



Hybrid ionogels derived from polycationic polysilsesquioxanes for lithium ion batteries



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ABSTRACT

A multifunctional crosslinkable and ionic-group functionalized ladder-like polysilsesquioxane was synthesized and utilized for the fabrication of hybrid ionogels for lithium ion batteries. The ionic-group functionalized ladder-like polysilsesquioxane combined the synergistic effects of hybrid materials in improving the thermal stability of conventional battery electrolytes, whilst maintain facile solution processability and chemically crosslinkable function in ionic conducting ionic liquid electrolyte media. Fabricated iongel electrolytes exhibiting exceptional thermal stability, mechanical properties, high ionic conductivity, and electrochemical stability. Lithium ion batteries fabricated with the hybrid ionic ladder-like polysilsesquioxane ionogels exhibited initial discharge capacities on par with neat liquid electrolytes, good rate performance, as well as stable cyclability and excellent Coulombic efficiency.

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1. Introduction

The development of polymeric materials for gel membranes in lithium ion batteries have been extensively researched in order to attain tandem lithium ion battery performance and offset safety concerns arising from electrolyte leakage, thermal shrinkage of separators, and instability towards lithium metal [1–4]. The inevitable difficulties in procuring a plethora of properties spanning surface hydrophilicity, thermal stability, electrochemical stability, ionic conductivity, mechanical robustness, and stability towards lithium metal have led to a high degree of complexity in material design and fabrication [5,6].

The vast majority of studies striving to achieve all of the requisite properties for lithium ion batteries detailed above have entailed the use of hybridized ionogel electrolytes either in the form of *in-situ* polymerization of inorganic precursors [7–11] to

yield metal-oxide based frameworks within the ion conducting medium, or *ex-situ* mixing [12–15] of well-defined inorganic or organic-based materials to either physically and or chemically crosslink the ion conducting media.

The *in-situ* method of fabricating hybrid ionogel electrolytes have been pioneered by the Vioux group, as elucidation of various synthetic conditions for fabricating highly mechanically pliant hybrid ionogels with high ionic conductivity, as well as their electrochemical device performance have been well-detailed [8,9] with inorganic matrix precursors such as tetraorthosilicate and titanium isopropoxide. Through polymerizing these precursors *in-situ* ionic liquid media, the oxide-based matrix was found to fully solidify the ionic liquid electrolyte and provide a thermally and electrochemically stable porous framework for electrochemical devices.

The *ex-situ* method of blending oxide-based particles with ion conducting solutions have also been extensively investigated [12–15]. The utility of being able to physically gel ion conducting solutions through mere blending to form so-called ‘soggy sand electrolytes’ [16–18], or to chemically solidify electrolyte solutions through surface modification of the inorganic oxide-based fillers with ion conducting/dissociating [13] or crosslinkable organic functional groups [19] have been recently been a key research fields

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in the development of hybrid ionogels.

However, both the *in-situ* polymerization method and *ex-situ* blending method lack practical fabrication of electrochemical devices. For the *in-situ* polymerization method, the extraction of solvents, acid catalyst, and alcoholic byproducts formed by polycondensation of alkoxide ligands cannot be achieved after device fabrication, and the *ex-situ* blending method requiring pasting of gelatinous ionogels during electrochemical device fabrication may lead to poor contact and wettability between electrodes, leading to difficult replicability in electrochemical device performance.

In order to develop hybrid ionogel electrolytes which possess the requisite thermal, electrochemical, and mechanical properties, while maintaining facile processability with regards to electrochemical device fabrication, we sought out to develop a completely soluble, chemically crosslinkable, ionic-group functionalized hybrid polymer with thermally stable ladder-like structured inorganic backbone [20–33]. This hybrid ionic polysilsesquioxane crosslinkable polymer with high molecular weight exhibited complete solution processability in ionic liquid electrolyte media, while the crosslinkable ionic groups helped to provide high ionic conductivity and enhanced lithium mobility through ionic dissociation of the newly introduced quaternary ammonium group from its counteranion [13,14,34–37].

2. Experimental

2.1. Materials

3-chloropropyltrimethoxysilane (Shin-Etsu, 98%), triallylamine (Sigma Aldrich, 98%), tetrahydrofuran (J.T. Baker, 99%), and dimethylformamide (J.T. Baker, 99%) were vacuum distilled prior to use. Potassium carbonate (Sigma Aldrich, 99.9%) was dried at 40 °C under vacuum overnight prior to use. *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsufonyl)imide (BMPTFSI) (>99.9%, battery grade) was purchased from CTRI, Korea. Azobisisobutyronitrile (AIBN) (Daejung, 98%) was recrystallized from methanol.

2.2. Synthesis of ionic ladder-like polysilsesquioxane

2.2.1. Synthesis and characterization of ionic ladder-like polysilsesquioxane

2.2.1.1. Synthesis of ladder-like poly(chloropropyl)silsesquioxane (LPCIPSQ). Synthesis of LPCIPSQ followed a modified literature procedure [20,38–40]. In a flame dried 250 mL round bottom flask, potassium carbonate (0.2 g, 1.45 mmol) dissolved in deionized water (24 mL, 1.3 mol) and dry THF (40 g) was stirred until a transparent solution was obtained. To this solution, 3-chloropropyltrimethoxysilane (78.5 g, 0.4 mol) was added dropwise under argon flow. The reaction mixture was then vigorously stirred for 3 days, when a white, tacky solid was obtained. After decanting the THF/water mixture, the white tacky solid was dissolved in dichloromethane and extracted with water several times to remove the base catalyst. After collection of the organic layers, drying over anhydrous magnesium sulfate, filtering, and evaporation of dichloromethane, crude LPCIPSQ was obtained in excellent yield (95%). Obtained crude LPCIPSQ was then dissolved in THF and precipitated in cold acetonitrile to remove low molecular weight resins. After filtering, high molecular weight LPCIPSQ was obtained in good yield (85%). Weight average molecular weight (M_w) of LPCIPSQ was 22,000 g mol⁻¹.

2.2.1.2. Synthesis of ladder-like poly(triallylpropylammoniumchloride)silsesquioxane (LTACISQ). In a flame-dried 50 mL round bottom flask, a magnetic bar, LPCIPSQ (1 g, 4.62 mmol chloropropyl

equiv), was dissolved in 10 mL of dry DMF. After LPCIPSQ was completely dissolved, triallylamine (0.52 g, 5.54 mmol) was added under N₂ flow. The brown reaction mixture was then heated to 40 °C, and vigorously stirred for 48 h, when the reaction mixture turned light orange, indicative of the quaternization of the tertiary amines. After confirmation that all of the chloropropyl groups have been converted to quaternary ammonium groups via ¹H NMR, the reaction mixture was left to cool at room temperature. After partial evaporation of the volatiles, the reaction mixture was precipitated in 100 mL of cold acetone to give ladder-like structured poly(-triallylammoniumchloride)propylsilsesquioxane, LTACISQ in good yield (88%). LTACISQ has a M_w of 25,000 g mol⁻¹.

2.2.1.3. Synthesis of ladder-like poly(triallylpropylammoniumTFSI)silsesquioxane (LTATFSISQ). The anion exchange method adopted in this study followed a modified literature procedure [41]. Typically, LTACISQ (1 g, 4.62 mmol triallylammonium chloride equiv.) was dissolved in 15 mL of deionized water. In another vial, LiTFSI (1.45 g, 5 mmol) was dissolved in 10 mL of deionized water. To this solution, the solution containing LTACISQ was precipitated very slowly with vigorous stirring. After stirring for 20 min, the solution was filtered off to give LTATFSISQ as a light yellow glassy solid in good yield (80%). LTATFSISQ has M_w of 32,000 g mol⁻¹.

2.3. Fabrication of hybrid ionogels

The fabrication of hybrid ionogels (HI) began with the dissolution of ionic ladder-like polysilsesquioxane, LTATFSISQ in the ionic liquid electrolyte, 1 M LiTFSI in BMPTFSI, along with 1 wt% AIBN with respect to LTATFSISQ as thermal initiator. This pregel solution was stirred vigorously at room temperature until completely homogeneous solutions were observed. The resulting pre-gel solution was thermally cured at 70 °C for 3 h to yield homogeneous ionogels, named as HILI-5, HILI-10 for hybrid ionogels derived from ionic ladder polysilsesquioxane content of 5 wt% and 10 wt% respectively.

2.4. Characterization and methods

Fourier transform infrared spectroscopy examinations were conducted with a Perkin-Elmer FTIR system Spectrum-GX. Thermal gravimetric analysis was carried out with TA instrument (TGA 2950) at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. The ratios of weight average molecular weight (M_w) and number average molecular weight (M_n), so called molecular weight distributions index (M_w/M_n) of the polymers, were measured using JASCO PU-2080 plus SEC system equipped with refractive index detector (RI-2031 plus), UV detector ($\lambda = 254$ nm, UV-2075 plus) and Viscotek SLS apparatus using THF as the mobile phase at 40 °C with a flow rate of 1 mL min⁻¹. The samples were separated through four columns (Shodex-GPC KF-802, KF-803, KF-804 and KF-805). ¹H NMR, ²⁹Si NMR spectra were recorded at 25 °C on a Varian Unity INOVA (¹H: 300 MHz, ¹³C: 75.43 MHz, ²⁹Si: 59.6 MHz). NMR spectra for LPCIPSQ and LTATFSISQ were recorded in CDCl₃, while those for LTACISQ in D₂O. Rheological properties were measured using a MCR 302 rheometer (Anton Paar, Austria) instrument with parallel plate geometry (25 mm diameter) with strain of 5%. All rheological examinations were performed in the linear viscoelastic region under nitrogen atmosphere. Solid-state ⁷Li NMR spectra were obtained on a Varian Unity (¹H: 400 MHz, ⁷Li: 155.45 MHz) with spinning frequency held constant at 10 kHz with a pulse delay time of 4 s. Samples were packed into 7.5 mm zirconia rotors and sealed with Kel-F short caps. WAXD patterns were obtained with a Dmax2500/PC (Rigaku) with CuK α radiation.

The ionic conductivity values were determined using a complex impedance analyzer (Bio-Logics, VMP3) over frequencies ranging

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