzer after being degassed at 50 °C for at least 3 h. The reaction of thermal polymerization was examined by using Fourier transform infrared (FT-IR) spectra on a PerkinElmer Spectrum GX instrument in the range of 4000–1000 cm⁻¹ at ambient temperature. The TEGDA-BA precursor solution (before gel) was dropped on the surface of KBr pellets. The TEGDA-BA/PAN (after gel) was finely ground and dispersed into KBr powder-pressed pellets. The mechanical properties were performed by assembling the GPE (dimensions: length = 40 mm, width = 20 mm) between two stainless steel clamps with a tensile speed of 1 mm min⁻¹ on texture analyzer (TA-Xt. Plus, SMS). The thermal stability of the electrolytes was analyzed by a thermogravimetric analyzer (TGA, TA 2920) in the temperature range from 25 to 200 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

The ionic conductivities were acquired by electrochemical impedance spectroscopy (EIS) method with AC amplitude of 5 mV over the frequency range of 100 KHz–0.1 Hz and a temperature range from –20 to 80 °C on a CHI660C Electrochemical Workstation (Shanghai Chenhua). The electrochemical stability window was measured by linear sweep voltammetry (LSV), consisting of a stainless steel blocking electrode as the working electrode and a lithium metal as the reference and the counter electrode at a scanning rate of 10 mV s⁻¹ from 2.0 to 6.0 V vs. Li/Li⁺. The interfacial stability was determined by sandwiching the GPE between two lithium electrodes to form a symmetrical Li|GPE|Li cell.

To illustrate the electrochemical properties, the cathode of two-electrode 2032 coin-type cells was prepared by dispersing LiFePO₄ (80 wt%), Super P (15 wt%) and PVDF (5 wt%) in N-

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