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Superior polymer backbone with poly(arylene ether) over polyamide for single ion conducting polymer electrolytes

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ABSTRACT

Effect of polyamide and poly(arylene ether) as backbones of bis(benzene sulfonyl)imide for single ion conducting polymer electrolytes on mechanical and electrochemical properties and device performance was investigated. Alternating copolymerization between 4,4′-fluorine bis(benzene sulfonyl)imide and 4,4′-dihydroxydiphenyl ether produced a poly(arylene ether) based polymer (LiPHFE). For comparison, 4,4′-dicarboxyl bis(benzene sulfonyl)imide was used to copolymerize with 4,4′-diaminodiphenyl ether to form a polyamide based polymer (LiPACA). Thermal stability, morphology, mechanical strength, electrochemical stability and battery performance were carefully measured. We conclude that the LiPHFE blend film is superior to the LiPACA blend film. Half-cells using $LiFePO_4$ (LFP) and $Li_4Ti_5O_{12}$ (LTO) incorporating the LiPHFE film as the electrolyte as well as the separator were tested separately at 1 C for 800 cycles. No obvious performance decay was observed, demonstrating exceptional device compatibility and stability. Finally, a full cell with the configuration of "LTO | LiPHFE | LFP" was assembled and subsequently tested at 0.5 C for 100 cycles. The device is capable of delivering a stable discharge capacity of 96 mAh g^{-1} normalized to the mass of LFP with the coulombic efficiency of 100%. This work paves a way for design of more robust single ion conducting polymer electrolytes to enable batteries to be operative with long cycle life and superior device safety.

1. Introduction

One of the most active subjects of battery research in recent years is on the development of single ion conducting all solid state batteries of high energy density and power density [1–5]. These batteries are promised to offer ultimate safety for device operation. Although tremendous efforts have been made for the battery development, there have been formidable challenges in materials and processes [6,7] that enable successful device fabrication at an industrial scale. One approach to the development of all solid state batteries is to utilize single ion conducting electrolytes in battery cells to replace the conventional liquid electrolytes made of a lithium salt dissolved in organic solvents, such as $LiPF_6$ in a mixture of ethylene carbonate and propylene carbonate, with electrodes separated by a polypropylene membrane [8]. A single ion conducting polymer electrolyte consists of an organic polymer with anionic charges anchored in the polymer network surrounded by electron withdrawing atoms to facilitate charge delocalization; lithium ions are separated from the anionic sites outside of the polymer network via weak charge pairing. This structural arrangement gives rise to high lithium ion mobility and suppresses anion motion [9–16]. Another important class of single ion conductors is comprised of nanocomposite polymer electrolytes made from lithiated transition metal fluorinated oxides dispersed with poly ethylene glycol (PEG) [17–19].

In recent years, significant efforts have been made to develop solid state single ion conducting polymer electrolyte materials for applications in lithium ion batteries [9–16,20,21]. The polymer electrolyte membranes allow relatively soft contacts between electrodes and the separator, and thus the interfacial resistance can be reduced. A few breakthroughs have been achieved to incorporate selected electrolyte membranes in all solid state batteries, although the devices were found to be operative only at elevated temperatures [8,17–19]. The inferior device performance at room temperature arises largely from the significantly smaller lithium ion mobility in a dry state. As a compromise, a single ion conducting polymer electrolyte membrane is often saturated with an appropriate organic solvent to facilitate lithium ion transport [22–30]. Consequently, the membrane becomes a gel electrolyte.

Chen et. al. assembled a working battery using a gel type single ion conducting polymer electrolyte in 2004 by replacing a commercial dual-ion based electrolyte with a lithium ion exchanged Nafion film swelled with a solvent made of propylene carbonate (PC) and ethylene

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carbonate (EC) [23]. Li et. al. [24] and Cui et. al. [31] confirmed that batteries utilizing gel type single ion polymer electrolyte membranes were in fact superior to batteries using conventional dual ion based electrolytes in terms of capacity retention. Wang et. al. developed a microporous single ion conducting polymer electrolyte with the ionic conductivity as high as 10^{-3} S m^{-1} at room temperature, four times higher than that of traditional liquid electrolytes incorporated with polyolefin separators [32]. Recently, Archer et. al. confirmed that a gel type single ion conducting polymer electrolyte is capable of suppressing lithium dendrite proliferation by galvanostatic cycling at various current density [33].

Despite the rapid advance in development of gel type single ion conducting polymer electrolytes, battery cells equipped with the electrolyte membranes with longevity over 200 cycles at an ambient temperature remain to be demonstrated due to the limited ionic conductivity of these materials at room temperature and the insufficient stability of the membranes for long time battery operation. As a matter of fact, variables, such as a choice of appropriate anions and their residing sites in polymers, backbones, ion exchange capacities, degrees of polymerization and microstructures, all significantly affect electrochemical and mechanical properties of single ion conducting polymer electrolyte membranes. Therefore, rational design of building blocks and appropriate combinations of these units are of essential importance for development of high performance single ion conducting polymer electrolyte materials for applications in lithium ion batteries.

One class of polyamide based gel type single ion conducting polymer electrolytes with bis(benzene sulfonyl)imide as the immobilized anion was recently found to be promising for battery applications [30,34,35]. Unfortunately, the comprehensive performance in terms of high ionic conductivity, adequate mechanical strength, electrochemical stability and necessary flexibility has to be further improved to enable high device performance. In the study of dual ion based gel polymer electrolyte, introducing the functional groups such as ether with high affinity towards organic solvent benefits for the uptake of organic solvents which facilitate solvation and transport of lithium ions [36,37]. In addition, ether based polymer backbone is more flexible than polyamide and thus a close contact between film and electrode can be formed. Therefore, design and measurement of ether based polymer containing delocalized anion such as bis sulfonyl imide as the gel type single ion conducting polymer electrolyte for lithium ion battery is worthily expected.

In this paper, a poly(arylene ether) based single ion conducting polymer electrolyte is studied in comparison with a polyamide based polymer electrolyte. The aim of the present study is to objectively evaluate the influence of poly amide and poly(arylene ether) as the polymer backbones on the mechanical and electrochemical properties as well as on the device performance, which may guide molecular design of single ion conducting polymer electrolytes that enable batteries to be operative with long cycle life and superior device safety. 4,4′-fluorine bis(benzene sulfonyl)imide was used to react with 4,4′-dihydroxydiphenyl ether through nucleophilic substitution to form a poly(arylene ether) based single ion conducting polymer. For comparison, a polyamide based single ion conducting polymer was also synthesized via copolymerization between 4,4′-dicarboxyl bis(benzene sulfonyl)imide and 4,4′-diaminodiphenyl ether. The chemical structure, thermal stability, mechanical strength, electrochemical properties (i.e. ionic conductivity, ion transference number and electrochemical window) of the polyamide and poly(arylene ether) based copolymer membranes and the battery performances of half cells of the materials were characterized and systematically evaluated. Finally, a full cell was assembled with LFP as the cathode, LTO as the anode and the membrane made of a poly(arylene ether) based single ion conducting polymer as the separator as well as the electrolyte and its cycle performance was carefully assessed.

2. Experimental

2.1. Materials

4-fluorobenzenesulfonyl chloride (97%), and 4-fluorobenzene sulfonamide (97%) were purchased from Chem Greatwall Co., Ltd. 4-methyl benzenesulfonyl chloride (AR), and 4-methyl benzenesulfonamide (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. 4,4′- dihydroxy diphenyl ether (97%) was purchased from Aldrich and recrystallized in hot toluene. 4,4′-diamino diphenyl ether was purchased from Aldrich without further purification. Anhydrous potassium carbonate (K_2CO_3, AR) and lithium chloride (LiCl, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. and vacuum dried at 150 °C for 24 h before use. Dimethyl sulfoxide (DMSO, AR) and toluene (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. and pre-dried using calcium hydride followed by reduced distillation. Pyridine (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. and dried with KOH followed by reduced distillation. Ethylene carbonate (EC, AR) and dimethyl carbonate (DMC, AR) were purchased from Aladdin and dried with molecular sieves followed by reduced distillation. Both EC and DMC were stored in a glove box before use. Lithium hydroxide monohydrate (AR), hydrochloric acid (AR), N-methyl-2-pyrrolidone (NMP, AR), methanol (98%), triphenyl phosphite (TPP) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification. Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP, average Mw~400,000 (bimodal distribution), average Mn~130,000) was purchased from Sigma Aldrich Co., Ltd. $LiFePO_4$ (> 97%) was purchased from Tianjin STL Energy Technology Co., Ltd. $Li_4Ti_5O_{12}$ (98%) was purchased from Kejing Co., Ltd.

2.2. Synthesis of precursors and copolymers

2.2.1. Synthesis of bis(4-fluorine benzene sulfonyl)imide

Bis(4-fluorine benzene sulfonyl)imide was synthesized following the procedures described in Refs. [38] Typically, a Hinsberg reaction between 4-fluorine benzenesulfonamide and 4-fluorine benzenesulfonyl chloride under a basic condition was conducted to synthesize bis(4-fluorine benzene sulfonyl)imide with a yield of 44.50%.

2.2.2. Synthesis of bis(4-carbonyl benzene sulfonyl)imide

The synthesis of bis(4-methyl benzene sulfonyl)imide followed the same procedure as that of bis(4-fluorine benzene sulfonyl)imide with a yield of 43.3%. Subsequently, the product was oxidized by 25% excessive $KMnO_4$ followed by acidification in a hydrochloric acid solution [39]. The yield of bis(4-carbonyl benzene sulfonyl)imide was 76.0%.

2.2.3. Synthesis of lithiated poly(bis(4-hydroxy benzene) ether-alt-bis(4-fluorine benzene sulfonyl)imide) ether (LiPHFE)

To synthesize the lithiated alternating copolymer poly(bis(4-hydroxy benzene) ether-*alt*-bis(4-fluorine benzene sulfonyl)imide) ether, we followed the procedure described in Refs. [40,41] as shown in Scheme 1(a). 2.02 g (10 mmol) of 4,4′-dihydroxydiphenyl ether, 3.33 g (10 mmol) of bis(4-fluorine benzene sulfonyl)imide and 2.76 g (20 mmol) of K_2CO_3 were introduced in a two-necked flask equipped with a Dean-Stark trap. 15 mL of DMSO as the solvent and 8 mL of toluene as the azeotropic agent were added respectively. The reaction mixture was initially refluxed at 160 °C under argon protection for 4 h and the temperature was further raised slowly to 180 °C, lasting for 12 h. Upon cooling to 100 °C, the mixture was poured into aqueous hydrochloride (1 M) to precipitate the product. The precipitate was washed with methanol several times followed by vacuum drying. The obtained copolymer was neutralized by aqueous lithium hydroxide followed by freeze drying under vacuum.