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An effectively inhibiting lithium dendrite growth in-situ-polymerized gel polymer electrolyte

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ABSTRACT

Polyacrylate polymer is a promising polymer matrix for gel polymer electrolyte (GPE) in lithium-ion batteries. Herein, *in-situ* polymerized poly(ethylene glycol phenyl etheracrylate) (PEGPEA) based GPE combined with 1 M LiPF6 in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (EC/DMC/EMC, 1:1:1 in volume) solvents was introduced. The maximum recoverable strain of the *in-situ* polymerized PEGPEA-GPE was up to 99%. The outstanding interfacial compatibility between PEGPEA-GPE and the lithium electrode was also obtained. Surprisingly, lithium dendrite was effectively suppressed in charge-discharge cycling because of polymer-enhanced solid electrolyte interphase (SEI) and excellent contact interface. Furthermore, the PEGPEA-GPE exhibited wide electrochemical stability window up to 4.9 V versus Li^+/Li, and achieved an ionic conductivity of 3.35×10^{-3} S cm^{-1} at 25 °C. When used as electrolyte, the $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$/PEGPEA-GPE/Li batteries showed high discharge capacity retention rate of 97.5% after 70 charge-discharge cycles and considerable discharge rate capability, i.e., 155 mAh g^{-1} 0.2C, 142 mAh g^{-1} 0.5C, 120 mAh g^{-1} 1C, 60 mAh g^{-1} 2C. These results demonstrate that this highly elastic *in-situ* polymerized PEGPEA-GPE is a potential electrolyte system for high-performance polymer electrolyte lithium-ion batteries and has excellent application prospects in wearable and flexible batteries.

1. Introduction

In recent years, secondary rechargeable lithium-ion batteries (LIBs) have drawn much attention and have been widely used in electronic vehicles and various portable digital devices [1–4]. Lithium metal, as an ideal anode material, has a low potential of −3.04 V (versus the standard hydrogen electrode) and a high theoretical specific capacity of 3860 mAh g^{-1}. However, its practical application has been prevented due to the potential explosion or ignition hazard caused by dendrite formation on the lithium metal anode surface during charge/discharge cycling in liquid organic electrolytes [5–9]. Gel polymer electrolytes (GPEs), containing polymer matrices and liquid electrolytes, offer several advantages such as excellent processing performance, flexibility, minimized dendrite growth, and enhanced endurance of the electrodes to volume change during charge/discharge process in LIBs [10,11]. Since the first report of GPEs in 1975, various polymers have been introduced into GPEs such as polyethylene oxide (PEO) [12–15], polyvinylidene fluoride & poly(vinylidene fluoride-hexafluoropylene) (PVDF & PVDF-HFP) [16–18], polymethyl methacrylate (PMMA) [19–22], polyacrylonitrile (PAN) [23–26], Polyvinyl chloride (PVC) [27–29], and polyacrylate [30–32]. In GPE systems, liquid electrolytes were immobilized into polymer matrix, which induces a high conductivity, and maintains a high mechanical stability as a separator in LIBs. Therefore, for LIB applications, it is important to ensure electrochemical stability of the electrolyte and high ionic conductivity as well as stability of the polymer network.

The common methods used for preparation of GPEs are solvent-casting techniques [33], phase-inversion techniques [34], ultraviolet-curing (UV) [35] and in situ polymerization strategies [36]. In particular, the *in-situ* polymerization synthesis of GPEs has become a popular strategy because the synthesis of the polymer electrolyte membrane and the batteries assembly can be achieved

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in one step [37]. The monomer and initiator fully dissolve in liquid electrolyte and the mixture are placed into a lithium battery case; a polymer network is then formed by cross-linking polymerization [38]. The low viscosity of the precursor solution makes it easy for the electrolyte and electrode material to be infiltrated, resulting in good interface performance with the electrode and electrolytes. The GPE consisting of poly(ethyl cyanoacrylate) and 4 M $LiClO_4$ in carbonate solvents was prepared by in situ polymerization [37]. The interface between in-situ generated GPE and the ex-situ GPE was also analyzed. The ionic conductivity of the gel was 2.7×10^{-3} S cm^{-1} at room temperature. And the electrochemical window was up to 4.9 V (versus. Li^+/Li).

Importantly, polymer electrolyte has an advantage over liquid electrolytes in inhibiting lithium dendrite growth. Some strategies have achieved inhibition of lithium dendrite, such as anion-immobilized polymer-inorganic compounds [39], soft-rigid protective layer [40], fluoroethylene carbonate additives [41], self-plasticization double-network structure [42]. However, lithium dendrite growth and unsatisfactory interface performance are still limiting the GPEs. In this work, those two issues had been taken into account. Highly ionic conducting, flexible, and stable GPE was prepared by an *in-situ* polymerization strategy. A precursor solution consisting of 2,2′-azobis-(2,4-dimethylvaeronitrile) (AIBN) as the initiator, 1 M LiPF6 in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (EC/DMC/EMC, 1:1:1 in volume) as the electrolyte, and ethylene glycol phenyl ether acrylate as a curable monomer, was evenly mixed and then cured under facile conditions to form a polymeric matrix. As a result, high compression variable (99%), high ionic conductivity (3.35×10^{-3} S cm^{-1}), wide electrochemical stability window (4.9 V), and outstanding interface compatibility with lithium metal of PEGPEA-GPE were obtained. Stable discharge capacity retention rate (97.5% after 70 charge-discharge cyclings) and considerable discharge rate capability (155 mAh g^{-1} 0.2C, 142 mAh g^{-1} 0.5C, 120 mAh g^{-1} 1C, 60 mAh g^{-1} 2C) of $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$/PEGPEA-GPE/Li were achieved. In brief, the *in-situ* polymerized highly elastic and reliable PEGPEA-based GPE is a potential electrolyte system for high performance LIBs, which possesses excellent application prospects in wearable and flexible batteries.

2. Experimental section

2.1. Materials

Ethylene glycol phenyl ether acrylate (EGPEA, Aladdin, 90%), 1 M solution $LiPF_6$ in EC-DMC-EMC (1:1:1 in volume, Ningbo, China), 2,2′-azobis-(2,4-dimethylvaeronitrile) (AIBN, Macklin, GR), nickel sulfate ($NiSO_4 \cdot 6H_2O$, aladin , 99.99%), manganese sulfate ($MnSO_4 \cdot H_2O$, aladin, 99.99%), cobalt sulfate ($CoSO_4 \cdot 7H_2O$, aladin, 99.99%), ammonia (NH_4OH, Xilong Scientific, AR), Sodium hydroxide (NaOH, Xilong Scientific, AR), lithium hydroxide monohydrate ($LiOH \cdot H_2O$, Macklin, GR) polyvinylidene fluoride (PVDF, Solvay, battery grade), Ketjen black carbon (Akzo Nobel N.V, battery grade), and N-methyl-2-pyrrolidone (NMP, aladin, GC) were commercially obtained. In addition, EGPEA was sealed and stored at 4 °C. Electrolyte solutions were stored in an argon glovebox.

2.2. Preparation of PEGPEA-GPE

The monomer EGPEA (200 μL), the liquid electrolyte (1 mL, 1 M $LiPF_6$ EC/DMC/EMC(1:1:1)), and initiator (AIBN, 0.3 wt% of monomer) were homogeneously mixed. The precursor solutions (150 μL) were cast onto the anode materials (0.5 mm thick Li metal and stainless steel current collector) and cathodes were suspended above the precursor solution. Then the polymerization was initiated at 55 °C for 3 h. Finally, the coin cells (CR 2025) were assembled. All experiments were conducted in an argon glovebox (water content $\leq$ 1 ppm). The areal loading of PEGPEA-GPE was 0.087 g cm^{-2}.

2.3. Preparation of $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$

The $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$ was prepared as the cathode material. First, the precursor $(Ni_{0.5}Co_{0.2}Mn_{0.3})(OH)_2$ was prepared as follows: $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot H_2O$ (molar ratio of Ni:Co:Mn = 0.5:0.2:0.3) were mixed in deionized water at a concentration of 3 mol/L. Certain amounts of NH_4OH solution (as a complexant), sulfate solution, and 10 mol/L NaOH solution (as a precipitant) were separately pumped into a continuously stirred (speed 800 r min^{-1}) tank reactor (CSTR, capacity of 5 L). The reaction process was controlled at 55 °C at a pH of 11 under a nitrogen atmosphere. The obtained hydroxide precursors were thoroughly washed, filtered, and dried at 60 °C for 12 h to obtain $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ powders. Second, the obtained precursor $(Ni_{0.5}Co_{0.2}Mn_{0.3})(OH)_2$ was thoroughly ground with the $LiOH \cdot H_2O$ powder. The mixture was initially heated at 480 °C for 5 h in air for infiltration of LiOH into the matrix, then calcined at 900 °C for 10 h in air and naturally cooled to obtain $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$ powders. The positive electrodes were prepared by mixing $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$, KB, and PVDF in a mass ratio of 80:10:10 (wt%). The resultant compound was dispersed in an appropriate amount of NMP. The slurry was deposited evenly on aluminum foil with a diameter of 10 mm and dried at 110 °C for 12 h under vacuum for use. The mass loading of obtained $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$ cathode was about 2.548 mg cm^{-2}.

2.4. Methods of characterization

The morphology and microstructures of PEGPEA-GPEs and lithium dendrite were studied by scanning electron microscopy (SEM, Phenom Prox). The free radical polymerization reactions were characterized using a Perkinelmer Frontier FT-IR spectrometer in the range 4000–400 cm^{-1} and Raman spectroscopy (Thermo Scientific) in the range 1650–1620 cm^{-1}. Compressive stress and strain of PEGPEA-GPEs were tested by applying a sustained pressure with a speed of 1 mm min^{-1} using an electronic universal tensile testing machine (Suns, UTM4203). Thermogravimetric analysis (TGA) of PEGPEA was carried out in the range of 30–600 °C with a heating rate of 10 °C min^{-1}.

Coin cells SS/PEGPEA-GPE/SS (SS, stainless-steel plate electrodes) were assembled to determining the ionic conductivity of the *in-situ* polymerized PEGPEA-GPEs at different temperatures (20–70 °C) by alternating current (AC) impedance measurements over the frequency range 1000 kHz to 0.1 Hz with a potential amplitude of 5 mV using an impedance analyzer (BioLogic,VSP-300). The coin cells Li/PEGPEA-GPE/SS were assembled to measure the electrochemical window of PEGPEA-GPE by cyclic voltammetry(CV) measurements at 25 °C over the potential range from −1 V to 5 V at a scanning rate of 0.1 mV s^{-1} using VSP-300. The interface impedance between lithium metal electrodes and PEGPEA-GPEs at different times (0–20 days) were carried out using coin cells Li/PEGPEA-GPE/Li (Li, lithium metal electrodes) by alternating current (AC) measurements in frequency range from 1000 kHz to 0.1 Hz and a potential amplitude of 5 mV. The coin cells Li/PEGPEA-GPE/Li were assembled to measure the plating and stripping of lithium ions with the current density of 0.1 mA cm^{-2} at 25 °C. The assembled $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$/PEGPEA-GPE/Li batteries determine the electrochemical performance of the *in-situ* polymerized PEGPEA-GPE using a LAND CT2001A battery test system. The cycle performance and rate performance of the batteries (Li