



A novel porous gel polymer electrolyte based on poly(acrylonitrile-polyhedral oligomeric silsesquioxane) with high performances for lithium-ion batteries



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ABSTRACT

A novel porous membrane, based on a polymer matrix of poly(acrylonitrile-polyhedral oligomeric silsesquioxane) (P(AN-POSS)), is prepared by phase inversion process, and the corresponding gel polymer electrolyte (GPE) is further fabricated by immersing the porous membrane into liquid organic electrolyte. The thermal stability and structure of prepared POSS and polymers are investigated. The research indicates that the P(AN-POSS) membrane with copolymerization content of 8 wt% POSS exhibits the better pore structure and superior electrolyte uptake compared with pure PAN membrane, which endows the corresponding GPE with remarkable comprehensive performances: the maximum ionic conductivity value of $6.06 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature, the sufficiently stable interface compatibility between GPE and electrode, the excellent lithium ion transference number of 0.59 and the higher electrochemical stability potential of 5.7 V (vs. Li/Li⁺). At 0.2 C, the GPE with 8 wt% POSS in polymerization based lithium ion battery shows a satisfactory discharge capacity of 148 mAh g⁻¹ and improved capacity retention of 93.7% after 80 cycles.

1. Introduction

Rapid consumption of traditional energy sources, such as fossil oil and gas, and air environmental pollution have forced the development of green new energy sources as a significant key to solve the problem [1]. Lithium ion batteries (LIBs), an efficient energy storage device with long cycle life and high energy density, have been deeply studied and widely applied in various portable digital devices and electric vehicles [2–6]. However, although commercial LIBs with liquid organic electrolyte exhibit satisfactory ion conductivity and cycling capacity, safety risks such as leaks, fire and explosions cannot be neglected [7–9]. Thus, inorganic solid electrolytes such as lithium phosphorus oxynitride (LiPON) electrolyte [10–12] and sulfide electrolyte [13,14] have been extensively studied by researchers. These electrolytes do not contain liquid and organic components, battery combustion and explosion and other safety incidents can be effectively avoided. However, the lower ionic conductivity of inorganic solid electrolyte and the poor compatibility between solid electrolyte and electrode are unsatisfactory [15–17]. Gel polymer electrolyte (GPE), a safer electrolyte in a state between liquid and solid, presents a series of advantages of shape

controllability, high ionic conductivity and sufficient electrochemical stability, which can be formed by immersing the polymer matrix membrane in the liquid electrolyte [18–26]. In recent reports related to GPE, poly(methyl methacrylate) (PMMA) [27–30], poly(vinylidene fluoride) (PVDF) [31–34], polyacrylonitrile (PAN) [35–38] and poly(ethylene oxide) (PEO) [39–42] have been explored to be suitable for polymer matrix to develop GPE.

PAN, as we all know, presents the excellent thermal stability and superior film forming property. Furthermore, a high level of $10^{-3} \text{ S cm}^{-1}$ of ionic conductivity has been confirmed in numerous related studies [43–46]. Nevertheless, a serious problem that has limited the further development of PAN based GPE is the higher crystallinity of PAN polymer, which is consistent with the interaction of strong polar groups -C≡N on the adjacent segments of PAN [47]. The larger crystal regions will give rise to a great block to the transference of charge carriers, the ion conduction capacity, lithium ion transference number and interface stability of GPE will be further significantly weakened. It can be found from the previous reports of polymer electrolytes that the crystallinity of polymer matrix can be decreased through incorporating inorganic nanoparticles (such as SiO₂, TiO₂ and

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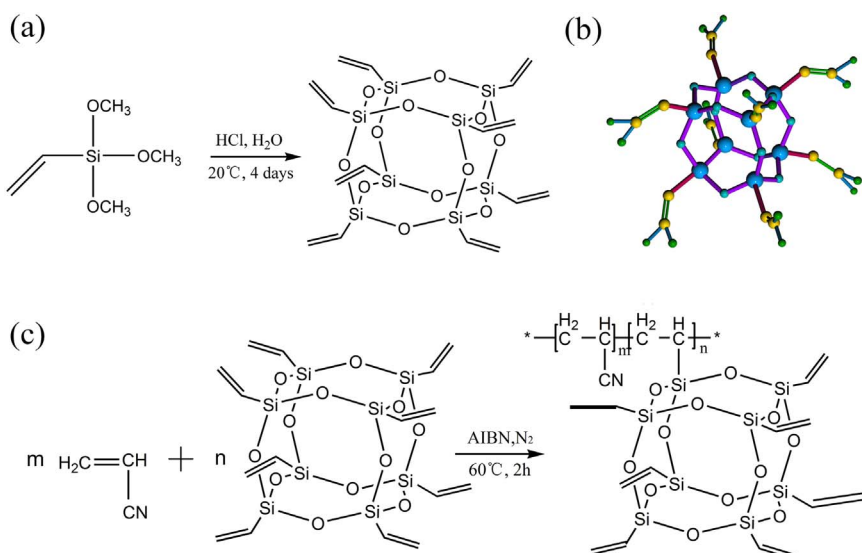


Fig. 1. (a) The synthetic method of POSS, (b) structural model of POSS and (c) the synthesis reaction of P(AN-POSS).

Al_2O_3) or polymerization with other monomers [4,48–50]. Accordingly, the combination of these two methods will be expected to play a significant role in reducing PAN crystallinity.

Polyhedral oligomeric silsesquioxane (POSS), a molecular-level intramolecular organic-inorganic hybrid nanoparticle, possesses a kind of particular structure of three-dimensional cage and general formula of $(\text{RSiO}_{1.5})_n$. In detail, n can be assigned the values of 8, 10 or 12, and R usually can be organic groups such as alkyl and vinyl group in the corners of POSS cage [51,52]. Therefore, the organic constituent and inorganic skeleton of Si–O–Si bonds constitute a mixed system of POSS. In particular, when the periphery of POSS cage is endowed with vinyl groups, the condition for copolymerization between POSS and acrylonitrile (AN) is created simultaneously. The introduction of POSS by the way of chemical polymerization reduces the possibility of nanoparticle agglomeration to a certain extent compared with the physical mixture of nanoparticles with polymer matrix. What more important is the involvement of organic double bonds of C=C in POSS disrupts the polymerization sequence of AN monomers and forms a network-like copolymer structure, which contributes to weaken the interaction of polar groups of $-\text{C}\equiv\text{N}$ between adjacent polymer segments, and an expanding amorphous region is created at the same time. Thus, this is exceedingly beneficial for the movement of charge carriers in GPE. Furthermore, the inorganic components of POSS are expected to play an important role in promoting the thermal performance of GPE as traditional inorganic nanoparticles [53]. Meanwhile, the steric hindrance of POSS inorganic skeleton cage will further favor the decrease of polymer crystallinity. Therefore, the performance improvement of P(AN-POSS) based GPE is worth to be expected compared with pure PAN based GPE.

In addition, the preparation technology of polymer membrane for GPE also exerts a profound impact on the performance of GPE. Solvent casting method [54], phase inversion method [55] and electrospinning technique [56,57] have been widely used in the preparation of membranes in recent reports. In these ways, the phase inversion method exhibits lots of merits such as low cost, easy operation and efficient, and the prepared polymer membranes often possess a distinct pore structure [19,58]. Consequently, taking into account all the above theoretical basis, a novel porous polymer membrane and the corresponding GPE base P(AN-POSS) were prepared through phase inversion technology. The comprehensive performances of the resulting dry membranes and GPEs were studied, and the effect of POSS on them was further investigated.

2. Experimental

2.1. Materials

N,N-dimethylformamide (DMF, AR), ethyl acetate (EA, AR), hydrochloric acid (HCl, AR), methanol (AR), acrylonitrile (AN, AR) dimethyl sulfoxide (DMSO, AR), 2,2'-Azobis(2-methylpropionitrile) (AIBN, AR), acetone (AR) were purchased from Chengdu Kelong Chemical Reagent Company. Vinyltrimethoxysilane (VTMS, CP) was purchased from Nanjing UP Chemical Co., Ltd. Liquid electrolyte (1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) = 3/7, v/v) was purchased from Shenzhen Kejing Star Technology Co., Ltd.

2.2. Preparation of POSS

30 ml VTMS and 130 ml EA were added to a flask and then placed in the water bath of 20 °C with continuous stirring of 30 min. A mixed acid solution consisting of 18 ml deionized water and 42 ml HCl was added dropwise to the flask. The mixture was subjected to a dehydration condensation reaction for 4 days under continuously vigorous stirring. Then a great amount of methanol was added to the mixed solution after the reaction to precipitate the crude product of POSS, and the crude product was washed with methanol at least two times. Finally, the white powder product of POSS was obtained by vacuum drying at 60 °C for 24 h. The synthetic method and structural model of POSS are shown in Fig. 1(a) and (b), respectively.

2.3. Preparation of P(AN-POSS)

The synthesis of the P(AN-POSS) copolymer was carried out in a four-necked glass reactor. AN, one of the reaction monomers, was firstly distilled under atmospheric pressure to remove the polymerization inhibitor. The prepared POSS as another reactive monomer was dissolved in a mixed solution consisting of DMSO and deionized water (DMSO/deionized water = 9/1, v/v) under vigorous stirring at 90 °C for 1 h. Then 1 wt% AIBN, as a free-radical initiator, and the purified AN were added to the reactor. The polymerization was continued at 60 °C for 2 h under N_2 flow and vigorous stirring. The resulting solution was firstly precipitated with methanol, and then the precipitate was subsequently washed with acetone. Finally, the P(AN-POSS) copolymer was obtained in the form of white powder by drying the precipitate in a vacuum oven at 60 °C for 12 h. In this synthesis process, for comparison, polymerization of AN and POSS with different mass ratios were carried out (AN/POSS = 100/0, 95/5, 92/8 and 90/10, respectively), and the

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