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Jeffamine® based polymers as highly conductive polymer electrolytes and cathode binder materials for battery application

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HIGHLIGHTS

- New comb polymer electrolytes synthesized by imide ring formation.
- Novel polymer electrolytes with EO/PO based chain structure (Jeffamine®).
- High ionic conductivity in fully amorphous solid polymer electrolytes.
- High cycle-ability of $LiFePO_4$ and sulphur cells based on these new polymer electrolytes.
- Jeffamine based polymers as alternative binders for Li based batteries.

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ABSTRACT

We report a simple synthesis route towards a new type of comb polymer material based on polyether amines oligomer side chains (i.e., Jeffamine® compounds) and a poly(ethylene-*alt*-maleic anhydride) backbone. Reaction proceeds by imide ring formation through the NH_2 group allowing for attachment of side chains. By taking advantage of the high configurational freedoms and flexibility of propylene oxide/ethylene oxide units (PO/EO) in Jeffamine® compounds, novel polymer matrices were obtained with good elastomeric properties. Fully amorphous solid polymer electrolytes (SPEs) based on lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and Jeffamine®-based polymer matrices show low glass transition temperatures around −40 °C, high ionic conductivities and good electrochemical stabilities. The ionic conductivities of Jeffamine-based SPEs (5.3×10^{-4} S cm^{-1} at 70 °C and 4.5×10^{-5} S cm^{-1} at room temperature) are higher than those of the conventional SPEs comprising of LiTFSI and linear poly(ethylene oxide) (PEO), due to the amorphous nature and the high concentration of mobile end-groups of the Jeffamine-based polymer matrices rather than the semi-crystalline PEO The feasibility of Jeffamine-based compounds in lithium metal batteries is further demonstrated by the implementation of Jeffamine®-based polymer as a binder for cathode materials, and the stable cycling of Li|SPE|$LiFePO_4$ and Li|SPE|S cells using Jeffamine-based SPEs.

1. Introduction

Li-ion batteries (LIBs) are widely used source of energy in many portable devices and lately in electrical vehicles (EV) or medium scale power banks. High volumetric energy density is achieved by the implementation of lithium-based compounds as cathode and graphitized carbon as anode in commercial LIBs. These systems have many advantages and have been widely explored for many years. However safety issue does not allow for the operation of these cells at elevated temperature (aging and safety) or the use of metallic lithium as anode due to dendrite formation. Since the first report of solvent-free solid polymer electrolytes (SPE) an extensive work has been done in this area [1,2]. Polymers give a possibility for: simplicity of cells construction and cell assembling, cost reduction, elevated temperature operation, usage of metallic lithium as anode, and lately shuttle effect diminution in lithium—sulphur (Li—S) batteries. Since 2011, solid polymer electrolytes (SPEs) have been successfully implemented in the "BlueCar" Electric Vehicle (EV) battery commercialized by Bollore [3] and its

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recent association with Peugeot Société Anonyme (PSA) automobile manufacturer will hasten their diffusion [4]. This already shows the great potential of polymers in Li° based batteries. Nevertheless, further improvement of polymer electrolytes in terms of ionic conductivity, electrochemical potential window, mechanical and thermal properties are still under progress. To date, numerous modifications have been proposed that can be simply divided into: i) additives to polymer network, ii) chemical modifications of polymer network.

The role of additives in polymer electrolytes is to improve the structural, electrochemical and mechanical properties. This can be achieved by decreasing the crystalline phase fraction present in high molecular weight PEO-based hosts by adding low molecular weight solvents whose effect is also a lowering of glass transition temperature (T_g) through improvement of the conformational freedom of polymer units. Other strategies rely on inorganic nanoparticles that interact with the anion (dispersoid polymer electrolytes (DPE)). The surface properties of the inorganic phase can be modified in terms of Lewis acid/base character as well as its hydrophilic/hydrophobic character [5–7]. Another approach is polymer alloy with different macromolecules: polystyrenes, poly(methyl methacrylate), poly(acrylamides) [8] or polymers with anion receptor additives [9,10]. Omitting miscibility problems, mechanical properties can be adjusted with the fraction of added polymer. It can be concluded that modification of polymer electrolytes by additive is relatively easy and the choice of additives is immense.

Chemical modifications are based on reaction within the polymer matrix yielding new type of polymer materials. This method could consist of block copolymerization in linear or comb like structure by bonding together functionalized polymers [11–14] or crosslinking of polymer network [15]. Chemical modifications are explored as well in liquid/gel electrolytes where different copolymers have been used as host together with plasticizing liquid solvents [16]. It has to be mentioned that a particular type of copolymer electrolytes based on polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) was analysed extensively [17–19]. In that type of polymer electrolytes significant improvements of mechanical and thermal properties were achieved due to micro phase separation. Mechanical properties are insured by the PS fraction whereas ion transport takes place according to Vogel-Tamman-Fulcher (VTF) model inside microstructure of PEO channels. Another significant improvement by chemical modification has been achieved by bonding anion to polymer network [20,21]. As added advantage, besides avoiding salt concentration polarization is the immobilization of anion that improves electrochemical performance of the electrolyte. However, the synthesis of these polyelectrolytes is not trivial.

Interesting approaches to chemical modifications were presented by several research groups where statistical copolymers based on poly(ethylene oxide)/poly(propylene oxide) (PEO/PPO) units were analysed [22–24]. It was shown that incorporation of propylene oxide units (PO) in polymer chains prevents crystallization while keeping good ion solvation properties. In those electrolytes glass transition temperature can be decreased whereas the ionic conductivity increases in comparison with ethylene oxide (EO)-only based electrolytes. Contrastingly, polymer electrolytes based only on PPO exhibit lower ionic conductivity versus PEO. In general the architecture of copolymer has to be set for low fraction of PO vs. EO repeat units preventing crystallization but at the same time keeping the solvation power of $-OCH_2CH_2O-$ unhindered in the polymer network. Unfortunately, these copolymers indicate a lower lithium-ion transference number (T_+) and a relatively low breakdown voltage (BV) with $T_+ \approx 0.1$ and BV ≈ 4 V, respectively [24]. For the implementation of these materials as electrolytes further modifications are needed. Ben Rabah et al. proposed the use of diamine–poly(oxyethylene–*co*–oxypropylene) (Jeffamine®) compounds in polymer electrolytes [25]. Fully amorphous electrolytes with low T_g temperature exhibit ionic conductivity in the range of 10^{-6} S cm^{-1} at room temperature for salt concentration O/Li = 8. This work showed new strategy of EO/PO based compounds implemented in polymer matrix. Lately Jeffamine® compounds were studied in solid organic-inorganic polymer electrolytes due to their facile fabrication [26]. Completely amorphous materials were synthesized with diamine-terminated Jeffamine® with molecular weight $M_w = 2000$. Ionic conductivity reached 6.23×10^{-5} S cm^{-1} at 30 °C. Another approach was shown by Brandell et al. [27] where Jeffamine T3000 (trifunctional polyether amine oligomer) was applied in polymer electrolyte destined to micro 3D battery. Good compatibility with cathode material was proven by SEM analysis. Micro batteries were tested in voltage range up to 4.2 V vs. Li° without visible side reaction effect. The role of polymers in solid batteries is essential for proper operation not only as an electrolyte. The polymer electrolyte is the ion-conducting separator between the positive and negative electrode, but also the binder of the positive electrode in Li° based cells. As it is known the compatibility of the cathode with electrolyte is critical for good electrochemical performance of battery. That is the main reason of implementation of polymer electrolyte as binders in cathodes in most SPE where wettability and impregnation of cathode by SPE is essential. Polymers used as binders for the cathode need to provide strong bonding strength to current collector and cathode components, high physical and electrochemical stability, low resistance and volume buffering properties for expansion/shrinkage of active material [28,29], in addition to low cost. Jeffamine® compounds, with their reactive NH_2 end group, give possibility for relatively easy modification of polymer/monomers, moreover compounds are commercially available in large scale. For instance reaction can be carried out through the very stable imide ring formation (chemistry extensively used since the 1960's). In this work, novel comb polymer materials are studied as the electrolyte matrices for electrolyte and binders in cathodes application. A new, one pot synthesis route starting with cheap and commercially available compounds is presented where the final product contains imide ring in polymer backbone. The reaction provides elastomeric material that can be modulated with respect to chemical composition where Jeffamine® compounds of various M_w are grafted to a rigid polymer backbone containing maleic anhydride. Another advantage of imide based materials should be a higher electrochemical stability, overall, yielding high performance, cost competitive and scalable polymer electrolytes. The application of this novel material as active binder for Li metal batteries and Li-S batteries is also presented.

2. Experimental

2.1. Synthesis of Jeffamine®-based polymer matrix

Two different routes were chosen to synthesize polymer material based on three different Jeffamine® compounds namely: Jeffamine M–1000, Jeffamine M–2070 and Jeffamine M–600 (all from Huntsman Company) where M signifies monoamine and number represents the approximate molecular weight. Samples acronyms are visible in Table 1. Operations were carried out in an inert atmosphere and components were dried prior to use in a Schlenk line. 5 mmol of Jeffamine® (Huntsman) was dissolved in dry acetonitrile (ACN 99,9%) with mass ratio 1:25, the solution was then slowly added into an equimolar (versus anhydride units) suspension of poly(ethylene-alt-maleic anhydride) (Sigma–Aldrich ref. 188050) in 20 mL of dry ACN. The reaction medium after adding