



Effect of OctaphenylPolyhedral oligomeric silsesquioxane on the electrospun Poly-m-phenylene isophthalamid separators for lithium-ion batteries with high safety and excellent electrochemical performance

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HIGHLIGHTS

- A novel hybrid Octaphenyl-POSS/PMIA membrane is successfully prepared.
- The separator has outstanding thermal stability and strength.
- The separator shows excellent ability to absorb and store liquid electrolyte.
- The separator has high ionic conductivity and stable electrochemical window.
- The battery presents high safety and excellent electrochemical performance.

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ABSTRACT

In this study, a hybrid Poly-m-phenyleneisophthalamide/Octaphenyl-Polyhedral oligomeric silsesquioxane (PMIA/Octaphenyl-POSS) membrane (HPPS) was fabricated by electrospinning technique and its application performance as lithium-ion battery separators was discussed. The organic-inorganic feature of Octaphenyl-POSS (OPS) endowed admirable compatibility of membrane matrix for the HPPS membranes. The nanofiber membranes with OPS nanoparticles were provided with commendable thermal stability, robust mechanical strength (21.79 MPa), high porosity and electrolyte uptake, which laid a good foundation for improving the safety and cycle performance of the cells with the separator. The lithium-ion battery with the HPPS separator displayed a high ionic conductivity of $1.93 \times 10^{-3} \text{ S cm}^{-1}$ and a stable electrochemical window of 4.98 V. More significantly, the HPPS nanofiber membrane based Li/LiCoO₂ cell exhibited excellent cycling stability with high first discharge capacity up to 157.9 mAh g⁻¹ and superior capacity retention of 89.04% after 100 cycles. Therefore, the HPPS separator has extraordinary potential to be used in high-performance lithium-ion battery.

1. Introduction

In the present era, the shortage of energy and pollution of the environment become more and more serious with the development of society. Confronting with the urgent problems of environmental pollution and resource exhaustion, the development of an alternate, sustainable and clean energy technology is extremely necessary. The lithium-ion battery, as an efficient and clean energy storage system, has attracted widespread attention for a wide variety of new energy

vehicles by virtues of its high energy density, low self discharge rate, excellent power density, long cycle lifetime as well as low memory effect and environmental friendliness [1–5]. It is widely recognized that lithium-ion battery is mainly composed of four parts including cathode, anode, separator and liquid electrolyte [6]. And separator plays an indispensable role in impeding the immediate contact of cathode and anode and providing the effective channels for the transmission of lithium-ions between electrodes, which has a significant influence on the safety performance and cycle capability of battery [7–10]. Currently,

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the polyolefin microporous membranes have become the main commercialized separators owing to their excellent mechanical property, prominent electrochemical stability and low cost, such as polypropylene (PP), polyethylene (PE) and their combinations [11,12]. However, their intrinsic limitations, including low porosity, poor electrolyte wettability and unsatisfactory thermal stability, make against the passing of lithium-ions and the guarantee of battery safety, so their application prospects were greatly restrict in the field of power battery [13–16].

To improve the performance of lithium-ion battery separators, a vast array of strategies have been proposed, including γ -ray irradiation method [17], solvent casting technique [18], thermally induced phase separation technique [19], phase inversion method [20] and electrospinning technique [21–23]. Among these methods, electrospinning is a widely used technology, which can fabricate nanofiber membranes directly and continuously [24,25]. Admirably, these electrospinning membranes are provided with fine fibers, strong electrolyte uptake, high porosity and large specific surface area [23,26,27], which have a great potential in the application of separator materials for commercialized lithium-ion batteries. For the past few years, various polymers with excellent properties have been developed to satisfy the need of lithium-ion battery separators by the electrospinning technology, including Polyvinylidene fluoride (PVDF) [28,29], Poly(vinylidene fluoride co-hexafluoropropylene) (PVDF-HFP) [30], Polyacrylonitrile (PAN) [31] and Polyethylene terephthalate (PET) [32] *etc.* In recent years, some heat-resistant polymers, like poly(phthalazinone ether sulfone ketone) (PPESK) [2], polyimide (PI) [33,34], Polyetherimide [35,36], Polyethylene [37], Ceramic [38,39] and so on, have obtained extensive attentions to act as the matrix of separators for lithium-ion batteries by electrospun technique.

To the best of our knowledge, Poly(m-phenylene isophthalamide) (PMIA) is provided with extremely high thermal stability up to 400 °C, because it is a polymer with meta-type benzene-amide linkages in its skeletal chain [40–42]. In addition, PMIA fibers also show outstanding mechanical property, excellent self extinguishment and chemical corrosion resistance. Therefore, some researchers believed that PMIA had definite potential to be used as a separator for lithium-ion batteries. Zhang et al. [43] adopted the aramid fibers as the separator of lithium-ion battery by the papermaking process, which exhibited better electrolyte wettability, excellent thermal resistance, and outstanding cycling performance than that of PP separators. In addition, Zhai et al. [44] constructed a sandwich-structured PVDF/PMIA/PVDF nanofibrous battery separator with an increased tensile strength up to 13.96 MPa via the electrospinning technique. Although the PMIA polymer membranes have certain capacity to act as lithium-ion battery separators, the electrolyte uptake and ionic conductivity still need to be further improved.

Various methods and strategies have been studied to improve the performance mentioned above of electrospinning separators, including blending modification, compound modification, adding inorganic nanoparticles, *etc.* Gopalan et al. [45] blended PVDF with PAN polymer to fabricate the electrospinning lithium-ion battery separator, and found that the electrolyte uptake of the mixed polymer membrane increased significantly compared with the pure PVDF separator. Moreover, Xiao et al. [46] prepared a PVDF/PMMA/PVDF tri-layer composite membrane, and the PVDF membrane on both sides was formed by electrospinning while the middle layer PMMA was constructed via the solution-casting method. Because high surface area of the electrospun fiber membrane, the prepared membrane can absorb more electrolytes and obtain higher ionic conductivity. Furthermore, the inorganic nanoparticles have large specific area, which can block the ordered arrangement of polymer segments and reduce the crystallinity of polymers, and then improve the electrolyte uptake rate. Juang et al. [47] coated the electrospun PP/PE/PP composite separator with TiO₂ nanoparticles, and thermal stability and liquid electrolyte wettability were greatly improved. Raghavan et al. [48] added the in situ SiO₂ to

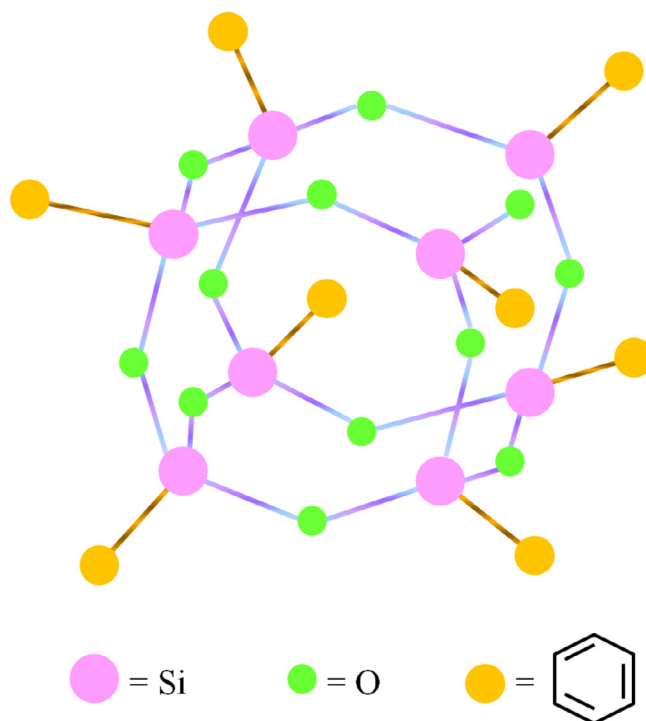


Fig. 1. Molecule structure of Octaphenyl-POSS.

the P (VDF-HFP) spinning solution, the electrospun nanofiber membrane displayed a high ionic conductivity up to 8.06 mS·cm⁻¹. In particular, the inorganic oxide nanoparticles, such as TiO₂, SnO₂, MgO, Al₂O₃ and SiO₂, not only possess excellent thermal stability, but also can enhance the film forming ability, which are conducive to improving the thermal-resistance and mechanical properties of the whole membranes [49].

Octaphenyl-Polyhedral oligomeric silsesquioxane (Octaphenyl-POSS) is an organic-inorganic intramolecular hybridization system at the molecular level in nature [50]. As shown in Fig. 1, Octaphenyl-POSS (OPS) has a special cage-shaped core/shell structure. The core of OPS is the cage-shaped inorganic kernel connected by silicon and oxygen element, thus it has natural attributes of inorganic nanoparticles such as large specific surface area and excellent adsorption electrolyte performance. And the internal inorganic structure endows OPS molecule the characteristics of superb thermal stability, fantastical oxidation resistance and outstanding rigidity. Meanwhile, the eight vertices of OPS can link with organic groups (–R), which is extremely advantageous to the compatibility with polymers. Bharadwaja et al. [51] had revealed that the interaction between the POSS nanoparticles and the polymer matrix was much larger than the molecular force between POSS particles via the molecular dynamics simulation of norbornene-POSS polymers, which was the main reason that POSS nanoparticles could be dispersed uniformly and stably in polymer matrix. The size of OPS is about 1–3 nm, which is much smaller than that of traditional inorganic nanoparticles, meanwhile, the OPS nanoparticles show the larger specific surface area than that of traditional inorganic nanoparticles [52]. In recent years, it has been found that OPS nanoparticles not only were used as a reinforced and heat resistance material, but also facilitated to improve the ionic conductivity and concentration polarization of lithium-ion batteries. Parameswara et al. [53] grafted the short chain polyethylene glycol (PEG) to the eight vertices of POSS and added into the electrolyte. Because of the cavity in the interior of POSS, the ion conductivity and the concentration polarization phenomenon can be improved effectively, leading to an increased charge-discharge efficiency and an extended cycle life for the battery. Furthermore, the binding effect on charge by the organic-inorganic hole structure of

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