



Effect of alumina on triethylene glycol diacetate-2-propenoic acid butyl ester composite polymer electrolytes for flexible lithium ion batteries



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HIGHLIGHTS

- Flexible CPE (TEGDA-BA/Al₂O₃) employing LiPF₆/(EC + DMC + EMC) are fabricated.
- The inorganic filler with average particle size (<50 nm) into CPE is very rare.
- The resulting CPE have high ionic conductivity up to $6.02 \times 10^{-3} \text{ S cm}^{-1}$.
- Al₂O₃ improves mechanical bendability and compatibility between CPE and Li metal.
- The influence on cycle stability at different temperatures is rarely investigated.

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ABSTRACT

Triethylene glycol diacetate-2-propenoic acid butyl ester (TEGDA-BA) based composite polymer electrolytes (CPE) are fabricated by incorporating alumina (Al₂O₃) nanoparticles (average particle size 10–20 nm) as inorganic filler via *in situ* polymerization. Effects of Al₂O₃ concentration on ionic conductivities, Li⁺ transfer numbers and charge/discharge properties are studied in details. Due to the uniformly dispersed Al₂O₃ nanoparticles, significant improvements in the mechanical flexibility and bendability are presented in the resulting polymer electrolytes. The CPE with 5 wt% Al₂O₃ nanoparticles exhibits the highest ionic conductivity up to $6.02 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C and the highest Li⁺ transference number (0.675), coupled with the most stable electrochemical window (>4.5 V vs. Li/Li⁺). With the presence of Al₂O₃, the growth of interface resistance is retarded, which increases the interface stability. The Li|CPE|Li₄Ti₅O₁₂ and Li|CPE|LiFePO₄ cells demonstrate remarkably stable charge/discharge performance and excellent capacity retention during cycling test. The results suggest that the CPE holds great application potential in flexible lithium ion batteries.

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1. Introduction

High-performance rechargeable lithium-ion batteries (LIBs) with long cycle life, high energy and power densities are attractive candidates for high energy density power sources in portable electronic devices, electric vehicles and energy storage systems due to their low cost and high safety [1,2]. The flexible LIBs with high flexibility, high specific power and energy density are urgently required for the development of bendable, implantable, and

wearable electronic products [3,4]. The flexible polymer electrolytes with high ionic conductivity are the key component for constructing flexible LIBs [5]. Common liquid electrolytes containing highly flammable organic solvents (usually carbonates such as dimethyl carbonate and ethyl carbonate) may cause fires or explosions due to short circuits or local overheating [6]. Dry solid polymer electrolytes (SPE), consist of polymer and lithium salt, generally offer very low ionic conductivity although various modification methods have been adopted, e.g., by adding inorganic fillers, forming copolymer, decreasing the crystallinity of polymer, in the order of 10^{-8} – $10^{-5} \text{ S cm}^{-1}$ at room temperature, which excludes this type of membrane from practical applications [7–10]. Gel polymer electrolytes (GPE), formed by immersing large amount

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of liquid organic electrolytes into polymer framework, have high ionic conductivities in the order of 10^{-3} S cm^{-1} at ambient temperature. However, a thin GPE film with low ionic resistance generally lacks some key properties, such as high reactivity with lithium metal, poor mechanical integrity and persistent structure, which are essential for facile cell assembly [11–14]. Many studies have demonstrated enhanced electrochemical and mechanical properties by incorporating a wide range of inorganic fillers such as TiO_2 [15,16], SiO_2 [17–20], Al_2O_3 [21–23], thus developing a new family of composite polymer electrolytes (CPE). The mechanical flexibility, ionic conductivity and electrolyte/electrode interface stability have been improved by the addition of inorganic fillers [24,25]. It has been reported that the inorganic particles promote electrochemical properties of the polymer electrolytes, but only by physical actions without directly contributing to the lithium ion transport process [26]. After facilitating suitable surface modifications of inorganic particles, it could also act as a source of charge carriers [27]. Also, densely packed nanoparticles can obviously suppress lithium dendrite growth in the CPE with unique microstructure [28].

In comparison, little attention has been devoted to discussing the effect of inorganic filler (<50 nm) on physical and electrochemical performance of the CPE, which is essential for improvement of mechanical compatibility. Also, the researches on the CPE formed by incorporating inorganic filler into GPE, which was prepared by *in situ* thermal polymerization, are rarely reported. Based on such consideration, a new type of free-standing CPE has been synthesized for flexible LIBs to fundamentally understand the influence of nanosized fillers. In our previous study [29], cross-linked GPE composed of triethylene glycol diacetate (TEGDA)-2-propenoic acid butylester (BA) copolymer and commercial liquid organic electrolytes via *in situ* polymerization has been reported. The two vinyl bonds at the end of TEGDA can form a three-dimensional network structure through the addition reaction. The liquid electrolytes that were well dispersed in the polymer matrix make the major contribution to the migration of Li-ions, which leads to high ionic conductivities and enhanced electrochemical properties. However, the presence of liquid electrolytes leads to serious deterioration of the mechanical strength of the polymer. Thus, Celgard 2400 is needed as the separator to absorb the gel precursor solution in the fabrication process of the testing cells. To overcome the contradiction between mechanical properties and ionic conductivity, a new flexible CPE was synthesized by incorporating inorganic nanoparticles Al_2O_3 (average particle size 10–20 nm) as a functional filler into the cross-linked TEGDA-BA polymer matrix. The significant improvements of dimensional stability and mechanical bendability are mainly attributed to the presence of Al_2O_3 nanoparticles, which could serve as a mechanical buffer to dissipate external stress. For flexible LIBs, in addition to provide Li^+ diffusion channels, the CPE can be also used as the separator to prevent electron transfer between anodes and cathodes. Electrochemical performance of the resulted CPE with different contents of Al_2O_3 nanoparticles are investigated with Li|CPE|LiFePO_4 and $\text{Li|CPE|Li}_4\text{Ti}_5\text{O}_{12}$ half cells, respectively. With the presence of Al_2O_3 , the growth of interface resistance is retarded, which increases the interface stability. Especially, the influence on the cycle stability at different temperatures, which is rarely investigated, is discussed in detail.

2. Experimental

2.1. Materials

Al_2O_3 (>99.9%, average particle size 10–20 nm) was purchased from Alfa Aesar. TEGDA ($\text{C}_{12}\text{H}_{18}\text{O}_6$), BA ($\text{C}_7\text{H}_{11}\text{O}_2$), 2, 2'-Azobis-(2, 4-

dimethylvaleronitrile) (ABVN, $\text{C}_{14}\text{H}_{24}\text{N}_4$) and 1 M LiPF_6 /ethylene carbonate (EC): dimethylcarbonate (DMC): ethylmethylcarbonate (EMC) (1:1:1, in volume) were obtained from Shenzhen Capchem Technology Co., Ltd. and used as received without further purification. LiFePO_4 was purchased from Aleees. The cathode materials $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared according to literature [30].

2.2. Preparation of composite polymer electrolyte

In a typical preparation, Al_2O_3 , TEGDA, BA and ABVN were mixed into 1 M LiPF_6 /(EC + DMC + EMC) to form precursor solution by ultrasonic stirring for 4 h. 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 Al_2O_3 in the prepared CPE varied from 0 to 10 wt%. Then, the precursor solution was cast onto a Teflon plate, followed by being sealed in a closed glass dish. Finally, the CPE were formed by heating the above mixture at 80 °C (30 min) for *in situ* thermal polymerization. Then, the precursor solution was cast into a Teflon plate sealed in a closed glass dish. Finally, the CPE was 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 ($\text{H}_2\text{O} < 1$ ppm).

2.3. Characterization of physical properties and electrochemical performance of the composite polymer electrolyte

The surface morphology was characterized by transmission electron microscopy (TEM, JEM-2011) and high field-emission scanning electron microscopy (FE-SEM, JSM-6330). The fourier transform infrared (FT-IR) spectra was recorded on a PerkinElmer Spectrum GX instrument in the range of 4000–1000 cm^{-1} at ambient temperature. The ionic conductivity was acquired by electrochemical impedance spectroscopy (EIS) method with AC amplitude of 5 mV over the frequency range of 100 KHz to 0.1 Hz and a temperature range from –20 °C to 80 °C on a CHI660C Electrochemical Workstation (Shanghai Chenhua). The electrochemical stability window was measured by linear sweep voltammetry (LSV) in a three-electrode system, which consisted 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 1 mV s^{-1} from 2.0 to 6.0 V (versus Li/Li^+). The interfacial stability of the CPE was sandwiched between two lithium electrodes to form a symmetrical Li|CPE|Li cell.

The two-electrode 2032 coin-type cells were fabricated by using LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as positive and negative electrodes, respectively, to illustrate the electrochemical properties. The slurry for preparing positive electrode was obtained by dispersing LiFePO_4 active materials (80 wt %), carbon black (Super P, 15 wt %) and PVDF (5 wt %) in N-methylpyrrolidinone solution. The slurry for preparing negative electrode was acquired by mixing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Super P with PVDF in a weight ratio of 80:10:10. Subsequently, the slurries were spread on an aluminum foil and a copper foil separately (used as current collectors) and dried at 60 °C to remove the solvent. After that, the electrodes were cut into disks (14 mm in diameter) and dried at 120 °C for 12 h in vacuum. The 2032 cells were assembled by sandwiching the CPE electrolytes-integrated LiFePO_4 cathode and a Li metal anode in an argon-filled glove box. Other testing cells were assembled using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as working electrode and Li foil as the counter electrode.

The charge–discharge capacity and cycle ability of the Li|CPE|LiFePO_4 cells were estimated at 0.1 C (1 C = 170 mAh g^{-1}) under a voltage range between 2.0 and 4.2 V by using a CT2001A cell test

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