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Composite Electrospun Membranes Containing Monodispersed Nano-sized $\text{TiO}_2@Li^+$ Single Ionic Conductor for Li-ion Batteries

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Abstract: In this work, we report novel composite electrospun membranes for Li-ion batteries. A monodispersed nano-sized $\text{TiO}_2@Li^+$ single ionic conductor containing a P(AAl-MMA) polymer layer grafted on nano-sized TiO_2 surface was prepared and used as functional fillers in composite membranes. The obtained results show that our material, based on the incorporation of nano-sized $\text{TiO}_2@Li^+$ single ionic conductor into a composite electrospun membrane is a new generation battery separator for application in lithium-ion batteries.

Keywords: Functional filler; Monodispersed; Composite electrospun membrane; Single ionic conductor; Li-ion batteries;

1. Introduction

Nowadays, Li-ion secondary batteries have been used as power sources in electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their high energy density, high power density and long cycle life [1, 2]. However, the majority of Li-ion batteries employ thin ($\sim 25 \mu\text{m}$) microporous polyolefin separators (e.g. Celgard and Tonen amongst others), of which the poor wetting capability, small porosities and small pore sizes usually cause a significant decrease in ionic conduction compared to pure liquid electrolyte solutions (e.g. the ionic conductivity of the electrolyte solution

is $1.2 \times 10^{-2} \text{ S cm}^{-1}$, but that of PE separator filled with the electrolyte solution is only about $0.65 \times 10^{-3} \text{ S cm}^{-1}$). The net results are significant decreases in charge-discharge properties of cells [3,4]. In addition to the poor ionic conductivity of polyolefin porous separator, the poor thermal stability is another serious problem, because the shrinking of separator by heating often causes short circuit, which may lead to ignition and explosion of power lithium-ion batteries and affect the safety performance of EVs [5, 6]. Therefore, separators used in power lithium-ion batteries still need improvement especially in terms of ionic conductivity at room temperature and thermal stability.

Electrospinning is widely regarded as an alternate, efficient and simple technology for the manufacture of new generation battery separators. Compared to the conventional microporous polyolefin separators, separators based on electrospinning can offer higher level of porosity, higher ionic conductivity and superior thermal stability [3-6]. Very recent applications of electrospinning separators or polymer electrolyte membranes for Li-ion batteries have been successfully prepared with submicron fibers from such polymers as PVdF [7-9], PAN [8,10], PVDF-HFP [2,6].

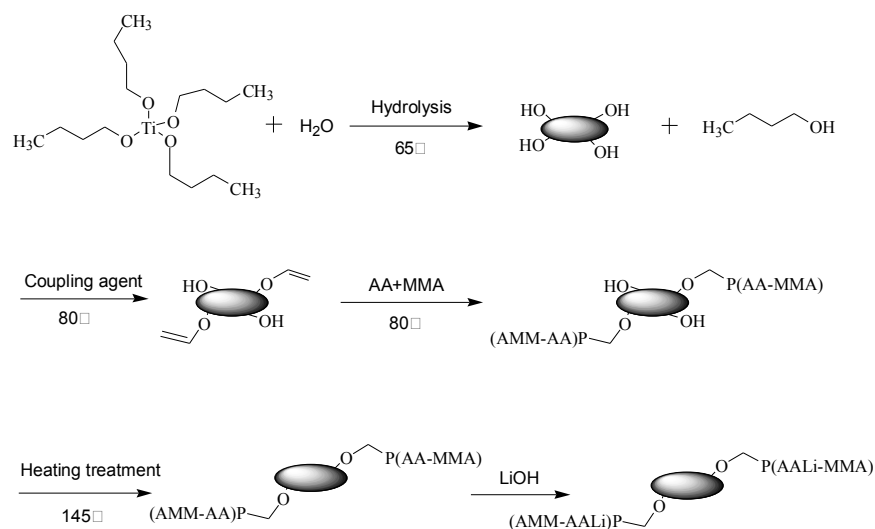
In this work, we synthesized a monodispersed inorganic-organic nano-sized $\text{TiO}_2@Li^+$ single ionic conductor. The obtained single ionic conductor was dispersed in a solution of PVDF-HFP (10 wt%) dissolved in DMF and then coated on a supporting layer of pristine PVDF-HFP electrospinning membranes to form composite membranes. The structures and properties of the composite electrospun membranes (CEMs) were investigated. The results reported in this work confirm the superior performance of the $\text{TiO}_2@Li^+$ single ionic conductor doped PVDF-HFP based CEMs compared to conventional PE separators.

2. Experimental

2.1 Synthesis of nano-sized $\text{TiO}_2@Li^+$ single ionic conductor

Fig. 1 illustrates the synthetic scheme of nano-sized $\text{TiO}_2@Li^+$ single ionic conductor prepared by in situ radical polymerization and crystallization. Tetrabutyl titanate (TBOT) is added into an aqueous alcohol solution, of which the pH is adjusted to 3-4 by using NH_4OH . The mixture is then hydrolyzed at 65°C to form titania sol. After completion of this reaction, vinyl triethoxy silane, acrylic acid (AA),

methyl methacrylate (MMA) monomers and benzoyl peroxide (as initiator) are successively added into the titania sol to polymerize for 4 hours at 80 °C to obtain a titania-PAA-PMMA dispersion. Then the dispersion is poured into a high pressure reactor to heat treatment at 145 °C. After heating treatment, the TiO₂-P(AALi-MMA) single ion conductor is performed by an acid-base reaction for -PAA and LiOH.



Scheme 1. Reaction scheme of nano-sized TiO₂@Li⁺ single ionic conductor prepared by in situ radical polymerization and crystallization.

2.2 Preparation of electrospun PVDF-HFP composite membranes

Pristine electrospun PVDF-HFP membranes (PEMs) prepared by a typical electrospinning method at room temperature, as described in previous reports [11, 12]. The thickness of the pristine electrospun membranes are controlled to about 35 μm. With PEMs as supporting layer, PVdF-HFP with TiO₂@Li⁺ fillers (mass rate = 1:1) are dissolved in N,N-dimethyl formamide (DMF) at 20 wt% concentration to form a homogenous casting solution. Then the solution is casted on one side of the supporting layer to form CEMs at room temperature. After casting, the CEMs are submerged into distilled water bath immediately [13]. The characterization of the CEMs are carried out after further submerged in absolute alcohol for 2 h and then dried in vacuum oven at 80°C for 24 hours. The thickness of the dried CEMs are about 45 μm.

2.3 Cell assembly and electrochemical measurement

LiCoO₂ electrode is prepared by coating a NMP-based slurry containing LiCoO₂, PVdF, acetylene black and graphite (mass rate = 8:1:1:1) on an Al foil. 1.0 M LiPF₆

dissolving in 1:1:1 (v/v/v) mixture of ethylene carbonate (EC), diethylene carbonate (DEC) and Dimethyl Carbonate (DMC) is used as electrolyte solution. LiCoO₂/Li 2032-type coin cells with PVDF-HFP electrospun composite membrane or PE separator are assembled in a an argon filled glove box, of which the C-rate performance are galvanostatically measured in a voltage range of 2.75-4.2 V at a constant charge current density of 0.1 C for the first 5 cycles and 0.5 C for all of the following cycles, and discharge is at various current densities ranging from 0.1 to 8 C.

3. Results and discussion

Fig. 2 shows the FTIR spectrum of TiO₂@Li⁺ single ionic conductor. TiO₂ is confirmed by -Ti-O-Ti- absorption band at 604 cm⁻¹. The peaks at 1730 cm⁻¹ and 1556 cm⁻¹ are the characteristic absorption of -C=O and -COO-, respectively, which are attributed to P(AALi-MMA). The peak around 918 cm⁻¹ is assigned to the stretching vibration band of -Si-O-Ti- which indicates that P(AALi-MMA) is grafted onto the TiO₂ surface via vinyl triethoxy silane [13,14]. Fig.3 shows the dispersing process for TiO₂@Li⁺ single ionic conductor. As 1 g TiO₂-P(AA-MMA) nanohybrid disperses in 20 mL DMF solution, a light yellow emulsion can be formed. After adding a certain amount of LiOH into this emulsion, heating at 80 °C for 30 min, the emulsion transforms into a homogeneous and transparent solution, showing Dyndall scattering [13,14]. Above results confirm that nano-sized TiO₂@Li⁺ prepared by in situ radical polymerization and crystallization possesses well dispersity in DMF and it costs a little amount of energy to obtain a well dispersion without assistant of ultrasonication.

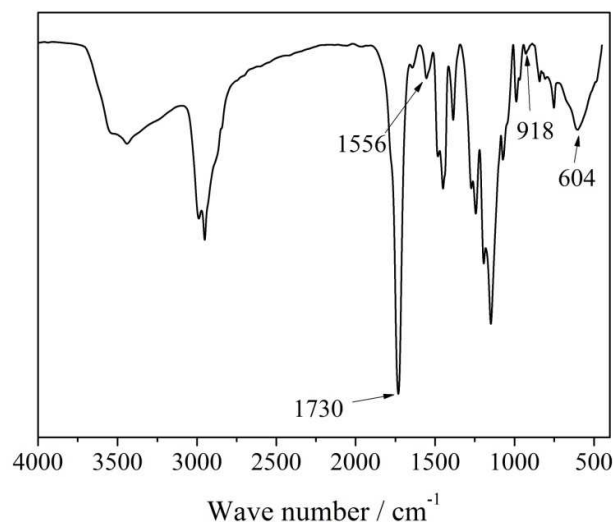


Fig. 2. FTIR spectra of nano-sized $\text{TiO}_2@Li^+$ single ionic conductor

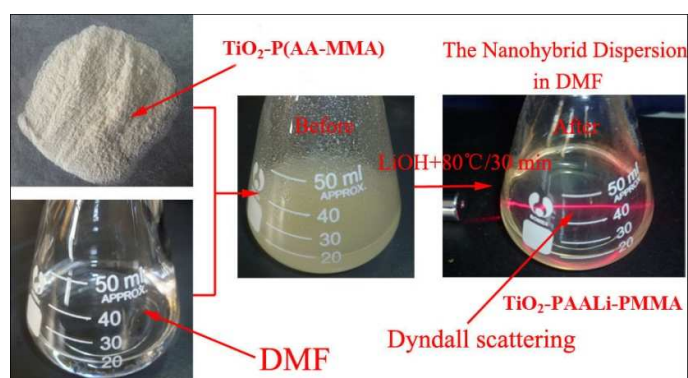


Fig. 3. The dispersing process for nano-sized $\text{TiO}_2@Li^+$ single ionic conductor

Fig. 4. shows the SEM images of PVDF-HFP based electrospun membranes. From figure 4-a, it can be found that PEM consists of nanofibers with smooth surfaces and well-controlled fiber diameter ranging from 200 to 400 nm. Meanwhile, the PEM exhibits big pore size and high porosities. After performing a CEM-separator by coating process (the casting solution soaks through the pristine PVDF-HFP electrospun membrane), as shown in Fig. 4-(b), (c) and (d), big pores are filled with $\text{TiO}_2@Li^+$ /PVDF-HFP blends and an about 10 μm thickness of inorganic-organic nanocomposite layer is formed on the upper surface of the CEM, of which the total thickness is controlled to about 45 μm .

Fig. 5 shows the photographs of PE separator and CEM-separator after being exposed to 150 $^\circ\text{C}$ for 2 h. PE separator is transformed into a transparent film with

thermal shrinkage of 25%, but the (area-based) dimensional change of CEM-separator is negligible after heating treatment at 150 °C heating treatment for 2 h. This confirms the superior thermal stability of CEM-separator as compared to PE separator. Table.1 lists the values of breaking strength, liquid uptake, ionic conductivity and lithium transport number of PVDF-HFP based electrospun membranes at room temperature. The stress at failure for the PVDF-HFP based electrospun membrane increase from approximately 8 MPa to approximately 39 MPa after compounding with TiO₂@Li⁺/PVDF-HFP blends. This indicates that CEM-separator with acceptable mechanical strength can be used in commercial Li-ion batteries. However, an intriguing finding is that CEM-separator shows a decrease in the liquid uptake (280%), but increases in ionic conductivity ($3.63 \times 10^{-3} \text{ S cm}^{-1}$) and lithium transport number (0.52) compared to PEM-separator. Generally speaking, improving liquid uptake can enhance the ionic conductivity of a polymer electrolyte membrane. Obviously, in here, this result is contradictory. Thus, it can be deduced that, when a composite membrane keeps enough liquid uptake, the improved ionic conductivity is related to the location of nano-sized fillers in membrane matrix but liquid uptake. In addition, the increased lithium transport number measured by combination of AC impedance and DC polarization for CEM-separator is attributed to the mobile lithium ions dissociating out of nano-sized TiO₂@Li⁺ single ionic conductor, as well as the activated composite gel membrane.

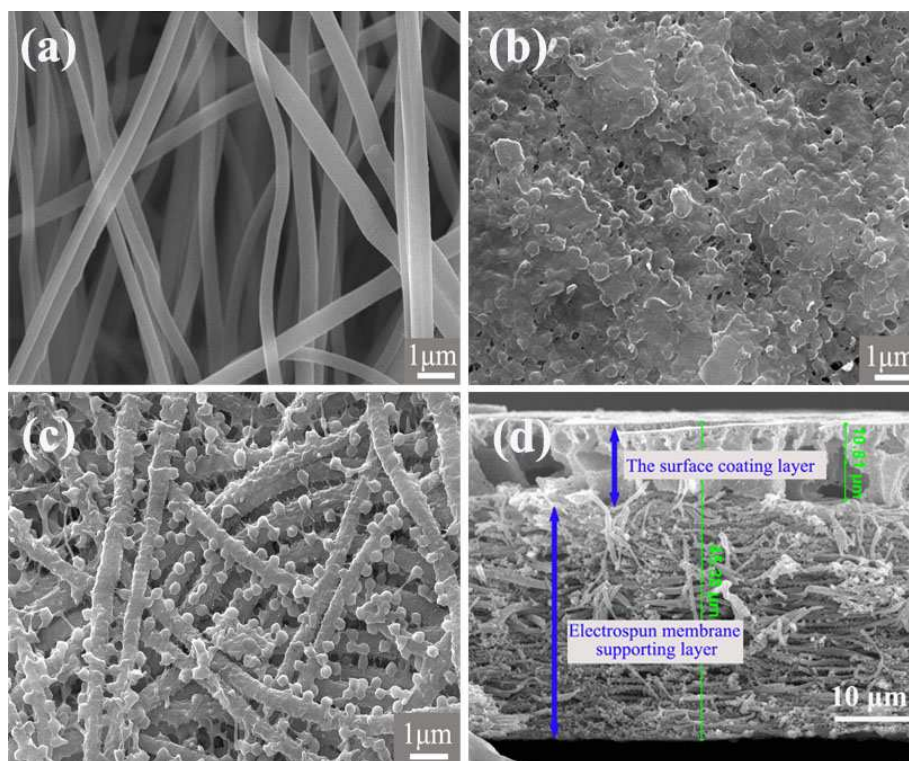


Fig. 4. SEM images of (a) PEM, (b) upside, (c) downside and (d) cross-section of CEM separator.

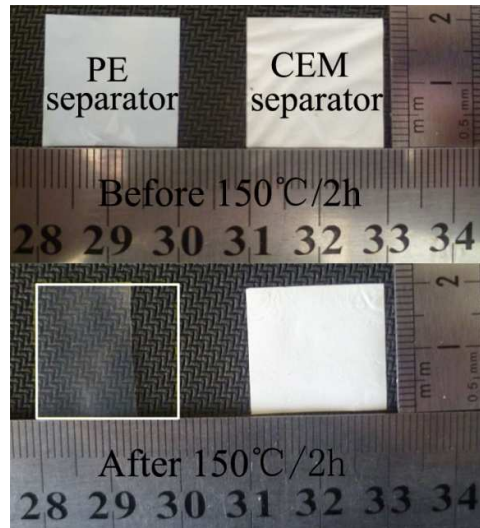


Fig. 5. Thermal shrinkage of PE separator and CEM separator after 150°C/2h treatment

Table 1. Breaking strength, liquid uptake, ionic conductivity and lithium transport number of PVDF-HFP based electrospun membranes at room temperature

Sample	Breaking strength (MPa)	liquid uptake (%)	ionic conductivity (S cm ⁻¹)	Lithium transport number
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PEM	8	350	1.56×10^{-3}	0.30
CEM	39	298	3.63×10^{-3}	0.52

The higher ionic conductivity of li-ion battery separator suggests a better rate performance and the C-rate performance of CEM-separator which is evaluated according to the assembled LiCoO₂/Li cells with CEM-separator. As a contrast, the cells with PE separator are also assembled, and all the cells are charged under a voltage range of 2.75-4.2 V at a constant charge current density of 0.1 C for the first 5 cycles and 0.5 C for all of the following cycles and discharged at various current densities ranging from 0.1 to 8 C. Fig .6-(a) and Fig.6-(b) show the discharge curves for cells with PE separator and CEM-separator, respectively. It is obvious that the C-rate discharge performance of cells with CEM-separator is enhanced compared to that with PE separator. Fig.6-(c) summarizes the aforementioned discharge capacities of the two kind separators as a function of the discharge current density (i.e., the discharge C-rate). An intriguing finding is that, the cell with CEM separator exhibits a lower initial discharge capacity than the cell with PE separator at 0.1C/0.1C charge/discharge current density, but the capacity recovers after 3 cycles. Indeed, after the assembled composite membrane fully soaked in the liquid electrolyte in a cell, a composite gel polymer electrolyte membrane will be formed, and the interfacial compatibility between electrode and composite gel polymer electrolyte membrane play an important role in the capacity of a cell [15]. Thus, a bad initial interface between the PVDF-HFP electrospun composite electrolyte membrane and the LiCoO₂ electrode leads to a low initial capacity of the cell, but the gradual recovered capacity may be attributed to the gradual improved interfacial compatibility produced by monodispersed nano-TiO₂ particle in membrane matrix during the charge-discharge process of cell.

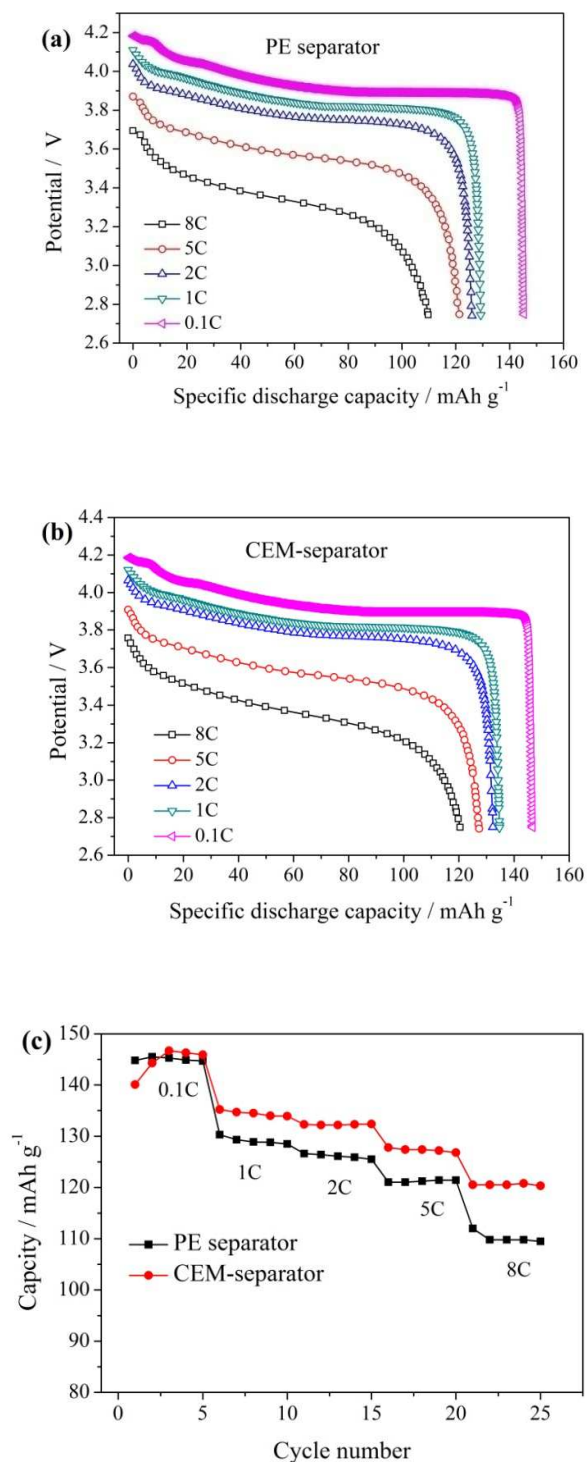


Fig. 6. The C-rate performance of cells: (a) and (b) are the discharge curves for cells with PE separator and CEM-separator, respectively; (c): Discharge specific capacity versus cycle number with different electrolytes.

4. Conclusions

A monodispersed nano-sized $\text{TiO}_2@\text{Li}^+$ single ionic conductor is successfully prepared by in situ radical polymerization and crystallization. The experimental results demonstrate that the PVDF-HFP based composite electrospun membranes containing $\text{TiO}_2@\text{Li}^+$ as fillers exhibit unique mechanical properties and battery performance, which confirms that the composite membranes are very promising separators for the use in rechargeable lithium-ion batteries, especially in power batteries.

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