



A dense transparent polymeric single ion conductor for lithium ion batteries with remarkable long-term stability



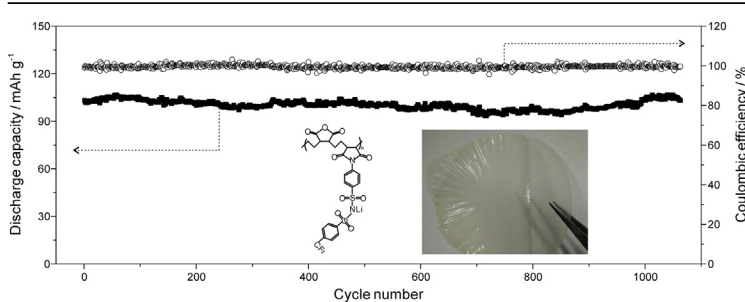
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HIGHLIGHTS

- A dense transparent polymeric single ion conductor for lithium ion battery.
- Ionic conductivity of 0.104 mS cm^{-1} at 25°C and Li^+ transference number of 0.92.
- A discharge capacity of 100 mAh g^{-1} at 1 C under room temperature for 1000 cycles.
- The cyclic imides and comb-like structure are responsible for the stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 August 2016

Received in revised form

6 October 2016

Accepted 8 October 2016

Keywords:

Single ion conducting polymer electrolyte

Transference number

Side chain grafting

Ion exchange capacity

ABSTRACT

We report an outstanding electrochemical performance of a gel type lithium ion battery with long cycle life enabled by a dense transparent polymeric single ion conductor. The polymer electrolyte was synthesized by a side chain grafting method with 4-amino-4'-trifluoromethyl bis(benzene sulfonyl)imide grafted on side chains of poly(ethylene-*alt*-maleic anhydride) with a grafting ratio of 50%. Blending lithiated ionomers with poly(vinylidene fluoride-*co*-hexafluoropropylene) via a solution cast method results in a dense transparent film. The fabricated blend polymer electrolyte film has an ionic conductivity of 0.104 mS cm^{-1} at room temperature, a tensile strength of 15.5 MPa and percent elongation at break of 5%. A gel type single ion conductive polymeric lithium ion battery was assembled using the blend film as the separator as well as the electrolyte, LiFePO_4/C mixed with ionomers as the cathode and a lithium foil as the anode. The battery delivers a reversible discharge capacity of 100 mAh g^{-1} at 1 C under room temperature for 1000 cycles without obvious decay. The stable cyclic imide and comb-like structure of the polymer is largely responsible for the excellent battery performance. The side chain grafted single ion conducting polymer electrolyte is well suited for large-scale production.

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1. Introduction

Demand for lithium ion batteries with high energy density and high power density has been growing rapidly in recent years.

Systems such as lithium sulfur [1,2], lithium air [3,4] and silicon-based lithium ion batteries [5,6] have been shown to be highly promising and thus have been intensely studied. While much progress has been made over the past decade, a few intrinsic problems remain to be resolved [7]. In particular, safety related issues arising from lithium dendrite formation in conventional lithium ion batteries utilizing dual-ion liquid electrolytes have become a serious public concern [8]. Enhancement of lithium ion transference

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number to unity to avoid concentration polarization and dendrite formation for lithium ion batteries has been recognized by both theoretical and experimental studies [9–12]. The main thrust of the recent development of single ion conducting materials largely aims at achieving this objective [13–20]. Although development of all solid state lithium ion batteries enabled by inorganic single ion conductors is deemed to be the ultimate goal, unstable electrochemical interface and low machinability of inorganic electrolyte have hindered the commercial development [21,22]. Polymeric single ion conductors offer a viable alternative with inexhaustible functional groups and structural variations to manipulate physical and chemical properties of electrolyte membranes for battery applications. All solid state lithium ion batteries using single ion conducting polymer electrolytes have been shown to work at elevated temperatures [12,23]. Applications of gel type single ion conducting polymeric electrolytes in lithium ion batteries have already been successfully demonstrated at room temperature [16,24–32]. Nevertheless, to date, most of the studies with single ion conducting polymer electrolytes have only remained in the demo stage to prove the concept with less than 200 cycles of device operation.

A highly effective single ion conducting polymer electrolyte requires a high degree of charge separation and anion immobilization. Charge separation can be achieved by placing electron withdrawing functional groups in the vicinities of the anions [13,20,31–34], which reduces cation-anion electrostatic interaction and further enhances ion dissociation. Anion immobilization can be realized by selecting appropriate anion species to form covalent bonds with polymer chains, which restricts the mobility of anions and thus maximizes the transference number of cations. Copolymerization of small molecules and post grafting of commercially available polymer are two important kinds of known synthetic strategies for preparing these types of materials, among which the former is the widely adopted because functional small molecules can be deliberately designed and diversely grouped. Bouchet et al. reported that lithium 4-styrenesulphonyl(trifluoromethylsulphonyl)imides (STFSILi) and PEO-based macroalkoxyamines with different ratios were copolymerized to form PSTFSILi-PEO-PSTFSILi triblock copolymers [12]. PEO-PSLiTFSI diblock copolymer was selected as the model to systematically study morphology-conductivity relationship [35,36]. Hu et al. reported a single ion conductor based on super delocalized anions synthesized by self-copolymerization of 4-styrenesulphonyl (trifluoromethyl(S-trifluoromethylsulfonylimino)sulfonyl)imide [13]. Long et al. reported a highly cross-linked single ion conductor via copolymerization between tetrakis(phenyl)borate and 1,4-diethynylbenzene (or tri(ethylene glycol)) [14]. Recently, Wang et al. reported a poly(arylene ether) based single ion conductor synthesized through copolymerization of sodium 2-(2',3',5',6'-tetrafluorophenoxy)perfluoroethanesulfonate, hydroquinone and 4,4'-biphenol followed by lithium ion exchange [15]. We also copolymerized 4,4'-dicarboxyl bis(benzene sulfonyl)imide and 4,4'-diamino bis(benzene sulfonyl)imide to obtain an AB alternating copolymer [16]. It was found that the purity of precursors, input ratio, reactivity of reaction sites profoundly affect the properties of final product such as the degree of polymerization, polydispersity and regularity. Post grafting of a commercially available polymer is also an important synthetic strategy especially for aqueous ion exchange membranes. For example, poly(ether ether ketone) is side chain grafted with either quaternary ammonium [37] or sulfonic acid [38] and used as polymer electrolyte membrane for energy conversion. This method is well suited for large-scale production because synthesis route is relatively simple and the industrially available raw materials are usually inexpensive and easy to obtain with well controlled quality. Therefore, we adopted the synthetic strategy to graft functional groups on side chains of a selected commercial polymer.

In this paper, we report a successful synthesis of a single ion conductor made of the commercially available poly(ethylene-*alt*-maleic anhydride) as the polymer backbone with maleic anhydrides providing the reaction sites for grafting with functional side chains. The flexible alkyl main chain ensures the mechanical stability. An asymmetric bis(benzene sulfonyl)imide molecule, i.e., 4-amino-4'-trifluoromethyl bis(benzene sulfonyl)imide is designed and synthesized for placement of selected anions on side chains. 4-amino-4'-trifluoromethyl bis(benzene sulfonyl)imide is grafted on the side chains of the polymer backbone via cyclic imides to obtain a comb like polymer as schematically illustrated in Scheme 1. Highly polar side chains where delocalized anions are anchored via covalent bonds are vertically attached to a flexible alkyl backbone. The polar chemical bonds of imide and anhydride in the side chains are more compatible with the polar solvents, which is beneficial for film swelling and lithium ionization. Interestingly, blending the lithiated side grafted poly(ethylene-*alt*-maleic anhydride) with poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) via a solution cast method results in a dense transparent film, different from commonly used porous Celgard film. Subsequently, a gel type polymeric lithium ion battery with the single ion conductor as the separator as well as the electrolyte for 1000 cycles at 1 C was performed. This work paves a way to use safer and more durable single ion electrolyte based lithium ion batteries for practical applications.

2. Experimental

2.1. Chemicals

4-nitrobenzenesulfonamide (97%) was purchased from Chem Greatwall Co., Ltd. 4-(trifluoromethyl)benzene-1-sulfonyl chloride was purchased from Adamas Reagent Co., Ltd. Poly(ethylene-*alt*-maleic anhydride) (average Mw 100,000–500,000, powder) and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP, average Mw ~400,00 (bimodal distribution), average Mn ~130,000) were purchased from Sigma-Aldrich Co., Ltd. *m*-Cresol (AR), isoquinoline (AR), *N*-methyl-2-pyrrolidone (AR), ethylene carbonate (AR), propylene carbonate (AR), Tin(II) dichloride dihydrate (AR), methanol (AR), dichloromethane (AR), hydrochloric acid (AR), sodium hydroxide (AR), lithium hydroxide (AR) and lithium foil (ϕ 16 mm) were purchased from Sinopharm Chemical Reagent Co., Ltd. LiFePO₄ (>97%) was purchased from Tianjin STL Energy Technology Co., Ltd. Poly(ethylene-*alt*-maleic anhydride) was preheated at 150 °C in the vacuum oven before use. Ethylene carbonate (EC) and propylene carbonate (PC) with the volume ratio of 1:1 were dried and stored with 4A molecule sieves in a glove box.

2.2. Polymer synthesis and characterization

2.2.1. Synthesis of 4-amino-4'-trifluoromethyl bis(benzene sulfonyl)imide

10.1095 g (0.05 mol) of 4-nitrobenzenesulfonamide was dissolved in a sodium hydroxide solution (2.05 g of sodium hydroxide dissolved in 600 mL of deionized water) to form a homogeneous solution. 6.1155 g (0.025 mol) of 4-(trifluoromethyl)benzene-1-sulfonyl chloride was added stepwise under stirring, lasting for around 1 h. The reaction was stirred at 90 °C for 12 h. Upon cooling, the suspension was filtrated and the filtrate was collected. Subsequently, concentrated hydrochloric acid was added to the filtrate to precipitate completely. The precipitate was collected by filtration and further purified by recrystallization in water. The yield was 40%.

9.48 g (0.4 mol) of tin(II) dichloride dihydrate was dissolved in 20 mL of methanol with an addition of 2 mL of concentrated hydrochloric acid. Subsequently, a solution of 1.31 g (3.2 mmol) of 4-

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