



A novel polyhedral oligomeric silsesquioxane based ionic liquids (POSS-ILs) polymer electrolytes for lithium ion batteries

Dapeng Shang^a, Jifang Fu^{a,*}, Qi Lu^a, Liya Chen^a, Jintao Yin^a, Xing Dong^{a,b}, Yufeng Xu^a, Rongrong Jia^a, Shuai Yuan^{a,*}, Yi Chen^a, Wei Deng^{a,c}

^a Nano-Science & Technology Research Center, Shanghai University, 99 Shangda Road, Shanghai 200444, PR China

^b School of the Environment and Safety Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang, Jiangsu Province 212013, PR China

^c School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, PR China

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ABSTRACT

A series of novel imidazolium-based polyhedral oligomeric silsesquioxane ionic liquids (POSS-ILs) have been successfully synthesized and used to develop new solid polymer electrolytes with high ionic conductivity and wide electrochemical windows. The POSS-ILs are added to the solid polymer electrolytes (SPEs) based on blend of polyethylene oxide (PEO), poly(vinylidene fluoride-hexafluoro propylene) (P(VDF-HFP)), propylene carbonate (PC) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) to alter the morphology, ionic conductivity, electrochemical windows properties. The results from scanning electron microscope (SEM), energy-dispersive x-ray spectrometry (EDXS) mapping and X-ray diffraction (XRD) indicate that POSS-ILs are uniformly distributed in the SPEs and form amorphous area by significantly inhibiting the crystallization of host polymer. The electrochemical studies indicate that the addition of POSS-ILs increases the ionic conductivity up to $3.9 \times 10^{-4} \text{ S cm}^{-1}$ at 22 °C and $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at 62 °C. The electrochemical windows of POSS-ILs based SPEs are stable up to 5.0 V. As a result, the lithium-ion battery cell prepared using the POSS-ILs-SPE showed a good cycle performance and reversible capacity recovery behavior. These indicate POSS-ILs based SPEs would be good candidate to replace the conventional organic liquid electrolytes for lithium ion batteries.

1. Introduction

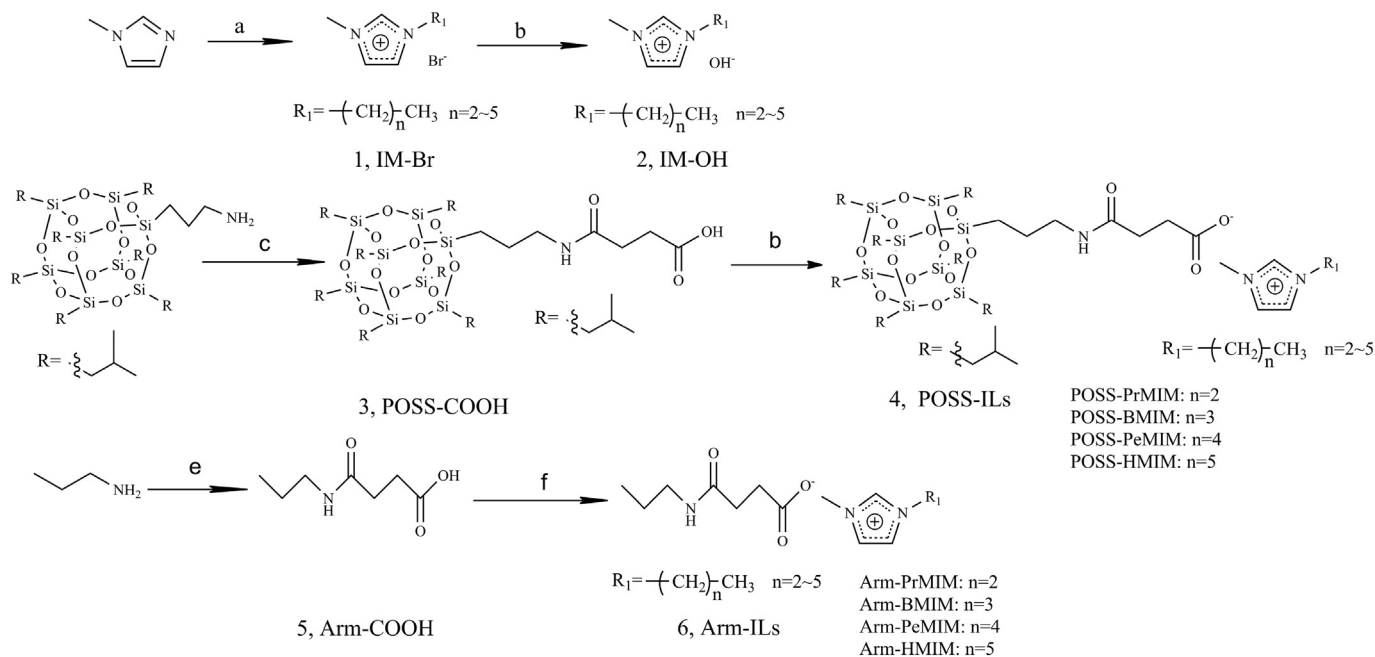
Electrolytes are one of the most important components in electrochemical devices such as lithium ion batteries, fuel cells, solar cells and supercapacitors [1–5], and they play a key role in determining devices performance, durability and safety [6,7]. However, traditional liquid electrolytes for most commercially electronic devices may bring a series of potential safety problems such as leakage, thermal decomposition and narrow electrochemical windows [8–10]. Recently, solid polymer electrolytes (SPEs) have been developed as excellent candidate to replace liquid electrolytes in electronic devices, in terms of the enhanced safety and many other distinct advantages, including low cost, light weight, good interface stability and excellent design flexibility [11–15]. Unfortunately, it must be mentioned that SPEs possess a main disadvantage, which is the low ionic conductivity compared to liquid electrolytes [16]. Different strategies have been explored to enhance SPEs with sufficient ionic conductivity and mechanical stability [17–22]. One strategy to improve the ionic conductivity of SPEs is modifying traditional polymer electrolytes with inorganic salt such as

ZrO₂, TiO₂ and SiO₂ [20,22–25]. Inorganic salts can hinder the re-organization of polymer chains and thus facilitate the dissociation of lithium salt and the motion of Li⁺ ionic species, finally leading to the improvement of the ionic conductivity [25–27]. However, high ionic conductivity can be obtained with high filler content, which results in poor processibility, mechanical properties and cell performance [25–27]. Another strategy is added plasticizers including ionic liquids, conventional organic electrolytes, solvents, compounds and monomer/oligomer units of polymer to traditional polymer based electrolytes [24,28–31]. The growing use of ILs in SPEs materials community is due to their unique properties, such as non-flammability, relatively high ionic conductivity and wide electrochemical window. The ion conductivity and electrochemical window of SPEs can be enhanced by introducing ILs to the polymer matrix [32,33]. However, a great quantity of ILs is needed to satisfy high ionic conductivity, which can cause some serious problems such as phase separation, leakage, deteriorated mechanical strength, lower dimensional and thermal stability during its applications [34,35].

Polyhedral oligomeric silsesquioxane (POSS) are unique inorganic-

* Corresponding authors.

E-mail addresses: fjshu@shu.edu.cn (J. Fu), S.yuan@shu.edu.cn (S. Yuan).



Scheme 1. Reagents and conditions: (a) propyl bromide, butyl bromide, pentyl bromide or hexyl bromide, 0 °C to r.t., 1 week; (b) Amberlite-IRA400, water, r.t.; (c) succinic anhydride, tetrahydrofuran, r.t., 4 h; (d) **2**, tetrahydrofuran, methanol, r.t.; 10 h. (e) succinic anhydride, dioxane, 80 °C, 1 h; (f) **2**, tetrahydrofuran, methanol, r.t.; 10 h.

organic nanoscale materials with well-defined cage-like nanometer-sized inorganic structures and organic functional groups [36,37]. Consequently, by introducing POSS core to ionic salts, the thermal stability properties of the ILs significantly improved and the ion transportation abilities of ILs also strengthened [38,39]. POSS based ionic liquids (POSS-ILs) combine advantages of ILs and inorganic salts. POSS based materials not only hinder the crystallization of host polymer, but also enhance the thermal and electrochemical stability of SPEs due to their inner inorganic silicon oxygen core that facilitate lithium ion conduction [40–42]. Z.S. Wang et al. [43] developed new POSS-based electrolytes with low glass transition temperatures for solid-state dye-sensitized solar cells, and POSS-based imidazolium iodide ionic conductors yield the highest power conversion efficiency of 6.98% at RT due to high conductivity of POSS-ILs.

In this work, novel solid polymer electrolytes containing POSS-ILs are proposed. A series of POSS based ionic liquids are designed and synthesized, as outlined in Scheme 1. The POSS-ILs not only retains the good electric properties of ionic liquids, but also enhances the thermal stability of imidazolium-based ILs by introducing POSS core to ionic salts. The blend of the PEO and P(VDF-HFP) can hinder the crystalline of the PEO and achieve a good combination of higher ionic conductivity and mechanical strength compared to PEO electrolytes, which suffer from a major drawback involving a very low conductivity at room temperature [23,31]. Then we added these POSS-based ionic liquids to PEO-P(VDF-HFP) blend-based electrolytes and characterized them involving complex impedance spectroscopic analysis with a view to understand the effect of incorporation of POSS-ILs into the blend-based polymer electrolytes. As expected, POSS-ILs increases the ionic conductivity and the electrochemical windows of blend-based polymer electrolytes, which make them good electrolyte candidates to replace the conventional organic liquid electrolytes for lithium ion batteries.

2. Experimental section

2.1. Materials

1-Methylimidazole, 1-bromobutane, 1-bromopentane, 1-bromohexane and anion change resin (Amberlite 717) were obtained from Aladdin Company. Succinic anhydride and *N,N*-dimethylformamide

(DMF), LiFePO₄ and carbon black were purchased from Sinopharm Chemical Reagent Co. Ltd. Aminopropylisobutyl POSS (POSS-NH₂) was obtained from Hybrid Plastics Company. Poly(vinylidene fluoride-hexafluoro propylene) (P(VDF-HFP)), (Mw ≈ 400,000) was obtained from Sigma-Aldrich chemicals limited. The polyethylene oxide (PEO, Mw ≈ 5,000,000), propylene carbonate (PC) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) were procured from Aldrich chemicals limited. Synthesis of Arm-COOH and Arm-ILs are seen in supporting information.

2.2. Synthesis of hydroxide of imidazolium cations

A series of bromide salt of imidazolium cations were synthesized according to the method described by K Tanaka et al. [44] 1-Bromoalkane was dropwisely to the 1-methylimidazole with vigorous stirring at 0 °C. The mixture was stirring for 1 week at ambient temperature. After that, the excessive 1-bromoalkane was decanted. Then, the molten salt was washed with ethyl acetate for three times, and then dried in vacuum at 60 °C for 24 h.

2.3. Synthesis of POSS-COOH

POSS-NH₂ (2.01 g, 2.298 mmol) was dissolved into 30 ml of tetrahydrofuran and then dropwisely into a solution of succinic anhydride (0.28 g, 2.800 mmol) in 30 ml tetrahydrofuran. The solution was stirred for 4 h at room temperature and then removing solvent by rotary evaporation. Then 30 ml cyclohexane was poured into the flask and excessive succinic anhydride was precipitated and filtrated, after that, the filtrate were evaporated under reduced pressure, finally the POSS-COOH was obtained as white solid after dried under vacuum at 60 °C.

2.4. Synthesis of POSS-ILs

Then, exact same equivalent of bromide anion **1** to the carboxy group was converted into **2** by anion change resin (Amberlite-IRA400) in water. The aqueous solution was concentrated with rotary evaporator and the residual liquid was freeze dehydrated to give the imidazolium hydroxide derivatives white solid. In a 100 ml flask, POSS-COOH (9.74 g, 0.01 mol) was dissolved in 30 ml anhydrous

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