



Lithium battery with solid polymer electrolyte based on comb-like copolymers



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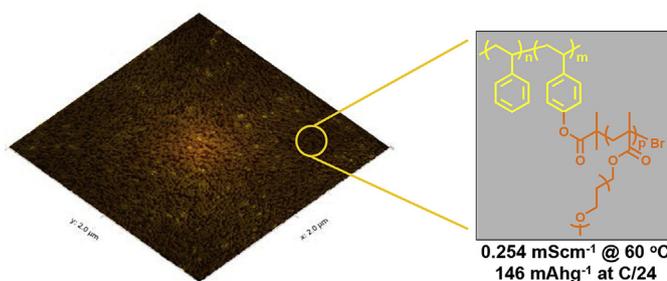
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HIGHLIGHTS

- Synthesis of comb-like copolymers and their promising use as solid polymer electrolytes.
- Micro and nano phase separation as a function of the ratio of grafting.
- Micro and nano phases have an impact on the energy of activation (E_a) and the ionic conductivity of the polymers.
- Good conductivities at room temperature by AC Impedance (10^{-5} Scm^{-1}).
- The batteries evaluated with these polymers exhibited good capacity (146 mAh g^{-1}) at C/24.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we report on the synthesis of comb-like copolymers as solid polymer electrolytes (SPE). The synthesis involved anionic polymerization of styrene (St) and 4-vinylanisole (VA) as the followed by grafting of poly(ethylene glycol) monomethyl ether methacrylate (PEGMA) by Atom Transfer Radical Polymerization (ATRP). The comb-like copolymer's structure was analyzed by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). The membranes were made by solvent casting and the morphologies were analyzed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). We observed that a nano and micro phase separation occurs which improves ionic conductivity. The ionic conductivities were determined by AC Impedance, which showed that the SPEs have good conductivities (10^{-5} Scm^{-1}) at room temperature owing to the negligible values ($<10 \text{ kJ mol}^{-1}$) of the activation energies for conductivity. The batteries with these polymers exhibit a capacity of 146 mAh g^{-1} at C/24, and no evidence of degradation after intense cycling was observed. However, poor cycle life was observed at C/6 and C/3, which is a consequence of several factors. We partially explain that behavior by arguing that whereas PEO lightly "solvates" Li^+ thus slowing Li-ion mobility, and PEGMA chains "solvate" Li ions too strongly, trapping and inhibiting their mobility.

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1. Introduction

One of the key solutions to curb climate change, pollution and greenhouse gas is to develop a fully electric transportation infrastructure. One of the most promising approaches is to use batteries such as those utilizing a lithium anode in electric vehicles. However, making these batteries safe can be problematic [1–3]. The liquid electrolytes in lithium batteries pose potential safety problems, and they can cause damage to the environment and human health if they explode [2]. These safety issues are minimized by using batteries containing a solid polymer electrolyte (SPE) with good lithium conductivity and mechanical properties [3]. The SPE in combination with a lithium anode can be safely used for the production of a high-power battery [4].

Since the first publication of Armand and co-workers [5], poly(ethylene oxide) (PEO) is the most studied polymer electrolyte owing to its capacity to dissolve lithium salts and excellent ionic conductivity above 70 °C. However, the conductivity is limited by the inherent crystallinity of PEO at room temperature [6,7]. The discovery of polymers with reasonable conductivity below 60 °C should advance the production of more energy-efficient batteries [8]. The issue with the crystallinity experienced with PEO is eliminated by the synthesis of branched polymers [9–12], copolymers with low molecular weight PEO [13–15] or by the incorporation of plasticizing agents [16,17]. But, one problem still remains unsolved: limiting the growth of dendrites on the lithium anode. Monroe et al. reported the possibility of impeding the formation of dendrite if the Young modulus of the polymer is increased to a suitable level [18–20]. However, an increase of the shear modulus can limit the motion of the chains, and this motion is essential for higher conductivity [21]. Incorporating cross-linking sites on the backbone can increase the hardness of rubbery polymers [15,22], although the reaction occurs during the preparation of the membrane. This can lead to residue from the initiator trapped inside the membrane, which may produce variation in the conductivity and act as plasticizers [23].

In order to improve the conductivity, the Kanamura group demonstrated the efficient use of oligooxyethylene pendant groups in a poly(styrene-*b*-oligooxyethylenemethacrylate-*b*-styrene) with micro phases separation [24,25]. PEO grafted on a polystyrene (PS) backbone produced excellent mechanical modulus (10^8 Pa at 30 °C) and a conductivity of 2×10^{-5} Scm⁻¹ at 25 °C [26]. Jannasch reported on the effectiveness of comb-shaped polyethers as polymer electrolytes with a conductivity of 10^{-5} Scm⁻¹ at room temperature [27]. These polymers were prepared by grafting ethylene oxide and propylene oxide by anionic polymerization on a polystyrene backbone. The Balsara group reported on the use of block copolymers of polystyrene and polyethylene oxide [13,28]. The crystallinity of high molecular weight PEO is not eliminated and contributes to a low conductivity below 80 °C. Balsara [28] and Park [29] showed the importance of rigid and fluid blocks to promote the formation of a micro phase suitable for good conductivity. The gyroid structure consists of ionic channels of PEO surrounded by PS, as observed by transmission electron microscopy (TEM). This structure is associated with a more straightforward displacement of lithium, thereby reducing dendrite growth [29]. Very recently, Bouchet et al. [30] described a series of BAB triblock polymers called single-ion polymer electrolytes. These polymers have two segments based on poly(styrene trifluoromethanesulfonylimide of lithium) and a landlocked PEO block. This material exhibited, in a prototype cell, good conductivity (10^{-4} Scm⁻¹) at 60 °C and promising charge/discharge cycles (50 cycles) at 60 °C [30].

2. Experimental

2.1. General information

All items of glassware used in the synthesis were dried overnight in an oven at 120 °C. 4-vinyl anisole (VA) was purified by vacuum distillation at 1 mm Hg and 100 °C over CaH₂. Styrene (St) was purified by passing 3 times over a bed of basic Al₂O₃ and CaH₂. The monomers were used immediately after purification. Anhydrous toluene was used without any further purification. A solution of polyethylene glycol methyl methacrylate (PEGMA, $M_n = 550$)-toluene was passed 3 times over a bed of basic Al₂O₃ and CaH₂ and degassed by bubbling with nitrogen for 1 h. The concentration of the solution was determined by ¹H NMR after purification. CuBr was purified by stirring in acetic acid (AcOH). The AcOH was removed by filtration and the solid was washed 3 times with diethyl ether and dried under vacuum for 12 h. All the other chemicals from Sigma Aldrich were used as-received.

2.2. Polymerization procedures

2.2.1. Typical procedure for anionic copolymerization of styrene and 4-vinylanisole

The procedures for the synthesis of polymers were carried out in a nitrogen atmosphere using standard Shlenk techniques. The polymerization of VA and St was already published by Westwood et al. [33]. No changes were made to the method. A typical result is a conversion of 75% with a yield of 13.2 g.

2.2.2. Typical procedure for polymerization of PEGMA by ATRP on poly(styrene-co-4- α -isobutyryl bromide styrene)

The synthesis of polymers was carried out in a nitrogen atmosphere using standard Shlenk techniques. 2.50 g poly(styrene-co-4- α -bromoisobutyryl styrene) with 4 mol% of functional monomers (VA) was introduced in a 50-ml Shlenk flask. The flask was degassed for 1 h under vacuum. 20.00 ml of PEGMA-toluene (32 % mol in PEGMA) solution was introduced into the flask under a constant flow of nitrogen and then stirred to ensure the complete solubilisation of the polymer. The flask was degassed using four freeze-pump-thaw cycles. 50.0 mg of CuBr and 100 μ l of N,N,N',N'-Pentamethyldiethylenetriamine (PMDETA) were added to the frozen solution under a constant flow of nitrogen. The solution was warmed at room temperature and stirred. The flask was degassed using four freeze-pump-thaw cycles. The solution was heated at 110 °C for 12 h under a slight vacuum, then the flask was cooled to room temperature and diluted with 25 ml of toluene. The solution was purged with air for 30 min and passed through a bed of basic alumina to remove the copper residues. If the solution was green after this step, the solvent was rotoevaporated and the solid was dissolved in 25 ml of distilled water, 5 ml 5 M HNO₃ and 5 ml urea (5% wt/vol). The solution was boiled for 5 min and cooled in an ice bath. Aqueous ammonia was added to the solution, drop by drop, until the complex Cu(NH₃)₄²⁺ (blue solution) was formed. Occurs, an excess of aqueous ammonia was then added, followed by concentrated H₂SO₄ which was added drop by drop until the blue color disappeared. Further steps involved the addition of 5 ml conc. H₃PO₄ and 4.0 g KI while stirring the solution for 10 min. During this step, CuI was formed. The aqueous solution was extracted 4 times with dichloromethane (DCM). The organic phases were combined and extracted 3 times with a solution of 10% potassium thiosulfate, and dried over MgSO₄ for 12 h and filtered to remove the solid. The filtrate was rotoevaporated under reduced pressure until the volume reached 20 ml, at which time it was poured into 350 ml of diethyl ether at -25 °C. The polymer precipitated and was recovered by centrifugation (7500 rpm for 10 min). To ensure the

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