



Short communication

Preparation and electrochemical properties of gel polymer electrolytes using triethylene glycol diacetate-2-propenoic acid butyl ester copolymer for high energy density lithium-ion batteries



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HIGHLIGHTS

- BA–TEGDA copolymer-based GPE were prepared by in situ thermal polymerization.
- The GPE had a well cross-linked framework and excellent mechanical properties.
- The in situ polymerization simplified the assembly process of batteries greatly.
- The GPE could satisfy the use of the high-voltage positive electrode material.

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ABSTRACT

Gel polymer electrolytes (GPE) composed of triethylene glycol diacetate (TEGDA)–2-propenoic acid butyl ester (BA) copolymer and commercial used liquid organic electrolyte are prepared via in situ polymerization. The ionic conductivity of the as-prepared GPE can reach $5.5 \times 10^{-3} \text{ S cm}^{-1}$ with 6 wt% monomers and 94 wt% liquid electrolyte at 25 °C. Additionally, the temperature dependence of the ionic conductivity is consistent with an Arrhenius temperature behavior in a temperature range of 20–90 °C. Furthermore, the electrochemical stability window of the GPE is 5 V at 25 °C. A Li|GPE(Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O₂) cell has been fabricated, which shows good charge–discharge properties and stable cycle performance compared to liquid electrolyte under the same test conditions.

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1. Introduction

Gel polymer electrolytes (GPE) have received increasing interest worldwide since they overcame the safety problems caused by liquid electrolyte such as the possibility of leakage [1,2]. Furthermore, due to the easily shaped properties, the gel polymer electrolytes permit the development of thin batteries with design flexibility. Nowadays, considerable efforts are being focused on the development of new types of advanced lithium-ion batteries with GPE. In order to provide high power density, GPE should have good mechanical properties, stable performance in the practical applications and high ionic conductivity at ambient temperature [3]. Since the first demonstration of GPE reported by Feullade and

Perche in 1975 [4], various polymers such as poly(acrylonitrile) (PAN) [5,6], poly(vinylidene fluoride) (PVDF) [7,8], poly(methyl methacrylate) (PMMA) [9,10], poly(vinyl chloride) (PVC) [11,12], poly(ethylene oxide) (PEO) [13,14] and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [15,16] have been widely used as polymer matrices for the preparation of GPE. In the GPE, the liquid electrolytes are retained in a polymer framework and contribute to the ionic conduction, whereas the host polymer provides dimensional stability to the gel electrolyte system. The most advantageous features of these electrolytes lie in their free-standing consistency and high ionic conductivities exceeding $10^{-4} \text{ S cm}^{-1}$, which is significant for battery applications.

It is critical to develop suitable GPE with good lithium interface stability, high electrochemical stability, high mechanical strength and high ionic conductivity for lithium ion batteries. As a common matrix polymer used in the GPE, PMMA has been proposed for lithium battery applications [17]. Meanwhile, its amorphous

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structure is beneficial to the ionic conduction ($1 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature). Besides, the PMMA-based gel electrolytes have exhibited excellent interfacial stability towards lithium metals. It has also been reported that gel electrolytes based on cross-linked PMMA can suppress the formation of lithium dendrite [18]. In order to form free-standing films with a high content of organic solvents, however, PMMA has to be blended with other polymers such as poly(vinyl chloride) (PVC) [19] and acrylonitrile–butadiene–styrene terpolymer (ABS) [20]. Besides, the GPE can be prepared by ultraviolet-curing (UV), solvent-casting techniques, phase-inversion methods and in situ polymerization. Particularly, in the case of in situ polymerization, the preparation of the electrolyte membrane and the assembly of the batteries could be achieved in one step, effectively improving the production efficiency and reducing the costs [21,22]. A precursor consisted of a curable monomer and a liquid electrolyte was directly put into the lithium ion battery cell, followed by curing to form a polymer network [23]. Due to the relatively low viscosity, the precursor can be easily wetted into the electrodes and separators, then resulting in good contact and affinity with the electrode and electrolytes.

In this work, in order to prepare highly conductive GPE with high mechanical strength, TEGDA–BA copolymer has been synthesized as the polymer matrix for the GPE, 2,2'–Azobis(–2,4-dimethylvaleronitrile) (ABVN) as the thermal initiator, and 1 M LiPF₆/ethylene carbonate (EC):dimethylcarbonate (DMC):ethylmethylcarbonate (EMC) (1:1:1 in volume) as the electrolyte. By using in situ polymerization, the precursor was directly put into the lithium ion battery cell, followed by curing to form a polymer network. The two vinyl bonds at the end of TEGDA can form a dense network structure, which leads to high mechanical strength for the polymer. The ionic conductivities and electrochemical properties of the GPE were examined. A high capacity cathode material (Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O₂) has been prepared to assemble the Li[GPE](Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O₂) cells and the electrochemical characteristics and cycling performance were evaluated.

2. Experimental

To synthesize the GPE, TEGDA and BA (CAPCHEM CO., LTD.) were prepared as the monomer mixtures in a weight ratio of 2:4. An appropriate amount of ABVN (CAPCHEM CO., LTD.) (1 wt% the monomer mixtures) was added as thermal initiator. A battery grade solution of 1 M LiPF₆/EC:DMC:EMC (1:1:1 in volume) (CAPCHEM CO., LTD.) was added and then the solution was further stirred. The amount of electrolyte solution (94 wt%) was added based on the total weight of the GPE composed of matrix polymer and liquid electrolyte. All the procedures were carried out in the glove box with argon gas. The GPE was synthesized after keeping the precursor in a water bath at 80 °C (30 min) for thermal polymerization.

The cross section morphology of the GPE membrane was observed by a scanning electron microscopy (SEM) on an EVO 18 system. Pore diameters of these membranes and their distribution were estimated based on SEM micrographs. Mechanical stress versus strain measurement of electrolyte was performed by applying stress with a compression speed of 0.5 mm min⁻¹ using a circular electrolyte plate with the diameter of 20 mm and the thickness of 1 mm on a WDS-5 electronic universal testing machine (Changchun Chao yang test instrument Co. LTD).

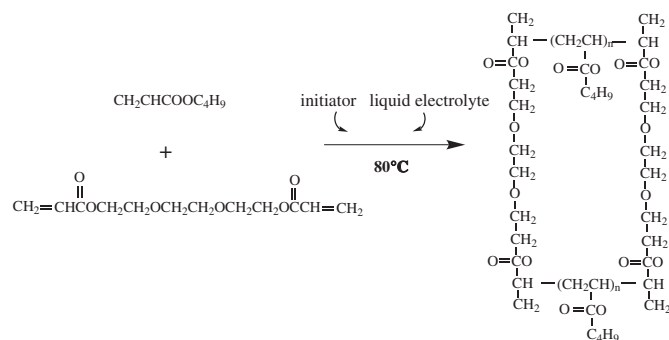
The GPE was sandwiched between two platinum electrodes to fabricate the testing cell for ionic conductivity measurement. The AC impedance measurement was performed using a CHI660C impedance analyzer over the frequency range from 10⁵ Hz to 1 Hz with the potential amplitude of 5 mV. In order to investigate the temperature dependence of ionic conductivity for GPE, the measurement was carried out in the range of 20–90 °C.

The electrochemical stability window of the GPE was measured by cyclic voltammetry at room temperature using stainless steel as the working electrode and lithium as both the counter and reference electrodes. Electrochemical stability was scanned in a potential range of –0.5 to 5 V versus Li/Li⁺ at a scanning rate of 1 mV s⁻¹.

The lithium nickel manganese oxide (Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O₂) cathode was coated on an aluminum foil consisted of 80 wt% active material oxide, 15 wt% acetylene black and 5 wt% PVDF. Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O₂ cathode active material was synthesized by the coprecipitation method followed by a high-temperature solid-state reaction. A carbonate precursor Ni_{0.3}Mn_{0.7}CO₃ was firstly prepared by the coprecipitation of a 2 mol L⁻¹ aqueous solution of Ni, Mn sulfate (Ni:Mn = 3:7 in molar) and a 2 mol L⁻¹ solution of Na₂CO₃ with 0.3 M NH₄OH added as a chelating agent. The pH of the mixed solution was adjusted to 8 and the co-precipitation temperature was controlled at 55 °C. The obtained Ni_{0.3}Mn_{0.7}CO₃ was washed with deionized water several times and subsequently dried in a vacuum oven. Thereafter the carbonate Ni_{0.3}Mn_{0.7}CO₃ was thoroughly mixed with Li₂CO₃ according to the stoichiometric ratio, and then annealed in air at 450 °C for 6 h to decompose the carbonate precursors followed by calcining at 850 °C for 10 h. The Li foil was used as anode and Celgard 2400 as the separator. A 2032 type of coin cell was fabricated in the glove-box filled with argon gas. In the fabrication process, the precursor, the blend of 6 wt% monomer mixtures, 1 wt% initiator, and 94 wt% liquid electrolyte, was added into the assembled cell. The assembled cells were settled for 4 h to ensure the precursor solution to be well wetted into the electrodes and then the cell was heated at the temperature of 80 °C (30 min) for polymerization. The charge and discharge cycling tests of the lithium-ion polymer cells were conducted at 25 °C, and the voltage range of the Li[GPE](Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O₂) cell was 2.0–4.8 V. For the comparison, the conventional battery with liquid electrolyte instead of precursor solution of GPE was also assembled, and tested under the same conditions.

3. Results and discussion

The GPE were prepared via the in situ polymerization by copolymerizing the monomers TEGDA and BA. As shown in Scheme 1, the primary radicals were firstly formed by the decomposition of the initiator, which open the double bonds of the vinyl monomers to form a monomer radical. Then, the monomer radicals continue to open the double bond of the other vinyl monomers for the addition reaction. After that, the polymer molecular chains gradually increase with the addition of the vinyl monomer chain, and ultimately formed a three-dimensional structure of the polymer backbone. It is well-known that both the industrial assembling method and practical application safety, mechanical properties are key factors [24]. The stress–strain curve of GPE is shown in Fig. 1a.



Scheme 1. Synthesis of the copolymer of 2-propenoic acid butyl ester (BA) and triethylene glycol diacrylate (TEGDA).

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