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Lithium Ion Batteries Fabricated with Ionic Ladder-Like Polysilsesquioxane Hybrid Ionogels

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A new cross-linkable ionic group-functionalized ladder-like structured polysilsesquioxane was utilized as crosslinker for fabrication of hybrid ionogels. The ionic ladder-like polysilsesquioxane was completely solution processable in ionic liquid electrolytes and through chemical crosslinking, hybrid ionogel electrolytes with high ionic conductivity and electrochemical stability were obtained. Lithium ion batteries assembled with these hybrid ionogels electrolytes exhibited excellent cell cycling performance at elevated temperatures, suggesting the highly utile nature of our hybrid ionogel electrolytes.

Keywords: Polysilsesquioxane, Ionic Liquids, Lithium Ion Batteries.

1. INTRODUCTION

With increasing demands for high performance lithium ion batteries, subsequent needs for enhanced safety have been a key issue and challenge for engineers. To mitigate the most common safety concerns of lithium ion batteries, which are electrolyte leakage and explosions derived from such leakage, are to develop solidified electrolytes.[1]

However, completely solid polymer electrolytes without liquid components lack the required ionic conductivities for practical industry application.[2] As such, gel polymer electrolytes and solidified ionic liquids, so-called ionogels, have received much attention.[3–5] Ionogels can be fabricated via chemical or physical crosslinking methods, but chemical crosslinking with highly soluble materials have been sought out as the most facile method.

However, a remaining problem with ionogels is their insufficient mechanical properties.[6] As such, the hybridization of ionogels with inorganic materials have been extensively investigated in several recent reports, most notably with the Vioux and Archer groups.[6,7]

As ladder-structured polysilsesquioxanes are known to exhibited superior thermal and mechanical properties[8] over organic-based and other hybrid materials with uncontrolled structure, all while having excellent solubility in organic solvents, we sought out to develop hybrid ionogels through synthesis of an ionic ladder-like structured polysilsesquioxane.

2. EXPERIMENTAL DETAILS

2.1. Materials

All materials were vacumm distilled or recrystallized prior to use. All solvents were used as received.

2.2. Synthesis of LPClSQ

The synthesis of LPClSQ followed our previous method[8] utilizing 3-chloropropyltrimethoxysilane as monomer.

2.3. Synthesis of LVImClSQ

To a solution of LPClSQ (1 g) in DMF (20 mL), 1-vinyl imidazole (0.2 g, 2.1 mmol) was added under Ar. The reaction mixture was heated to 60 °C for 24 h and purified through repeated precipitations in hexane.

2.4. Synthesis of LVImTFSISQ

LVImClSQ (1 g) was dissolved in deionized water (5 mL) and precipitated in a previously prepared solution of LiTFSI (0.72 g, 0.25 mmol) in deionized water (5 mL). The precipitates were collected via vacuum filtration and LPVImTFSI stored at 40 °C prior to use.

2.5. Fabrication of Hybrid Ionogels

LVImTFSISQ was dissolved in an ionic liquid electrolyte (ILE) solution of 1M LiTFSI in *N*-butyl-*N*-methylpyrrolidiniumbis (trifluoromethylsulfonyl)imide (BMPTFSI) and thermally cured with AIBN as radical initiator (1 wt% of LVImTFSISQ) at 70 °C for 3 h to

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yield hybrid ionogels. The hybrid ionogels were named LIE-5, LIE-10 and LIE-20 according to LVImTFSISQ crosslinker weight percentage of 5 wt%, 10 wt%, and 20 wt%, respectively.

2.6. Electrochemical Measurements

The ionic conductivity was determined using a complex impedance analyzer (Bio-Logics, VMP3) over frequency range from 1 Hz to 1 MHz at AC amplitude of 10 mV. The electrochemical stability of the hybrid ionogel electrolytes was examined using a linear sweep voltammetry system. In the experiments, a stainless steel working electrode was used with lithium metal as both the counter and reference electrodes. The voltage was swept at a scan rate of 1.0 mV s^{-1}. Electrochemical measurements of the gel polymer electrolyte were conducted using 2032 coin cells consisting of a separator, Li metal and a $LiFePO_4$ cathode (90 wt% $LiFePO_4$, 5 wt% carbon black, 5 wt% PVDF). All the cells were assembled in argon-charged glove box. After fabrication, the cells with pre-gel solution were subjected to thermal cross-linking for 3 h at 70 °C. The galvanostatic charge–discharge experiments were carried out with voltage range of 2.5–4.2 V using a battery cycler (Wonatech, WBCS3000) at 50 °C.

3. RESULTS AND DISCUSSION

The synthesis of ionic ladder-like polysilsesquioxane with crosslinkable functional groups followed the synthetic scheme shown in Figure 1. As shown, the ladder-structured polymer backbone with chloropropyl groups was first obtained by our previously developed method[8–11] and the vinylimidazolium groups introduced through quaternization reaction in DMF media. Through simple anion exchange in water, LVImTFSISQ was obtained as a viscous brown liquid with excellent yields (~88%).

Figure 2 shows the characterization results for the various intermediary products and final ionic ladder-like structured polysilsesquioxane, LVImTFSISQ. As shown, all of the chloropropyl groups were quantitatively substituted with the vinyl imidazolium group as indicated by the shift in $-CH_2$-peak characterized as *c* to *c*′, as well as the new peak *d* and *d*′ attributed aromatic proton of vinyl imidazolium in Figure 1(a). Moreover, the ^{13}C NMR of LVImTFSISQ in Figure 1(b) revealed the presence of $TFSI^-$ anion as shown by the new sharp peaks at 113, 118, 122, and 127 ppm and the trifluorosulfonyl vibrations (1193 cm^{-1} and 1043 cm^{-1}) in the FTIR spectra in Figure 1(c).

FT-IR analysis was also carried out to characterize the chemical structures of the cured ionogels. As presented in Figure 3, the characteristic peak around 1640 cm^{-1} from the C═C stretching mode of the vinyl group of LVImTFSI disappeared after thermal treatment, indicating the crosslinking reaction was complete.

The room temperature ionic conductivities of the fabricated hybrid ionogels were shown in Figure 4 as a function

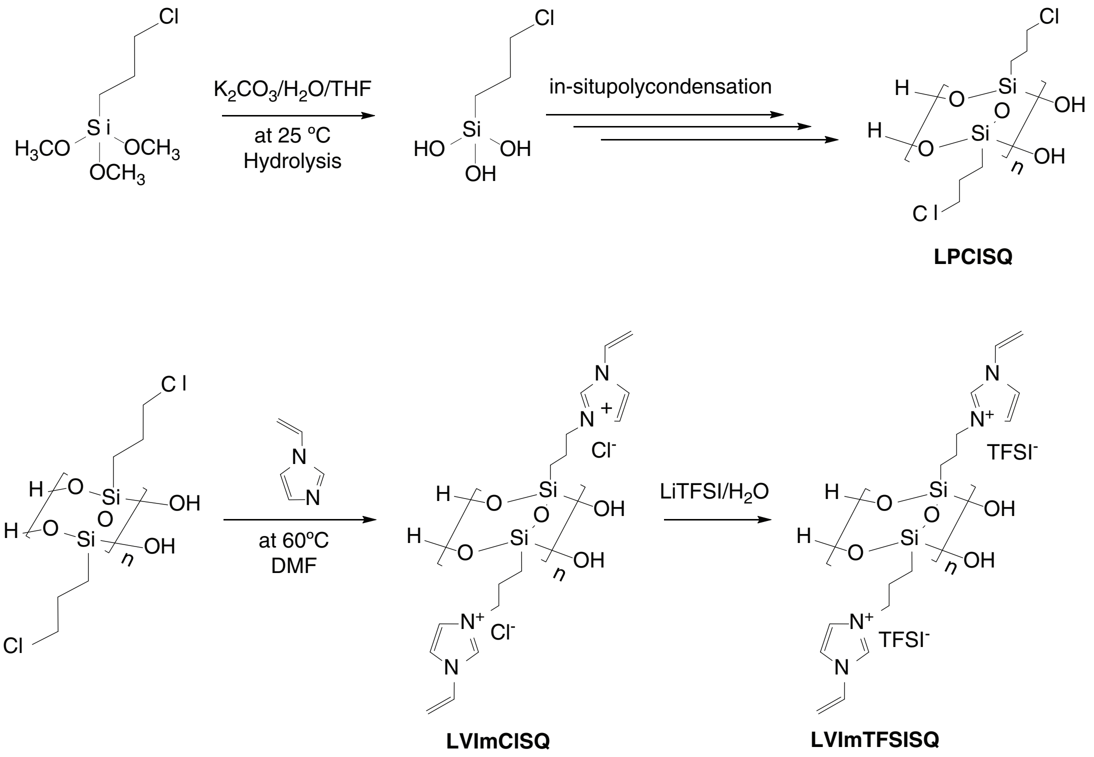

Figure 1. Synthetic scheme for LPClSQ, LVImClSQ and LVImTFSISQ.

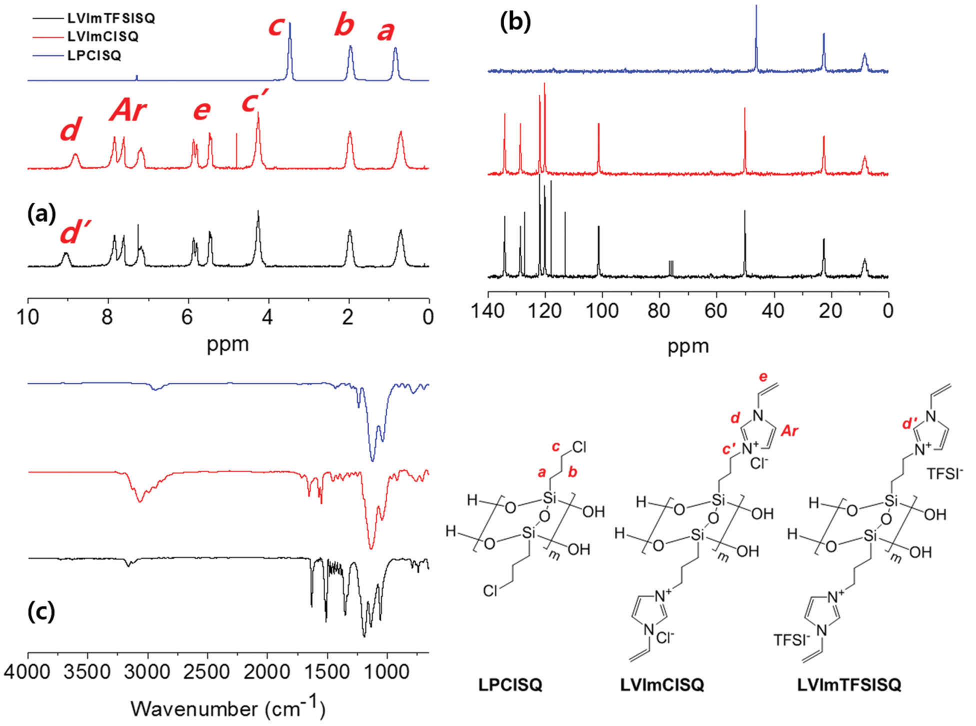

Figure 2. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) FTIR spectra for LPClSQ, LVImClSQ and LVImTFSISQ.

of crosslinkable ionic ladder-like polysilsesquioxane. As shown, the ionic conductivities for the hybrid ionogels decreased as a function of ionic ladder-like polysilsesquioxane due to the increasing rigidity of the network structure. However, LIE-10 hybrid ionogel electrolyte fabricated with only 10 wt% of ionic ladder-like polysilsesquioxane, LVImTFSISQ, exhibited high ionic conductivity (~0.3 mS/cm), a most practical value for application in lithium ion battery cells.

Next, the electrochemical stability of the LIE-10 was measured through linear sweep voltammetry in Figure 5. As shown, the hybrid ionogels fabricated with crosslinkable ionic ladder-like polysilsesquioxane exhibited high electrochemical stability (up to 5 V vs. Li+/Li) which led

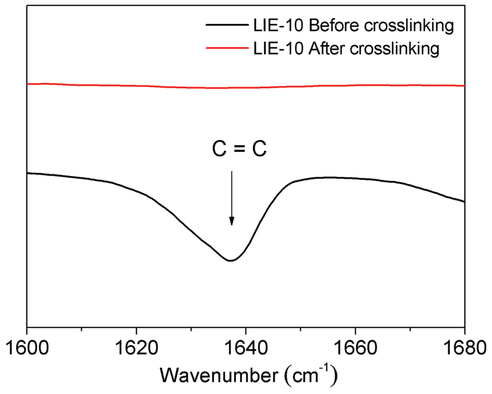

Figure 3. FTIR spectra of LIE-10 before and after thermal treatment.

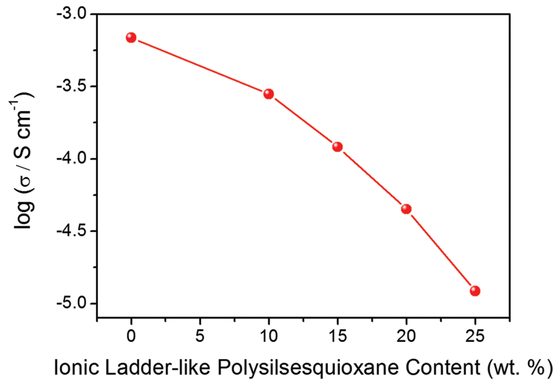

Figure 4. Room temperature ionic conductivities of hybrid ionogels as a function of ionic ladder-like polysilsesquioxane crosslinker.

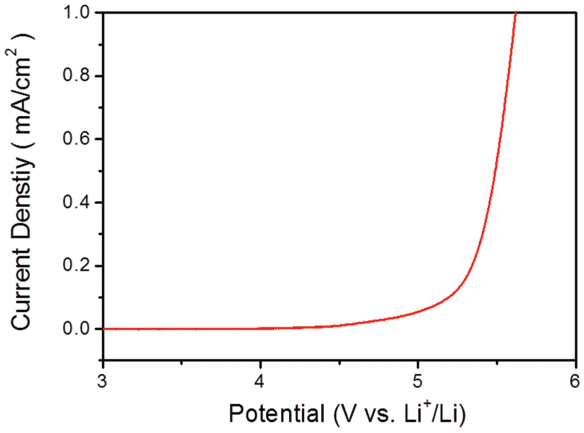

Figure 5. Linear sweep voltammetry curves for LIE-10.

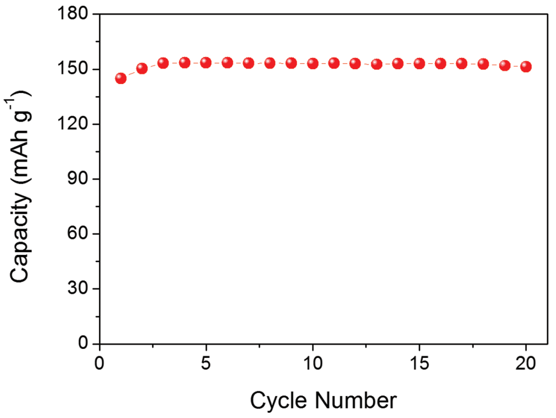

Figure 6. Cyclability of hybrid ionogels LIE-10 at 0.1C–0.2C (charge–discharge) at 80 °C.

us to believe that these hybrid ionogels would be suitable for lithium ion batteries.

Lithium ion batteries were fabricated with a $LiFePO_4$ cathode, Li metal anode, and a PP separator sandwiched between with LIE-10. Under conditions of 0.1C–0.2C (charge-discharge) at 80 °C, the cyclability of the LIE-10 hybrid ionogel electrolyte was extremely steady, giving a near ideal capacity for 20 cycles,[11–13] as shown in Figure 6. This promising lithium ion battery performance was attributed to the high ionic conductivity and exceptional electrochemical stability of the ionic ladder-like polysilsesquioxane crosslinker.

4. CONCLUSION

In conclusion, we successfully synthesized an ionic ladder-like structured polysilsesquioxane and utilized it as crosslinker for the fabrication of hybrid ionogel electrolytes for lithium ion batteries. The developed hybrid ionogel electrolytes exhibited high ionic conductivity, good electrochemical stability, and lithium ion battery performance revealed promising cycling behavior.

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