



Synthesis, dynamic properties and electrochemical stability of organic-inorganic hybrid polymer electrolytes with double core branched structures based on polyether, cyanuric chloride and alkoxysilane



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ABSTRACT

A new organic-inorganic solid hybrid electrolyte based on 2,4,6-trichloro-1,3,5-triazine, triblock co-polymer poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) bis(2-aminopropyl ether), poly(ethylene glycol) diglycidyl ether, and 3-(glycidyloxypropyl)trimethoxysilane doped with LiClO₄ salt is synthesized by a sol-gel process. Fourier transform infrared spectroscopy and ¹³C NMR results reveal the successful synthesis of the organic-inorganic hybrid electrolyte. The conductivity of the hybrid electrolyte follows a VTF (Vogel-Tamman-Fulcher)-like behavior, implying that the diffusion of charge carriers is assisted by the segmental motions of polymer chains. The Li-ion mobility is determined from ⁷Li static NMR linewidth and diffusion coefficient measurements; both are correlated with their ionic conductivities. The maximum ionic conductivity of $9.5 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C is obtained for the hybrid electrolyte with the [O]/[Li] ratio of 32. The electrochemical stability window of 4 V ensures the hybrid electrolyte as a potential candidate for low voltage lithium ion batteries.

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1. Introduction

The global energy crisis and increase in environmental pollution have prompted the researchers toward development of electrochemical devices, such as lithium-ion batteries, dye-sensitized solar cells, supercapacitors, electrochromic devices, etc. [1–4]. In all these devices, electrolytes play a pivotal role in the enhancement of device efficiency. Among the electrolytes, solid polymer electrolytes (SPEs) are the materials of choice in electrochemical devices as they offer safety, leak proof, mechanically and thermally stable, and structurally flexible design. However, a major limitation of these electrolytes to be used in lithium-ion batteries is their relatively low ionic conductivity as compared to liquid electrolytes.

To date, poly(ethylene oxide) (PEO) based electrolytes are extensively studied because of their effective ion solvating properties and ionic conductivities higher than $10^{-4} \text{ S cm}^{-1}$ above 70 °C [5,6]. However, the ionic conductivity of PEO-based electrolytes decreases drastically at room temperature because they are prone to crystallization, which prohibits their use in electrochemical devices [7]. As a result, various approaches have been adopted, for example, addition of micron/nano-sized particles, synthesis of rubbery block co-polymers, blends, development of branched/star-branched/comb structures, and incorporation of plasticizers, to reduce crystallinity while retaining the solvating properties [8–12]. Although these techniques help to enhance the room temperature ionic conductivity, some are lack of structural integrity and high conductivity that requires for commercial applications. During the last decades, the organic-inorganic hybrid materials have emerged as a promising research area, since this type of materials combines the advantageous properties of inorganic components such as hardness and mechanical resistance with those of organic

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ones, such as flexibility and impact resistance [13,14]. The development of organic-inorganic hybrid electrolytes via the *in-situ* formation of inorganic components within the polymeric matrix provides an effective method for the improvement of the electrochemical properties [15–18]. The combination of appropriate processing conditions with correct choices for the organic and inorganic components controls the morphology, molecular structure and characteristics of the resulting hybrid materials. These hybrid materials offer a useful basis for the production of new low-cost electrolyte materials to use in electrochemical devices. Among the various organic-inorganic hybrids, the hybrid based on 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride, CC) is particularly important as it provides bridging site to form a branched structure [19,20].

In the present work, an organic-inorganic hybrid electrolyte was synthesized by the reaction of cyanuric chloride with poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) bis(2-aminopropyl ether) (ED2003) by sequentially and selectively replacing the chloride atoms. Poly(ethylene glycol) diglycidyl ether (PEGDGE) was further reacted with the amine end groups of ED2003 to link a double core structure. The cross-linker, 3-(glycidyloxypropyl)trimethoxysilane (GLYMO), was added to react with the other amine end groups of ED2003 to form the silicate network in the hybrid structure, which was then followed by doping with LiClO_4 . Cyanuric chloride acts as the core while synthesizing the double core based branched structure. The silicate network makes the membrane mechanically stable and gives a composite nature to the membrane by forming *in-situ* sub-micron sized particles. The present work investigates the structural properties, the dynamic properties such as ionic conductivity, lithium-ion mobility, diffusivity, and the electrochemical stability of the organic-inorganic hybrid electrolytes.

2. Experimental

2.1. Materials

Triblock copolymer $\text{H}_2\text{N}-(\text{PPG})_x(\text{PEG})_y(\text{PPG})_z\text{NH}_2$ (commercially designated by Jeffamine ED2003 with $M_w = 2000 \text{ g mol}^{-1}$ containing $x + z = 6$; $y = 39$), PEGDGE, cyanuric chloride, GLYMO and lithium perchlorate (LiClO_4) were purchased from Aldrich. The polymers ED2003, PEGDGE and LiClO_4 were dried at 70°C in a vacuum oven for 2 days prior to use. Cyanuric chloride and GLYMO were used as received. Lithium foil from Alfa Aesar was used as electrode material. Tetrahydrofuran (THF) was distilled from sodium/benzophenone prior to use.

2.2. Synthesis of organic-inorganic hybrid electrolytes

The synthesis procedures of the double core organic-inorganic hybrid electrolyte are described in Scheme 1. In the first reaction step, 0.75 mmol of ED2003 and CC were dissolved in a small amount of THF separately and then mixed together and stirred at 0°C for 2 h to form the CED precursor. The NH_2 end group of ED2003 reacted with one Cl atom of CC to form the CED precursor by releasing HCl. In the second reaction step, 0.75 mmol of PEGDGE was added to the solution and continuously stirred at 0°C for 2 h. The epoxide ring opening reaction was occurred due to the reaction between one epoxide ring of PEGDGE and the remaining NH_2 group of the CED precursor to form the complex. After 2 h, 0.75 mmol of the CED precursor was added to the above solution at 0°C and stirred for another 4 h. Again, the NH_2 end group of the CED precursor reacted with the other epoxide ring of the PEGDGE based complex to form the basic linear structure comprising of two CC units linking with ED2003 and PEGDGE polymer chains. In the third reaction step,

the temperature of the solution was raised to room temperature and 1.5 mmol (two times of 0.75 mmol) of ED2003 was added and stirred for 24 h to replace the second Cl atom from both CC cores. In the same way, the NH_2 end groups of ED2003 reacted with the both CC units by replacing the Cl atom to further enhance the linear structure and releasing HCl as byproduct. After that, 1.5 mmol of GLYMO was added and stirred for another 24 h at room temperature to react with another amine end group of the ED2003. The ring opening reaction of GLYMO was occurred because of the reaction of epoxide ring with the NH_2 end group of ED2003, which attached to the CC units and became an extended linear structure comprised of organic and inorganic groups. In the fourth step, the temperature of the mixed solution was raised to 130°C and 1.5 mmol of ED2003 was added and stirred for 24 h to replace the remaining Cl atoms from both CC cores. In this way, all Cl atoms were replaced from the CC cores by linking the ED2003 polymer chains with CC units and forming the branched structure. HCl was again released from the reaction. In the fifth reaction step, the temperature was brought down to room temperature and 1.5 mmol of GLYMO was added to the mixture and stirred for 24 h. Again, the epoxide ring of GLYMO reacted with the amine end group of ED2003 to form the complete double core branched structure. The byproduct HCl, which was released during the synthesis, helped to carry out the hydrolysis and condensation reaction and obviated the use of H_2O for hydrolysis. In the last reaction step, appropriate amounts of LiClO_4 were added into the solution to achieve the desired $[\text{O}]/[\text{Li}]$ ratios and stirred for 24 h to form the hybrid electrolyte complex. The resulting viscous solution was cast onto Teflon dishes and dried in a vacuum oven at 70°C for 2 days to get hybrid electrolyte film with good mechanical strength and flexibility. The hybrid electrolyte films were stored in an argon atmosphere inside a glove box (Innovative technology, PL-HE-2GB with PL-HE-GP1 inert gas purifier) for further characterization. The solid hybrid electrolytes were designated as CPEG-X, where C represents cyanuric chloride, P corresponds to PEGDGE, E stands for ED2003, G for GLYMO and X indicates the number of ether oxygen atoms (only for polymer) per Li^+ cation, $[\text{O}]/[\text{Li}]$. The thickness of the electrolyte films was controlled to be in the range of 80–100 μm .

2.3. Characterization methods

The thermal property of the solid hybrid electrolytes was measured by DSC in the temperature range from -60 to 120°C using Perkin-Elmer Pyris 6 DSC at a heating rate of $10^\circ\text{C min}^{-1}$. The sample weights were maintained in the range of 5–7 mg and hermetically sealed in aluminum pans.

FTIR spectra were obtained from a Bio-Rad FTS155 spectrometer over the range of $4000\text{--}500 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} using the KBr wafer technique. Band deconvolution of the resulting spectra in the range of $600\text{--}650 \text{ cm}^{-1}$ was conducted to obtain the best fit for the band envelope. Mechanical properties of the hybrid electrolyte membranes were evaluated using a Lloyd instruments' single column tensile testing machine (Model LS1). All the tests were conducted at a crosshead speed of 5 mm min^{-1} .

AC impedance measurements of the solid hybrid electrolytes were performed using an Autolab/PGSTAT302 frequency response analyzer (Metrohm Autolab B.V., Netherlands) over a frequency range of 1 Hz to 100 kHz with an amplitude of 10 mV. All the samples were sandwiched by two polished stainless steel blocking electrodes in an argon atmosphere inside a glove box for conductivity tests. The measurements were performed in the temperature range of $15\text{--}80^\circ\text{C}$. Each sample was thermally equilibrated at each selected temperature for at least 30 min prior to taking measurements. Complex impedance plots were computed from the experimental data. The intercept at the real impedance axis in the Nyquist plots corresponds to the bulk electrolyte resistance (R_b)

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