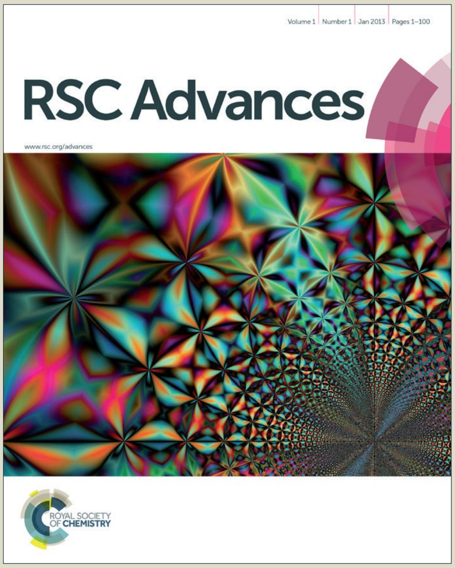
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

REVIEW

Recent advances in composite membranes modified with inorganic nanoparticles for high-performance lithium ion batteries

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Qiaohuan Cheng,[a] Wen He,[a]* Xudong Zhang,[a]* Mei Li [a] and Xin Song[b]

Separators with excellent physical and electrochemical performances are in urgent demand for higher power-density and energy-density lithium ion batteries(LIBs). This implies that the separators must possess high porosity, thin thickness, large electrolyte uptake, good thermal stability and mechanical property. Thus, the single component separators are difficult to satisfy all of these requirements. Recently, the composite membranes modified with inorganic nanoparticles have attracted great interest as the LIB separators, which show better physical and electrochemical performances compared with pure separators. In this article, recent advances, the main types, their manufacturing and performances of the composite membranes are thoroughly reviewed, covering three important types: inorganic particle-coated composite membranes, inorganic particle-filled composite membranes and inorganic particle-filled non-woven mats. The outlooks and future direction are also described in this review paper. This review will hopefully stimulate more extensive and insightful studies for fabricating and designing new LIB separators with excellent physical and electrochemical performances.

Introduction

With the reduction of fossil fuel energy and the deterioration of global warming, it has profound significance in the development, research and application of renewable energy resources. Lithium ion batteries (LIBs) have attracted more attention, which possess higher energy-density, power-density and long cycling life,[1-6] fulfilling the demand of green energy and achieving the purpose of environmental protection simultaneously. Nowadays, LIBs are used widely in our daily life, such as cellular phones, laptops, digital cameras.[7] There is no doubt that LIBs play an important role in our life and production, becoming an indispensable part of our life.

LIBs are usually comprised of anode, cathode, separator and electrolyte (Fig. 1). Separator is an crucial component, so stricter requirement is needed for its performances. First, separator provides a physical barrier to prevent electrical short circuits resulting from the physical contact between anode and cathode. Second, separator must have electrical insulation to avoid internal short-circuits and afford channels for the migration of lithium-ion between the two electrodes.[8, 9] Third, separator must be chemically and electrochemically stable to electrolyte and electrodes since most of the electrolyte is organic system with strong corrosive.[10] Fourth, separator should be inert, that is to say, it must not participate in chemical reactions when the battery is fully charged and discharged. Finally, ideal separators of LIBs should satisfy the following properties, good mechanical property, good wettability with liquid electrolyte, high porosity, high permeability and low internal resistance.

The separator can greatly impact the electrochemical performances of the LIBs, which is close related to the capacity,

---

[a] Institute of Materials Science and Engineering, Qilu University of Technology, Jinan 250353, China
[b] State Key Laboratory of Microbial Technology, Shangdong University, Jinan 250100, China
† E-mail: zxd1080@126.com, hewen1960@126.com; Fax: +86 531 89631518; Tel: +86 531 89631080

Wen He is currently a full professor in the Department of Materials Science and Engineering at Qilu University of Technology. She received her PhD degree in Department of Materials Science and Engineering from South China University of Technology in 2009. Her research interests focus on material chemistry and, technology for lithium batteries.

Qiaohuan Cheng graduated from Qilu University of Technology in 2014. In 2014, she moved to the Institute of Materials Science and Engineering, Qilu University of Technology as a postgraduate student, and majored in materials science and engineering.

RSC Advances

REVIEW

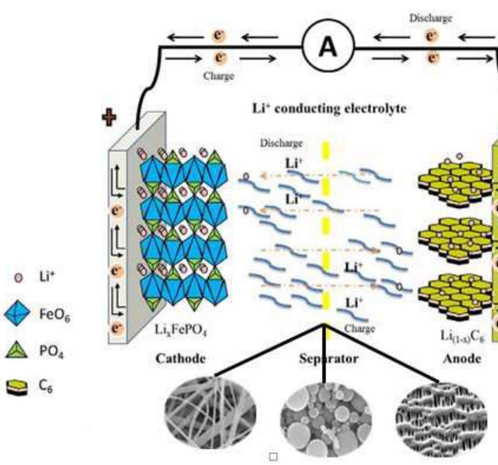


Fig. 1 Schematic illustration of typical lithium ion battery.

internal resistance, cycling capability and safety performance of batteries.[11-14] With the development of technology and the increasing demand of human, the application of LIBs is more and more extensive. The performance improvement of LIBs has made great progress, but still faces great challenges. In particular, when LIBs are used in large-sized devices, the high rate capability, long-term stability and high heat-resistant should be further improved. Thus, the performance improvement of separators also confronts with greatness challenges. The requirements for the performances of separators are various when LIBs are applied to different areas, containing porosity, wettability, thickness, thermal stability. Especially the LIBs with liquid electrolyte increase the potential risk and there will be even a fire or explosion.[15, 16] So, separators must have better physical and electrochemical performances to meet the various demands of LIBs. The conventional single component separators, such as polyolefin-based separators,[17] poly(viylidene fluoride) (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP),[18-21] polyacrylonitrile (PAN),[22] polyethylene terephthalate (PET)[23] and other non-woven fabrics, are not meeting the numerous and stringent requirements of LIBs.

For example, the PVDF and its copolymer PVDF-HFP are usually employed as host polymers to prepare separators, which have good chemically and mechanically stable. They are usually prepared by the conventional casting method,[24] Bellcore technology method,[25] phase inversion technique,[26] or electrospinning process. However, PVDF-based separators show low ionic conductivity and electrochemical stability, which can be attributed to the crystalline part of PVDF to prevent the migration of lithium ion, resulting in the LIBs show poor elcctrochemical performance.[27] Polyolefin-based separators, which are used widely in LIBs and have been realized industrial production, possess excellent mechanical strength, good electrochemical and chemical stability.[28, 29] However, their inherent characteristics prevent their application in high power and capacity LIBs,[30, 31] such as poor affinity with electrolytes, extensive shrinkage especially at high temperature. And the non-woven fabrics are usually fabricated by electrospinning method,[32-35] such as PAN,[36-38] PVDF,[39, 40] PVDF-HFP.[41-43] The electrospun separators have high porosity to ensure the electrolyte uptake enough and the migration of lithium ion. However, the discharge capability of pure electrospun separators has been limited at high discharge rate due to polymer degradation and the leakage of organic liquid electrolyte since these electrospun separators only possess macroporous structures (pore size > 1 μm) and do not have mesoporous structures (2 nm < pore < 50 nm).[44]

Hence, the separators with single component exist some disadvantages when they are applied to LIBs, and they can hardly meet the requirements of the high-power LIBs. Therefore, it is highly desirable to fabricate a kind of separator, which has relative high ionic conductivity and thermostability to ensure the security of battery when it was used in high-power devices even in harsh environment. And we expect that the separators possess excellent electrochemical performances when they are assembled into LIBs. Thus, many researchers have done a vast amount of works to overcome the drawbacks of single component separators mentioned above. Some researchers proposed that the single component separators can be modified to fabricate composite membranes by introducing inorganic nanoparticles,[45-47] which can improve the physical and the electrochemical performance of separators effectively. And the results indicated that the composite membranes had better physical and electrochemical performance than pristine separators. That is to say, the pure separators can be modified successfully by introducing inorganic nanoparticles. In this paper, we introduce the composite membranes with inorganic nanoparticles, which can be divided into three types: inorganic particle-coated composite membranes, inorganic particle-filled composite membranes and inorganic particle-filled non-woven mats.[48] The physical and electrochemical performance of composite membranes compared with bare separators are investigated.

Inorganic particle-coated composite membranes

It has been reported that the nanosized inorganic particles were coated on the surface of separators with binders to modify separators. The inorganic particles have aluminum oxide (Al_2O_3), silicon dioxide (SiO_2) and titanium dioxide (TiO_2).[49-52] The inorganic nanoparticles can significantly improve thermal stability of separators and reduce thermal shrinkage of the composite membrane. It can also enhance mechanical property and optimize electrochemical performance of LIBs. And it is easy to form highly porous structure and well-connected interstitial voids between nanosized inorganic particles,[53-55] which play an important role on improving the performance of LIBs. The ionic conductivity and wettability of composite membranes were also improved due to high surface area and high hydrophilicity of inorganic particles. Furthermore, the binders bonding the inorganic particles on the surface of separators are also important to prepare inorganic particle-coated composite membranes. The binders directly influence the performance of composite membrane and the electrochemical performance of LIBs. The binders are various, including PVDF, PVDF-HFP, poly(methyl methacrylate) (PMMA), phenolphthalein polyetherketone (PEK-C) [56].

The dip-coating process is most common and simple method to prepare inorganic particle-coated composite membranes. J. H. Park et al.[53] developed a novel composite membrane by using this method and synthesized a close-packed SiO_2/PMMA binary nanoparticles-coated polyethylene (PE) separator by introducing SiO_2 and PMMA binder nanoparticles. These composite membranes can effectively improve the thermal stability and the electrochemical performance of separator due to the formation of unique structure of separators, which possess highly porous structure, well-connected interstitial voids between the binary SiO_2 and PMMA nanoparticles. This special structure had well-wettability of liquid electrolyte because of the high surface area and high hydrophilicity of inorganic particles, so the discharge capacity and C-rate capability of cells were improved significantly. P. Zhang et al.[57] coated one side of a commercial PE separator with one–dimensional silica tubes (ST), which improve the thermal stability of separators due to the formation of interpenetrating network in the separator. The brief preparation methods of this composite membranes are as follows: the ST, styrene butadiene rubber (SBR), carboxyl methyl cellulose(CMC), and other reagents were mixed together to form the slurries, then the slurries were coated onto one side of the PE membrane using an automatic coating machine. These composite membranes coated with ST can effectively enhance thermostability at elevated temperature compared to the separator coated with spherical silica particles and pristine PE separator. H. S. Jeong et al.[54]coated both sides of PE separators with ceramic coating layer to improve thermal shrinkage by simple dip-coating process, the coating layer was composed of SiO_2 nanoparticles and PVDF-HFP binders. Fig. 2a, b, c and d show the surface morphologies and thermal shrinkage of the composite separators, indicating that they have well-developed porous structure. This porous structure is formations of well-connected interstitial voids between SiO_2 nanoparticle and improves the ant-thermal shrunk of the composite membranes, resulting in the composite membrane to be more resistant to rising temperatures than conventional PE separator (135 °C). What is more, they even explored the effects of nanoparticles' size (530 nm and 40 nm) on the performance of composite membrane. They found that the composite membranes with small-sized SiO_2 possessed better properties, the porosity of 40- nm SiO_2 was 68%, it was higher than the pristine PE separator, which was only 45%.

In addition to solvent evaporation directly, inorganic particle coated composite membranes can also be obtained by phase inversion technique. H. S. Jeong et al.[58] prepared composite membrane, which introduced coating layers onto both sides of PE separator to improve thermal shrinkage. The coating layers were composed of Al_2O_3 nanoparticles and PVDF-HFP polymeric binders. PVDF-HFP and Al_2O_3 nanoparticles (50/50 by weight) were mixed in acetone, here, water was added into the coating solution as nonsolvent to control microporous structure by phase inversion technique. They found that the coating layers with higher content of nonsolvent possessed more developed microporous structure, leading to the excellent electrochemical performance. The same year, H. S. Jeong et al.[59] published another article about the Al_2O_3/PVDF-HFP/PE composite membranes, the details were the same as above-mentioned, the different aspect was that they explored the effect of phase inversion, especially the solvent-nonsolvent miscibility, on the microporous structure of the coating layers of composite membrane. The coating layers were divided into three types according to the system of solvent and nonsolvent, actone-isopropyl alchohol system, acetone-butyl alchohol system and acetone-water system. The results indicated that not only the content of nonsolvent but also the types of nonsolvent can affect the performance of composite membrane. The performance of composite membranes were getting better in the following order: actone-isopropyl alchohol system, acetone-butyl alchohol system and acetone-water system. And all of these composite membranes showed good thermal stability and excellent electrochemical performance due to the stable microstructure of inorganic particle-coating layers.

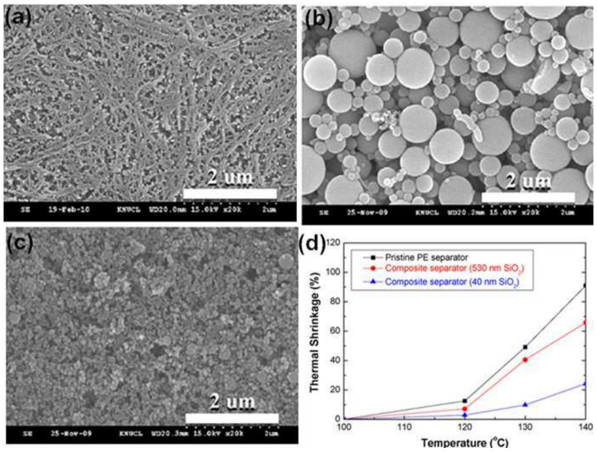


Fig. 2 FE-SEM photographs of surface morphologies for: (a) pristine PE separator, (b) 530 nm SiO_2-coated composite separator, and (c) 40 nm SiO_2 coated composite separator, (d) Thermal shrinkage of composite separators and pristine PE separator as a function of heat-treatment temperature.[54]

Recently, M. Kim et al.[60] employed chemical vapor deposition method to modify PE separator, which deposited SiO_2 nanoparticles onto PE separator. The thin SiO_2-coated layers formed on the PE separator enhanced significantly their thermal and dimensional stability. R. S. Juang et al.[61] developed microwave method to modify tri-layered polymeric membranes (PP/PE/PP) by depositing TiO_2 onto polymeric membranes. The TiO_2 particle-coated layers can effectively improve thermal and dimensional stability due to the formation of robust skeleton. X. Li et al.[62] synthesized the composite membrane by coating the PP separator with ceramic layers, which were composed of SiO_2 nanoparticles and PVDF-HFP binders. The polymer matrix was not directly used as it was mentioned above, the PP separator needed to be pretreated. 2, 2, 3, 3, 4, 4, 5, 5-octafluoropentyl methacrylate (OFPMA) was grafted on the surface of PP separator by plasma treatment, which can improve the adhesion between PP separator and PVDF-HFP. And then the coating solutions were coated on the PP separator. The composite membranes presented an increased electrolyte uptake

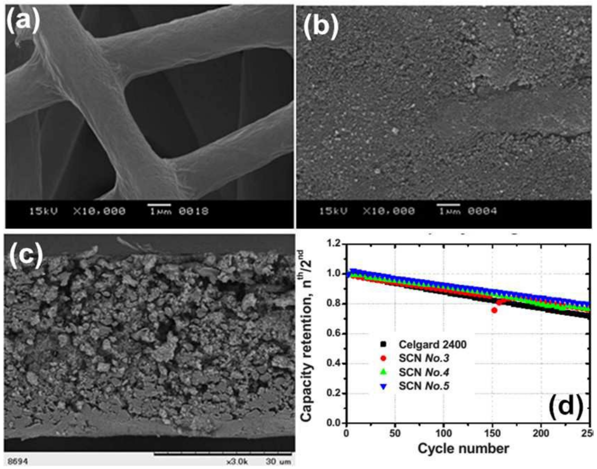


Fig. 3 SEM photographs of (a) the silica-free nonwoven. (b) and (c) are surface and cross section of the silica-composite nonwoven,respectively. (d) capacity retention ratios as a function of cycle number of cells at the C rate of 0.5.[63]

of 290 wt% and ionic conductivity of 1.76 mS cm^{-1} at room temperature. The discharge capacity of $LiFePO_4$/Li half cells based on this composite membranes kept about 150 mAh g^{-1} after 100 cycles. T. H. Cho et al.[63] developed SiO_2 coated-composite membranes by means of an air-laid method. They found that SiO_2 particles were homogeneously distributed over all the composite membrane, filling the large pore (Fig. 3). These composite membranes had excellent thermal stability, cycling performance and wettability than polyolefin-based separator and non-woven separators. S. M. Eo et al.[64] prepared composite membrane that PE separator was coated PVDF-HFP by simple dip-coating method firstly, then the PVDF-HFP coated separators were immersed in liquid electrolyte, which contained small amount of inorganic additive (aluminum fluoride, aluminum iodide, lithium fluoride and lithium iodide). They found that the capacity retention and cycling performance of cells with composite membranes were improved due to the formation of protective layers to cover active material in the electrode during cycling, which reduced the electrolyte decomposition, so that the structural stability of active material can be enhanced. And the performance of obtained composite membranes with various inorganic additives had a little different.

Although most of works focus on modifying polyolefin separators, efforts have been taken on the modification of other polymeric separators. M. Kim et al.[65] developed a novel trilayer composite membranes, ceramic coating layers/PMMA/ceramic coating layers, here, the ceramic coating layer was composed of Al_2O_3 nanoparticles and PVDF-HFP binders. The coating solutions were prepared by dispersing Al_2O_3/PVDF-HFP (90/10 by weight) in acetone, then they were applied to PMMA polymer matrix by simple dip coating method. The schematic diagram and the cross-section morphology of composite membranes are shown in Fig. 4a and b. These figures displayed that the composite membranes had porous structure and the inner PMMA layers were imporous resulting in high electrolyte uptake. They found that the as-prepared composite membrane had higher ionic conductivity and thermal stability than pristine PMMA separator. Fig. 4c and d show that the cells assembled with this composite membrane have excellent electrochemical performances, but the capacity of cells decreased as the current rate increased, this can be attributed to the electrical polarization caused by a serial resistance increase. And the composite membranes experienced less capacity drop at high discharge current densities.

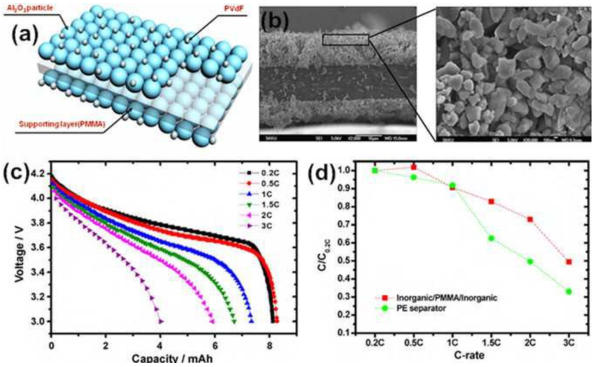


Fig. 4 (a) Schematic diagram of organic/inorganic trilayer separator. (b) Cross-section SEM of inorganic particulate film/PMMA/inorganic particulate film trilayer.) (c) Discharge capacities of unit cell (anode + inorganic/PMMA/inorganic separator + cathode) at various discharge rates after charging at 0.2C, (d) comparison of rate performance of cells with PE separator and those with an inorganic/PMMA/inorganic separator at various discharge rates (ratio of capacities at various rates normalized against that at 0.2C).[65]

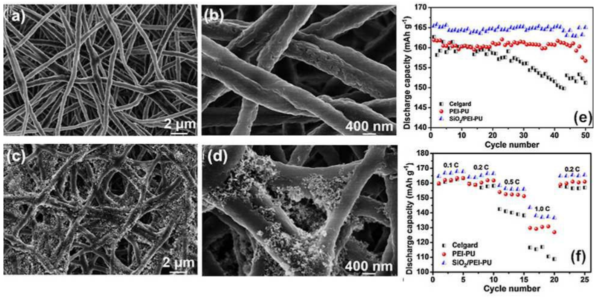


Fig. 5 FE-SEM images of as-prepared (a and b) PEI-PU and (c and d) SiO_2/PEI-PU composite membranes with (a and c) low and (b and d) high magnification. (e) Cycling stabilities of Li/$LiFePO_4$ cells using Celgard, PEI-PU and SiO_2/PEIPU composite membranes at 0.2 C rate. (f) Comparison of discharge rate capabilities.[66]

Y. Zhai et al.[66] constructed SiO_2/polyetherimide-polyurethane (PEI-PU) composite membranes via eletrospinning technique followed by dip-coating process. The surface morphology images of these composite membranes in Fig. 5a, b, c and d show their high porosity and interpenetrating network structure. These composite membranes possessed excellent mechanical strength (15.63 MP) and high ionic conductivity (2.33 mS cm^{-1}). The Li/$LiFePO_4$ cell assembled with SiO_2/PEI-PU membranes exhibited excellent cycling stability. The cell had the capacity retention of 98.7% after 50 cycles at 0.2 C rate and better rate capability compared with the cell based on Celgard membrane (Fig. 5e and f). E. S. Choi et al.[55] developed SiO_2/PVDF-HFP-coated polyethylene terephthalate (PET) nonwoven composite membranes. These membranes had unusual porous structure and well-connected interstitial voids formed between close-packed SiO_2 nanoparticles. These porous structure can be tuned by controlling the SiO_2 particle size (40 nm and 530 nm nanoparticles). Fig. 6a, b, c and d show the surface morphologies of the composite membranes with different particle size. The novel structure formed in this composite membranes helped improve thermal stability and liquid electrolyte wettability. Specifically, the composite membranes with 40 nm SiO_2 nanoparticles offered higher ionic conductivity due to the ion transport was more easier in the channel with higher porosity and shorter tortuous path. Fig. 6e and f show schematic diagrams of Li^+ transport path in the NC separators (a ceramic layer-coated non-woven composite separator) with different size of SiO_2 particle, respectively. They indicated that Li^+ transport can be tuned by controlling the SiO_2 particle size.

Above all, the physical and electrochemical performance of separators had been significantly improved by coating its surface with the inorganic particles to form the inorganic particle-coated composite membranes. The mechanical strength, thermal stability, electrolyte uptake are also enhanced remarkable compared with pristine separators, but the porosity reduced with the increasing the thickness of separator because of introducing the ceramic coated layers.

Inorganic particle-filled composite membranes

The inorganic particles not only can be coated on the surface of separators, but also can be incorporated directly into polymer matrices. The composite membranes formed by directly introducing the inorganic nanoparticles into the polymer matrix are called the inorganic particle-filled composite membranes, which is another effective way to improve the performance of separators. Various kinds of inorganic particles can be used in this composite membrane, including lithium aluminate ($LiAlO_2$), manganese oxide (MgO), Al_2O_3, TiO_2 and SiO_2. For example, Al_2O_3 has been filled into PVDF separator to form this composite membrane, which has excellent thermal stability and cycling performance.[67] D. W. Kim[68] developed SiO_2-filled poly(ethylene-co-methyl acrylate) (PE-co-MA) composite membrane, its ionic conductivity can reach 5.8×10^{-4} S cm^{-1} at room temperature. The cell assembled with the carbon/composite membrane/ $LiCoO_2$ delivered discharge capacity of 124 mAh g^{-1} at the rate of 0.1 C and 120 mAh g^{-1} at 0.5 C. Besides, $LiAlO_2$, Al_2O_3, MgO have been used as fillers in PVDF-HFP polymer matrix and the performances of separator for LIBs were improved significantly.[69]

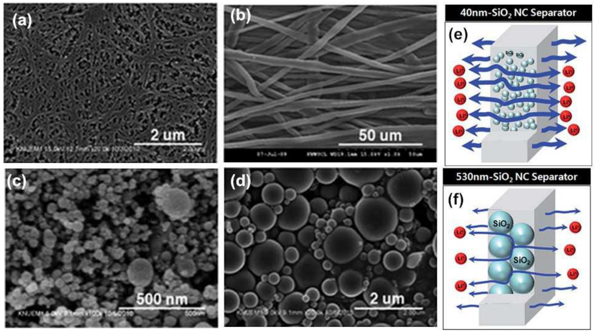


Fig. 6 FE-SEM photographs (surface) of: (a) PE separator; (b) pristine PET nonwoven; (c) 40 nm-SiO_2 NC separator; (d) 530 nmSiO_2 NC separator.Schematic illustrations explaining the SiO_2 powder size-dependent porous structure of the NC separators and its influence on iontransport: (e) 40 nm-SiO_2 NC separator; (f) 530 nm-SiO_2 NC separator.[55]

P. Yan et al.[70] prepared TiO_2/PVDF-HFP inorganic composite membrane by non-solvent evaporate method, TiO_2 was employed as fillers to reduce the crystallinity of composite membranes. Fig. 7a show the preparation process of this composite membrane. The effect of nano-TiO_2 on the crystallinity of porous polymer membrane was studied. They found that the crystallinity of polymer membrane was reduced with the introducing of TiO_2, resulting in increasing number of charge carriers and ionic conductivity. The $LiFePO_4$/Li cell assembled with this composite membrane exhibited stable electrochemical performance and excellent rate capability (Fig. 7b, c and d). For example, the discharge capacity of the cell was 164, 157, 143, and 122 mAh g^{-1} at 0.1 C, 0.5 C, 1 C, and 3 C, respectively. And the cell had only about 6% discharge capacity loss at 1 C after 50 cycles.

The preparation process of above-mentioned composite membranes were described as follows, inorganic nanoparticles, polymer matrix and solvent (some with nonsolvent) were mixed together to form slurry according to a precalculated proportion of materials. Then the slurry was cast on a clean glass plate. After evaporation of the solvent (or nonsolvent) in the slurry, the separator was separated from the glass plate and the composite membrane with a certain thickness was obtained. But the intrinsically microporous structure features of these composite membranes limited the absorbing capacity of liquid electrolyte to a certain extend. Therefore, some researchers have proposed the phase inversion method to prepared composite membranes, which had highly porous structure to get enough liquid electrolyte. For example, K. M. Kim et al.[71] developed PVDF-HFP-based composite membrane by phase inversion technique, which filled with TiO_2 nanocrystalline particles. PVDF-HFP and TiO_2 in a certain ratio were dispersed into the N-methyl-2-pyrrolidone (NMP) (solvent) to make the slurry. The slurry was spread on a clean glass plate, then the glass plate was dipped into a flowing water bath rapidly, the composite membranes were peeled off from glass plate after the onset solidification, finally the composite membranes were obtained after drying. The obtained composite membranes showed excellent electrochemical properties, higher ionic conductivity, better wettability and enhancing interfacial stability than cast PVDF-HFP separators. A. D. Pasquier et al.[72] developed SiO_2-filled PVDF-HFP composite membrane by phase inversion, acetone and ethanol were employed as solvent and non-solvent, respectively. The SiO_2 was uniformly dispersed in the separator resulting in the formation a stable porous structure, which reinforced the mechanical property of separator. The composite membrane exhibited high electrolyte uptake, which was beneficial to the discharge and rate capacity of LIBs. A. Subramania et al.[73] prepared PVDF-HFP-based micro-porous composite membrane by phase inversion that ZrO_2 was used as fillers. These kinds of membranes showed excellent performance, such as high ionic conductivity, good compatibility and high discharge capability.

Furthermore, the effect of different solvent and nonsolvent, filled amounts of inorganic particles on the performances of composite membranes fabricated by phase inversion process were also investigated. R. Miao et al.[74] researched the effect of different solvent and non-solvent system on the performances of PVDF-HFP-based composite membrane in which TiO_2 nanoparticles were used as fillers. The system of solvent and nonsolvent was divided into seven types: acetone and ethanol, tetrahydrofuran (THF) and water, THF and ethanol, acetone and water, N-methyl pyrrolidone (NMP) and acetone, NMP and acetone and water, NMP and acetone and ethanol. The results showed that the composite membranes prepared with different solvents and nonsolvents exhibited different properties, including morphology, electrolyte uptake, porosity and mechanical performance. And the system of acetone and water possessed good pore structure and pore size resulting in high electrolyte uptake. Z. Li et al.[75] have been studied the effects of different content of Al_2O_3 nanoparticle on the performances of the PVDF-HFP-based composite membranes prepared by the phase inversion process using N, N-dimethyl formamide (DMF) as solvent and distilled water as non-solvent. The results showed that the crystallinity of composite membrane decreased with the addition of Al_2O_3 and the amorphous phase content increased accordingly. This may attribute to the cross-linking centers formed by the interaction of Lewis acid group ceramics (e.g. the –OH groups on the alumina surface) with the polar groups (e.g. the –F atoms of the polymer chains), which hindered the reorganization of polymer chains. On the other hand, the electrochemical properties of composite membrane filled with Al_2O_3 nanoparticles were improved significantly. For example, lithium-ion transference number increased with the rise of Al_2O_3 content (the mass fraction of Al_2O_3 is below 10%), because the addition of Al_2O_3 nanoparticles can weaken the interaction between Li ions and F atoms of polymer chains.

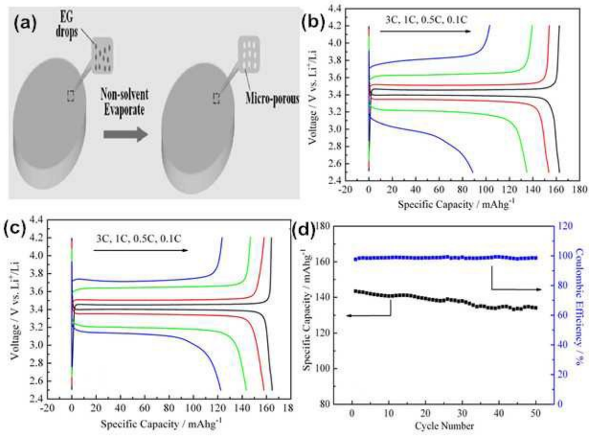


Fig. 7 (a) Picture of the fabrication process of composite micro-porous polymer membrane; (b) The charge–discharge profiles of Li/PVDF-HFP/$LiFePO_4$ at different rates; (c) The charge–discharge profiles of Li//$LiFePO_4$ with TiO_2/PVDF-HFP composite membrane at different rates; (d) The cycle performance of Li//$LiFePO_4$ with TiO_2/PVDF-HFP composite membrane at 1C.[70]

As we all know, because there are inevitably some acidic HF in the $LiPF_6$-based electrolytes now widely used in the LIBs, corrosion of HF on cathode materials is one of the important reasons of capacity fading.[76, 77] To resolve this problem, S. S. Zhang et al.[78] studied a novel inorganic composite membranes, which were composed of alkali calcium carbonate ($CaCO_3$) powders and a small amount of polytetrafluoroethylene (PTFE) polymer binder. They selected alkali $CaCO_3$ as the main component for the composite membrane because it can neutralize acidic products in situ. The results showed that the composite membranes had high ionic conductivity and excellent wettability due to the high porosity and good capillarity, and the LIBs with this composite membrane exhibited stable capacity retention and good high-rate performance.

However, the single component polymer matrix still could not completely satisfy the numerous requirements of separators, such as good mechanical strength, wettability as well as thermal stability. Considering of these factors, some researchers developed the blend polymer matrix to improve the performance of separators, and this blending was easy to control of the properties of separators by adjusting the content of blended polymer matrix.[79-82] N. T. K. Sundaram et al.[83] prepared the PVDF-HFP/polyvinyl alcohol (PVA) blend composite membranes by phase inversion method that $LiAlO_2$ nanoparticles were used as fillers. The results showed that the ionic conductivity was enhanced due to the increasing of the electrolyte uptake resulted from increasing of pore size, surface area and porosity. The composite membranes also showed excellent ionic conductivity of 8.12×10^{-3} S cm^{-1} at room temperature. H. Huang et al.[84] developed PVDF-HFP/polystyrene (PS)-based composite membrane that SiO_2 was employed as filler. The porosity of the composite membrane increased with increase of content of PS, consequently, the ionic conductivity was improved.

The means of direct addition of inorganic particles in the polymer matrix can enhance mechanical strength as well as absorb adequate liquid electrolyte, improve the affinity of separator and electrolyte, enlarge the contact surface of them, reduce internal resistance and increase the ionic conductivity. Inorganic nanoparticles can not only act as a solid plasticizer hindering the crystallization and reorganization of polymer chains but also interact with polar groups of polymer chains by Lewis acid-base effect,[85-88] which play a vital role in improving the ionic conductivity, interfacial stability and electrochemical stability of the composite membranes.

As discussed above, inorganic particles can be coated on the surface of separators as well as can be incorporated with polymer matrix directly to fabricate composite membranes, the physical and electrochemical performances of these two kinds of composite membranes were improved significantly. However, certain problems exist in the inorganic particle-coated composite membranes: (1) it is inevitable that the thickness was increased and the porosity reduced with the introducing inorganic particle-coating layers on the separator, resulting in higher internal resistance and lower energy and power density;[48] (2) the adherence strength between the inorganic particle-coating layer and the polymer matrix is weaker, due to the difference of their physical and chemical properties; (3) the inorganic particle-coating layers on this separator can chip off easily during charge-discharge cycles because of the difference of expansion coefficient between the inorganic particle-coating layer and the polymer matrix. Nevertheless, the inorganic particle-filled composite membranes can solve these problems well. So, the results show that the comprehensive performances of the inorganic particle-filled composite membranes are superior to that of the inorganic particle-coated composite membranes.

Inorganic particle-filled non-woven mats

Nonwoven-based separators have attracted much attention, which have large porosity and low cost compared with microporous polyolefin-based separators. It has potential to replace polyolefin membranes. However, most traditional non-woven separators have large pore size, leading to safety concerns when they are directly used in LIBs. Recently, electrospinning technology has been developed to prepare non-woven separator, which consists of micron and submicron fibers. The electrospun separators possess large porosity with fully interconnected pore structures and high surface area, resulting in high electrolyte uptakes and facile transport of lithium ion. It has been widely used in LIBs with high rate capability.[89-91]

However, one fateful shortcoming of electrospun non-woven separators is their poor mechanical stability, thus, it cannot withstand the large tension developed by the winding operation used during battery assembly. Besides, the high crystallinity of polymer separators is another major disadvantages.[92] All of these limited their use in LIBs. Some researches proposed that non-woven separators can be modified by introducing inorganic nanoparticle fillers to fabricate inorganic particle-filled non-woven mats, which can significantly improve the performance of separators. Inorganic nanopartiles, such as barium titanate ($BaTiO_3$), ZrO_2, Al_2O_3, TiO_2 and SiO_2, can incorporate along with polymer matrix to fabricate composite membranes. [93-99]

The introducing of inorganic fillers into non-woven separators can improve the ionic conductivity of separator by reducing the crystallinity of the polymer matrix and introducing Lewis acid/base interactions between the polar surface group on the filler surface and the ionic species in the liquid electrolyte.[100, 101] The inorganic fillers can also enhance the mechanical properties of the separator, improve the cation transference number and enhance interfacial stability between the liquid electrolyte and lithium metal electrode.[102, 103]

Y. Ding et al.[104] developed PVDF/TiO_2 composite membranes by electrospinning process using tetrabutyl titanate as the source of the TiO_2. They investigated the effect of TiO_2 on the morphology, crystallinity and electrochemical behavior of composite membranes. The results showed that the ionic conductivity and cycling performance of electrospun composite membranes were improved, its ionic conductivity can reach 1.4×10^{-3} S cm^{-1} at room temperature. M. Yanilmaz et al.[105] prepared SiO_2/PVDF hybrid composite membranes by electrospraying of SiO_2 dispersion and electrospinning of PVDF solution simultaneously. And the unique morphology of SiO_2/PVDF composite membrane that loading with the large amount of SiO_2 nanoparticles on fiber surface can be observed from SEM images (Fig. 8a, b, c and d). The research results showed that SiO_2/PVDF composite membranes had better physical and electrochemical performance than both pristine PP separator and PVDF nanofiber membranes, such as better wettability, higher ionic conductivity, lower interfacial resistance and better cycling performance. And we can find that the composite membranes with 24% SiO_2 exhibited better C-rate and cycling performance than others. P. Raghavan et al.[106] prepared PVDF-HFP-based composite membranes with different content of SiO_2 by electrospinning process, the electrospinning solution contains in situ generated SiO_2. These novel composite membranes possessed high porosity due to the formation of fully interconnected pores, high electrolyte uptake, high ionic conductivity, low interfacial resistance and excellent cycling performance. Especially the composite membranes with 6% in situ silica showed a maximum ionic conductivity of 8.06 mS cm^{-1} at 20 °C.

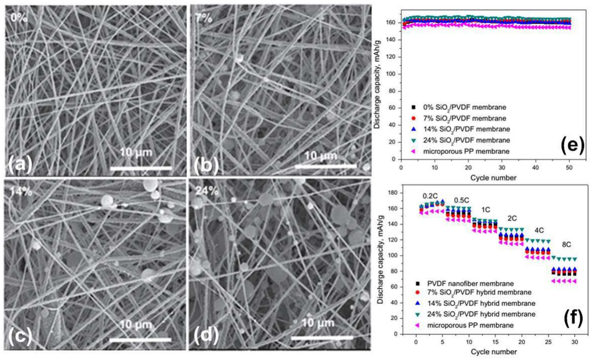


Fig. 8 (a-d) SEM images of SiO_2/PVDF nanoparticle/nanofiber hybrid membranes with different SiO_2 contents. (e) Cycling performance of Li/$LiFePO_4$ cells containing SiO_2/PVDF nanoparticle/nanofiber hybrid membranes and microporous PP membrane at 0.2 C. (f) C-rate performance of Li/$LiFePO_4$ cells containing SiO_2/PVDF nanoparticle/nanofiber hybrid membranes and microporous PP membrane.[105]

The effects of types and content of inorganic nanoparticles were also investigated in detail. J. K. Kim et al.[107] investigated the effect of different content of SiO_2 nanoparticles on the performance of composite membranes prepared by electrospinning method. The morphologies of SiO_2/PVDF-HFP composite membranes are shown in Fig. 9a, b and c, indicating the composite membranes with SiO_2 possess large porosity to ensure adequate electrolyte uptake. After activating with 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) (BMITFSI), the composite membranes with 6% SiO_2 not only showed excellent physical and electrochemical performance, the ionic conductivity also reached 4.3×10^{-3} S cm^{-1} at 25 °C. The discharge capacity of Li/$LiFePO_4$ cell assembled with this composite membrane can reach 170 mAh g^{-1} at 0.1 C, which equal to theoretical specific capacity of $LiFePO_4$, and the cells showed very stable cycle performance (Fig. 9d and e). P. Raghavan et al.[108] investigated the effect of different inorganic fillers on the performance of PVDF-HFP-based composite membranes prepared by electrospinning technique. The inorganic nanoparticles in this composite membrane have $BaTiO_3$, Al_2O_3 and SiO_2. The resultant composite membranes showed well-interconnected porous structure (Fig. 10a, b, c and d) and high electrolyte uptake, also improved their mechanical stability and ionic conductivity. Especially the composite membranes with $BaTiO_3$ showed highest electrolyte uptake, ionic conductivity and electrochemical stability. For example, the Li/$LiFePO_4$ cell assembled with the $BaTiO_3$ -filled composite membranes delivered a discharge capacity of 164 mAh g^{-1} and excellent cycling performance (Fig. 10e and f). All of these can be attributed to its better interaction with the polymer matrix and compatibility with lithium metal.

In addition to PVDF and its copolymer can be employed as host polymer, PAN[106, 109-111] can also be used as polymer matrix to fabricate inorganic-filled non-woven composite membranes since PAN has superior mechanical stability and fast lithium ion transport. Y. Liang et al.[112] prepared Lithium lanthanum titanate oxide (LLTO)/polyacrylonitrile (PAN)-based composite membranes by electrospinning technology. And a series of tests were carried, it was found that the composite membranes with 15 wt% LLTO provided the highest ionic conductivity of 1.95×10^{-3} S cm^{-1}. The obtained composite membranes had greater liquid electrolyte uptake, lower interfacial resistance and excellent electrochemical performance compared with pristine PAN separators. H. R. Jung et al.[97] developed hydrophilic fumed silica (SiO_2)/PAN composite membranes with different SiO_2 contents by electrospinning technology. Among them, the composite membrane with 12 wt% SiO_2 had highest porosity, largest surface area and highest ionic conductivity (1.1×10^{-2} S cm^{-1}). And the graphite/$LiCoO_2$ cell assembled with this composite membrane delivered the discharge capacity of 139 mAh g^{-1} for initial cycle, and retained a high value of 127 mAh g^{-1} after 150 cycles, which is significantly higher than pristine PAN separators.

Most of the above-mentioned composite membranes were mostly prepared by electrospinning method. Another method

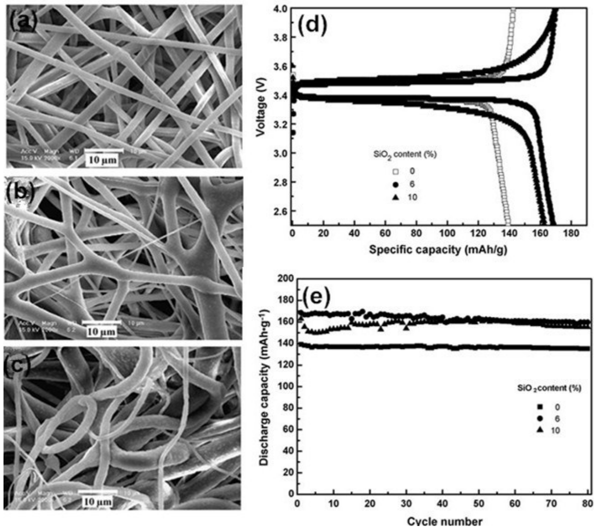


Fig. 9 SEM images of electrospun P(VDF-HFP) membranes with varying SiO_2 contents: (a) 0 wt.%, (b) 6 wt.%, and (c) 10 wt.%. (d) First cycle charge and discharge capacities of Li/$LiFePO_4$ cells with PEs based electrospun P(VDF-HFP) membranes containing varying SiO_2 contents(25 °C, 0.1 C, 2.5‑4.0 V). (e) Cycle performance of Li/$LiFePO_4$ cells with PEs based electrospun PVDF-HFP membranes containing varying SiO_2 contents (25 °C, 0.1 C, 2.5‑4.0 V).[107]

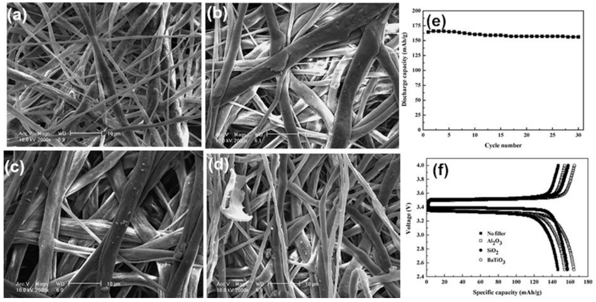


Fig. 10 SEM images of electrospun P(VDF-HFP) membranes with (a) no filler, (b) SiO_2, (c) Al_2O_3, and (d) $BaTiO_3$. (e) Initial charge‑discharge properties of Li/NCPE/$LiFePO_4$ cells with polymer electrolytes based electrospun P(VdF-HFP) membrane containing different ceramic fillers (25 °C, 0.1C, 2.5‑4.0 V). (f) Cycle performance of Li/NCPE/$LiFePO_4$ cells with polymer electrolyte based electrospun P(VdF-HFP) membrane containing 6% of $BaTiO_3$ (25 °C, 0.1 C, 2.5‑4.0 V).[108]

fabricated high-performance fiber-based separators is centrifugal spinning, which is a fast, cost-effective and safe method.[113, 114] M. Yanilmaz et al.[115] developed SiO_2/PAN composite membranes by the centurifugal spinning. The preparation process comprises the following steps. First, PAN was dissolved into DMF. Then SiO_2 powders were added to the above solution in certain ratio to form homogeneous solution. Finally, the SiO_2/PAN composite membranes were obtained by centrifugal spinning technology. Fig. 11g show the schematic of centrifugal spinning process. Fig. 11a, b, c, d and e show SEM images of the SiO_2/PAN composite membranes with different contents of SiO_2. From Fig. 11a, b, c, d and e, the morphologies of composite membranes with SiO_2 naoparticles have no obvious difference compared with bare PAN separators. But it is found that the average fiber diameters decreased with the increase of SiO_2 content because the repulsive force of SiO_2 can minimize the entanglement of polymer chains and increase porosity. Meanwhile, the obtained composite membranes showed better wettability, higher ionic conductivity, higher electrolyte uptake, lower interfacial resistance, better rate capability and cycling performance compared with pristine PAN separators. And the lithium/lithium iron phosphate cells based on composite membranes exhibited good cycling performance and rate capacity (Fig. 11f).

In addition to the electrospun composite membranes that were applied directly to LIBs, the non-woven polymer combined with other polymer matrix can also be used as coating layers. Their unique structures can enhance physical and electrochemical performance of separators. For example, M. Yanilmaz et al.[116] prepared a novel composite membrane by coating PP separator with an electrospun SiO_2/PVDF nonwoven mats. The results showed that the addition of SiO_2 nanoparticles improved the physical and electrochemical performance of separators, including wettability, ionic conductivity, electrochemical stability, interfacial resistance and cycling performance. They also found that the composite membranes with 15% SiO_2/PVDF provided highest ionic conductivity of 2.6 × 10^{-3} S cm^{-1}. T. H. Cho et al.[30] synthesized a non-woven composite membrane by a hot roll press method at 150 °C, which combine a PAN nano-fiber nonwoven with ceramic (Al_2O_3 or SiO_2). Fig. 12a show the hot roll press method and the SEM images of composite membranes. From Fig. 12a, the ceramic powder is sandwiched between the PAN nano-fiber nonwoven and the polyolefin non-woven layer, forming a stable structure of three layers. They investigated the physical, electrochemical and thermal properties of composite membranes. The results indicated that the as-prepared composite membrane had higher porosity, air permeability and thermal stability than commercial polymer separators. The $LiCoO_2$/graphite cells assembled with this composite membranes showed better rate capabilities and cycling performance(Fig. 12b and c), which had high capacity retention of about 88% covering 200 cycles, and no obvious thermal shrinkage was observed when it was exposed at 150 °C.

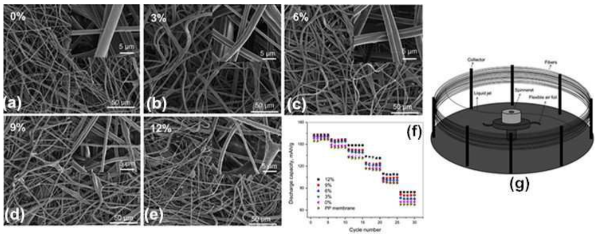


Fig. 11 (a-e) SEM images of SiO_2/PAN membranes with different SiO_2 contents. (f) C-rate performance of Li/$LiFePO_4$ cells containing SiO_2/PAN membranes with different SiO_2 contents and microporous PP membrane. (g) Schematic of centrifugal spinning process. [115]

Thus, introducing inorganic nanoparticles into non-woven fabrics (PVDF and its copolymer PVDF-HFP, and PAN, polyethylene oxide (PEO),[117, 118] poly(ethylene) glycol (PEG)[119], PVDF[120] and a blend of PEO/PVDF-HFP[121]) can fabricated the composite membranes with high performance. These composite membranes were sandwiched between anode and cathode to assemble cells. The cells showed excellent electrochemical performances, good C-rate performance and high cycling stability. Meanwhile, some researchers also suggest that the separators can also be modified successfully by introducing coating layers without inorganic particles. For example, S. Y. Xiao et al.[122] prepared the composite membrane by coating electrospinning PVDF membranes on the two sides of methyl cellulose(MC)-based host polymer. Fig. 13a, b, c and d are SEM images of this composite membrane, showing the porous structure of the as-prepared composite membranes with outer PVDF layers. This porous structure resulted in high electrolyte uptake. The MC layer was sandwiched between two PVDF layers, forming three layer structure. The results showed that the ionic conductivity of composite membranes can reach 1.5 mS cm^{-1} at room temperature, which is much higher than pure MC membranes. These composite membranes also exhibited good mechanical property, high lithium ion transference number and excellent thermal stability. The Li/LiFePO$_4$ cells assembled with the PVDF/MC/PVDF composite membranes showed high discharge capacity and good rate capacity (Fig. 13e and f). For example, its discharge capacity was about 158 mAh g^{-1} at 0.1 C, which was also higher than that for bare MC separators, about 138 mAh g^{-1}. When tested at different current densities such as 0.2 C, 0.5 C and 1 C, its discharge capacity was still higher than MC separators. And after 40 cycles there was still no evidence capacity fading at 0.2 C.

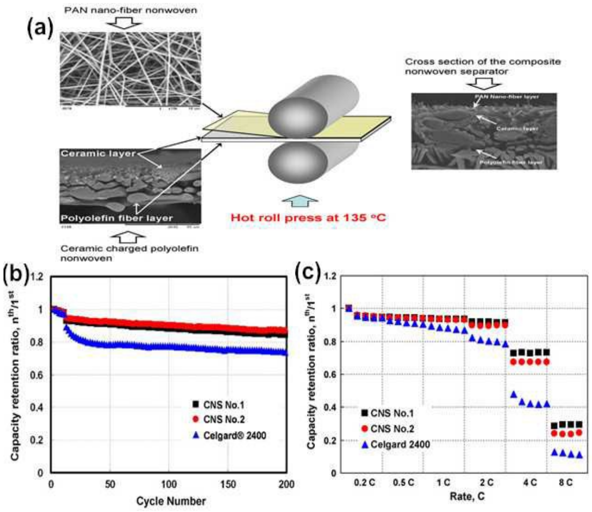


Fig. 12 (a) Schematic depiction of combining process. (b) Discharge capacities vs. cycle numbers of the test cells. (c) Results of rate capability tests for the cells with the Celgard 2400, the CNS No. 1 (composite membranes with SiO$_2$ fillers) and No. 2 (composite membranes with Al$_2$O$_3$ fillers).[30]

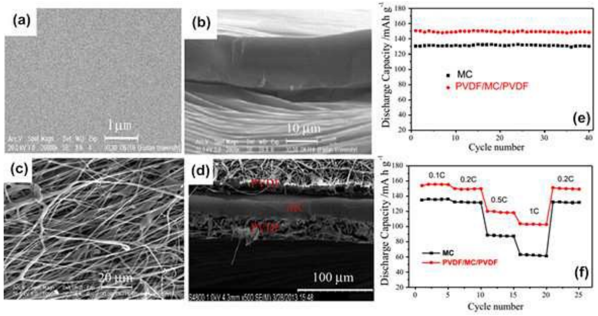


Fig. 13 SEM micrographs of (a) the surface and (b) cross section of MC, (c) the surface of PVDF and (d) the cross section of the sandwiched membrane PVDF/MC/PVDF. Electrochemical performance of LiFePO$_4$ tested by using MC and the PVDF/MC/PVDF sandwiched membrane as separators, respectively, saturated with 1 mol L^{-1} LiPF$_6$ electrolyte and Li metal as the counter electrode: (e) rate behavior, and (f) cycling behavior.[122]

G. Ding et al.[123] had successfully modified the cellulose non-woven membranes by coating a single ion polymer electrolyte via a dip-coating process. This membrane was composed of polymeric lithium tartaric acid borate salt (PLTB) and PVDF-HFP. This composite membrane with unique coating layer exhibited higher conductivity, better flame retardancy and better thermal stability compared with pristine PP separator and pure cellulose membrane. Moreover, the as-prepared composite membranes showed high lithium ion transference number of 0.48, good rate capability and excellent cycling performance. C. Cao et al.[124] prepared hydrophilic electrospun PVDF composite membranes by coating mussel-inspired polydopamine (PDA), the schematic of preparing the composite membrane is shown in Fig. 14a. They investigated the morphology, physical and electrochemical performances of the obtained composite membranes. The results showed that the surface of obtained composite membranes is hydrophilic, while the PVDF is hydrophodic, resulting in increasing of electrolyte uptake and ionic conductivity, improving the electrochemical performances of cells. The charge-discharge capability, C-rate capability and cycling performance were also investigated. In the cells assembled with the PDA-PVDF composite membranes, the LiMn$_2$O$_4$ was used as cathode materials and a lithium metal was employed as anode. The discharge capacity of this cell was 104.5 mAh g^{-1}, which was better than that of the cells using PVDF separators, about 101.1 mAh g^{-1} at 0.5 C(Fig. 14b). The cell also exhibited very good stable cycling performance as well as PVDF nanofiber. The results of the rate test in Fig. 14c show that the PDA-PVDF composite membranes have higher capacity retention compared with the retention of PVDF separators at various rates.

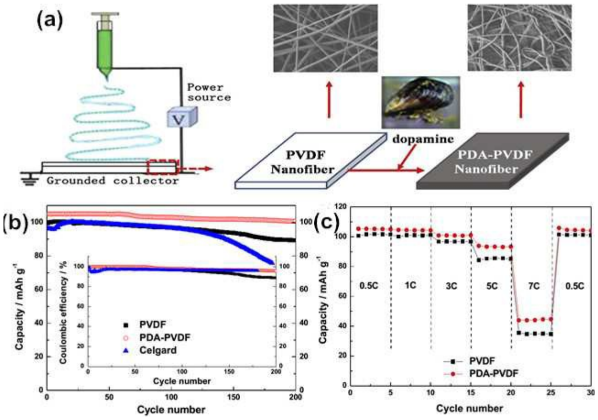


Fig. 14 (a) Schematic illustration of the mussel-inspired polydopamine coated PVDF nanofibrous membranes. Dopamine self-polymerizes in the aqueous solution at pH 8.5 and the resultant polydopamine coated surface becomes hydrophilic. Electrochemical characterizations for the Li/separator/LiMn$_2$O$_4$ cells using the PVDF nanofibrous membranes with and without polydopamine coating as separators. (b) Cycling stability and coulombic efficiency of with different separators at 0.5 C. (c) Discharge capacity profiles of the cells at various rates.[124]

Summery and outlook

Separators play an important role in LIBs. The primary function of the separator is to insulate anode and cathode to avoid the internal short-circuit of LIBs. The ideal separator must have excellent physical and chemical properties, such as larger porous structure with greater tortuosity to prevent the growth of dendritic lithium, thinner thickness, higher mechanical strength, higher electrolyte uptake, reservoir to allow the transfer of lithium ion, lower internal resistance and good thermal stability. In order to satisfy different applications of high performance LIBs, it is important to adjust the structure and properties of separators.

Currently, the most common single separators are polyolefin-based separators, which were prepared mainly by two different manufacturing methods: wet process and dry process. Some polyolefin separators have been industrialized, such as PP, PE and PP/PE/PP, but their physical and chemical properties are still need to be further improved, such as cycling capability, wettability and thermal stability for high performance of LIBs. Other microporous separators, such as PVDF, PVDF-HFP, PAN and MC, can be prepared by simple casting method and phase inversion technique. These separators can meet the fundamental requirements of LIBs, they possess a certain of porosity, electrolyte uptake, thermal stability and electrochemical performances. However, the poor ionic conductivity, lower charge/discharge capacity and high crystallinity hinder its application in higher performance of LIBs. And the other most common separators, electrospun separators, have also been used in LIBs. The electrospun separators possess many advantages, such as large porosity, high electrolyte uptake and large surface area. However, one fateful shortcoming is its poor mechanical stability. As above-mentioned, there is no single component of separators can meet all requirements of different battery application.

In order to address these issues, some researchers proposed introducing inorganic particles (such as SiO_2, Al_2O_3, TiO_2 and ZrO_2) into these polymer matrix to fabricate composite membranes by appropriate methods. This is because the inorganic particles have high surface area, high mechanical stability and good thermal stability. The modified separators can be divided into three main types: inorganic particle-coated composite membranes, inorganic particle-filled composite membranes and inorganic particle-filled non-woven composite membranes.

Recent studies have shown that the performances of separators are greatly improved by introducing inorganic nanoparticles with high surface area and absorbing ability. These inorganic nanoparticles can improve mechanical stability and reduce crystallinity, which is beneficial to the transportation of lithium ion. All of these result in improving effectively the physical and electrochemical performances of separators. So, the modified separators exhibit higher porosity, higher electrolyte uptake, stronger mechanical strength, higher ionic conductivity and better thermal stability than pristine separators. Furthermore, compared with the single component separators, these separators have better rate capability and cycling performance when they are assembled into half-cells or all-cells. Some of them even have the perfect effect of inflaming retarding at higher temperature. Thus, the excellent performance of modified separators make it possible to apply to high-power and high-density LIBs and to have better market.

However, although introducing inorganic particles into polymer matrix or on the surface of separators is an effective way to obtain high-performance LIBs separators with excellent physical and electrochemical properties, but the introducing of inorganic particles can also effect the performances of separators and result in other problems. For example, the inorganic coating layers increased the thickness and the internal resistance of separators, reduced the porosity of separators and limited the application of LIBs, even though the inorganic particle-coated composite membranes possess the above superior performances. The results also indicated that the interfacial bonding between the inorganic particles and polymer matrix is poor in the inorganic particle-filled composite membranes and inorganic particle-filled non-woven composite membranes due to the different physical and chemical properties of inorganic and organic materials. Based on those problems, this paper provides some suggestions to promote the further development of composite membranes. First, the study and understanding of the mechanism of interfacial bonding between the inorganic particles and polymer matrix should be strengthen. Next, the inorganic fibre-filled composite membranes should be developed so as to reduce the thickness and the internal resistance of separators and increase the permeability of separators by forming nanoporous network structure. Third, it should be investigated that the effects of the surface structures and features of inorganic particle on pore structure, permeability and mechanical performance of composite membrane. Finally, the development of new simple preparation methods, such as low cost, high-yield and safety, is important for business applications of composite membranes. By comparing the three composite membranes modified with inorganic particles mentioned above (Table 1), it is found that the inorganic particle-filled composite membranes prepared by phase inversion method have more outstanding properties, simple preparation process and lower cost. These composite membranes could effectively improve electrochemical performances using in LIBs because their highly porous structure has the good permeability to liquid electrolyte.

The batteries assembled by using above-mentioned three composite membranes as separators exhibit excellent rate capability, discharge capacity and cycling performance. However, the organic solvents in these batteries have high vapor pressures, it is easy to cause the battery to short circuit and thermal runaway. These are all very dangerous things because they can easily lead to fires and explosions. To address this issue, many researches turn to pay more attention on the electrolyte membranes, which is ionically conductive and can act as both separators and electrolyte within LIBs. However it still exist many problems need to be solved to improve the mechanical strength and ionic conductivity of these separators.

With the development of industrialization, it has higher requirement on LIBs, the performance of the separators also need to be improved. According to the above-mentioned, the modified composite membranes can be a potential candidate for the high-performance LIBs. Of course, it is necessary to continue improving the performance of the composite membrane. In the future, the new separator structure and techniques are needed to achieve advanced LIBs with excellent electrochemical performance.

Acknowledgements

The authors thank Natural Science Foundation of China (Grant No. 51272144, 51472127 and 51172132,) for the financial support. They also thank the Projects Supported by the State Key Laboratory of Microbial Technology (No. M2013-20) and the Key Laboratory of Pulp and Paper Science and Technology of Ministry of Education (No. KF2014-22).

Notes and references

1 Y. S. Zhu, F. X. Wang, L. L. Liu, S. X. Xiao, Z. Chang and Y. P. Wu, *Energy Environ. Sci*., 2013, **6**, 618–624.
2 J. Lee, C. L. Lee, K. Park and I. D. Kim, *J. Power Sources*, 2014,

248, 1211–1217.
3 Y. Li, G. Xu, Y. Yao, L. Xue, M. Yanilmaz, H. Lee and X. Zhang, *Solid State Ionics*, 2014, **258**, 67–73.
4 M. Dirican, M. Yanilmaz, K. Fu, Y. Lu, H. Kizil and X. Zhang, *J. Power Sources*, 2014, **264**, 240–247.
5 K. Fu, Y. Lu, M. Dirican, C. Chen, M. Yanilmaz, Q. Shi, P. D. Bradford and X. Zhang, *Nanoscale*, 2014, **6**, 7489–7495.
6 M. Li, X. Wang, Y. Wang, B. Chen, Y. Wu and R. Holze, *RSC Adv*., 2015, **5**, 52382–52387.
7 X. Liang, Y. Yang, X. Jin, Z. Huang and F. Kang, *J. Membrane Sci*., 2015, **493**, 1–7.
8 P. Yang, P. Zhang, C. Shi, L. Chen, J.Dai and J. Zhao, *J. Membrane Sci*., 2015, **474**, 148–155.
9 W. Xiao, L. Zhao, Y. Gong, J. Liu and C. Yan, *J. Membrane Sci*., 2015, **487**, 221–228.
10 C. H. Tsao, P. L. Kuo, *J. Membrane Sci*., 2015, **489**, 36–42.
11 Y. Liang, S. Cheng, J. Zhao, C. Zhang, S. Sun, N. Zhou, Y. Qiu and X. Zhang, *J. Power Sources*, 2013, **240**, 204–211.
12 X. Zhang, L. Ji, O. Toprakci, Y. Liang and M. Alcoutlabi, *Polym. Rev*., 2011, **51**, 239–264.
13 Y. Liang, Z. Lin, Y. Qiu and X. Zhang, *Electrochim. Acta*, 2011, **56**, 6474–6480.
14 H. Lee, M. Alcoutlabi, J. V. Watson and X. Zhang, *J. Appl. Polym. Sci*., 2013, **129**, 1039–1951.
15 C. J. Orendorff, T. N. Lambert, C. A. Chavez, M. Bencomo and K. R. Fenton, *Adv. Energy Mater*., 2012, **3**, 314–320.
16 K. Xu, *Chem. Rev*., 2004, **104**, 4303–4418.
17 H. S. Jeong, S. C. Hong, S. Y. Lee, *J. Membr. Sci*., 2010, **364**, 177–182.
18 J. K. Kim, L. Niedzicki, J. Scheers, C. R. Shin, D. H. Lim, W. Wieczorek, P. Johansson, J. H. Ahn, A. Matic and P. Jacobsson, *J. Power Sources*, 2013, **224**, 93–98.
19 Shalu, S. K. Chaurasia, R. K. Singh and S. Chandra, *J. Phys. Chem. B*, 2013, **117**, 897–906.
20 J. Pitawala, M. A. Navarra, B. Scrosati, P. Jacobsson and A. Matic, *J. Power Sources*, 2014, **245**, 830–835.
21 A. Manuel Stephan, *Eur. Polym. J*., 2006, **42**, 21–42.
22 T.H. Cho, M. Tanaka, H. Onishi, Y. Kondo, T. Nakamura, H. Yamazaki, S. Tanase and T. Sakai, *J. Power Sources*, 2008, **181**, 155–160.
23 J. Hao, G. Lei, Z. Li, L. Wu, Q. Xiao and L. Wang, *J. Membr. Sci*., 2013, **428**, 11–16.
24 E. Quartarone, M. Brusa, P. Mustarelli, C. Tomasi and A. Magistris, *Electrochim. Acta*, 1998, **44**, 677–681.
25 A.S. Gozdz, C.N. Schmutz, J.M. Tarascon and P.C. Warren, US Patent, 1995, 5,456,000.
26 H. Strathmann and K. Kock, *Desalination*, 1997, **21**, 241–255.
27 K. M. Kim, N. G. Park, K. S. Ryu and S. H. Chang, *Polymer*, 2002, **43**, 3951–3957.
28 H. Lee, M. Alcoutlabi, J. V. Watson and X. Zhang, *J. Polym. Sci. B:Polym. Phys*., 2013, **51**, 349–357.
29 M. Alcoutlabi, H. Lee, J. V. Watson and X. Zhang, *J. Mater. Sci*., 2013, **48**, 2690–2700.
30 T. H. Cho, M. Tanaka, H. Ohnishi, Y. Kondo, M. Yoshikazu, T. Nakamura and T. Sakai, *J. Power Sources*, 2010, **195**, 4272-4277.
31 P. Arora and Z. Zhang, *Chem. Rev*., 2004, **104**, 4419–4462.
32 K. Gao, X, Hu, C. Dai and T. Yi, *Mat. Sci. Eng. B-Solid*, 2006, **131**, 100–105.
33 P. Carol, P. Ramakrishnan, B. John and G.Cheruvally, *J. Power Sources*, 2011, **196**, 10156–10162.
34 Y. Ding, P. Zhang, Z. Long, Y. Jing, F. Xu and W. Di, *J. Membrane Sci*., 2009, **329**, 56–59.
35 A. L. Gopalan, P. Santhosh, K. M. Manesh, J. H. Nho, S. H. Kim, C. G. Hwang and K. P. Lee, *J. Membrane Sci*., 2008, **325**, 683–690.
36 L. Lu, X. Han, J. Li, J. Hua and M. Quyang, *J. Power Sources*, 2013, **226**, 272–288.
37 P. Raghavan, J. Manuel, X. Zhao, D. S. Kim, J. H. Ahn and C. Nah, *J. Power Sources*, 2011, **196**, 6742–6749.
38 M. M. Atabaki and R. Kovacevic, *Electron. Mater. Lett*., 2013, **9**, 133–153.
39 G. L. Ji, B. K. Zhu, Z. Y. Cui, C. F. Zhang and Y. Y. Xu, *Polymer*, 2007, **48**, 6415–6425.
40 S. W. Lee, S. W. Choi, S. M. Jo, B. D. Chin, D. Y. Kim and K. Y. Lee, *J. Power Sources*, 2006, **163**, 41–46.
41 K. S. Kim, S. Y. Park, S. Choi and H. Lee, *J. Power Sources*, 2006, **155**, 385–390.
42 A. M. Stephan, S. G. Kumar, N. G. Renganathan and M. A. Kulandainathan, *Eur. Polym. J*., 2005, **41**, 15–21.
43 D. Bansal, B. Meyer and M. Salomon, *J. Power Sources*, 2008, **178**, 848–851.
44 H. R. Jung,D. H. Ju ,W. J. Lee, X. Zhang and R. Kotek, *Electrochim. Acta*, 2009, **54**, 3630–3637.
45 Y. S. Lee, Y. B. Jeong and D. W. Kim, *J. Power Sources*, 2010, **195**, 6197–6201.
46 Y. Liu, J. Y. Lee and L. Hong, *J. Power sources*, 2004, **129**, 303–311.
47 W. Xiao, Y. Gong, H. Wang, L. Zhao, J. Liu and C. Yan, *Ceram. Int*., 2015, **41**, 14223–14229.
48 H. Lee, M. Yanilmaz, O. Toprakci, K. Fu and X. Zhang, *Energy Environ. Sci.*, 2014, **7**, 3857–3886.
49 M. Y. An, H. T. Kim and D. R. Chang, *J. Solid State Electr*., 2014, **18**, 1807–1814.
50 S. H. Chung, Y. Wang, L. Persi, F. Croce, S. G. Greenbaum, B. Scrosati and E. Plichta, *J. Power Sources*, 2001, **97/98**, 644–648.
51 W. K. Shin and D. W. Kim, *J. Power Sources*, 2013, **226**, 54–60.
52 J. A. Choi,S. H. Kim and D. W. Kim, *J. Power Sources*, 2010, **195**, 6192–6196.
53 J. H. Park, J. H. Cho, W. Park, D. Ryoo, S. J. Yoon, J. H. Kim, Y. U. Jeong and S. Y. Lee, *J. Power Sources*, 2010, **195**, 8306–8310.
54 H. S. Jeong and S. Y. Lee, *J. Power Sources*, 2011, **196**, 6716–6722.
55 E. S. Choi and S. Y. Lee, *J. Mater. Chem*., 2011, **21**, 14747–14754.
56 J. Wang ,Z. Hu, X. Yin, Y. Li, H. Huo, J. Zhou and L. Li, *Electrochim. Acta*, 2015, **159**, 61–65.
57 P. Zhang, L. Chen, C. Shi, P. Yang and J. Zhao, *J. Power Sources*, 2015, **284**, 10–15.
58 H. S. Jeong, D. W. Kim, Y. U. Jeong and S. Y. Lee, *J. Power Sources*, 2010, **195**, 6116–6121.
59 H. S. Jeong, S. C. Hong and S. Y. Lee, *J. Membrane Sci.*, 2010, **364**, 177–182.
60 M. Kim and J. H. Park, *J. Power Sources*, 2012, **212**, 22–27.
61 R. S. Juang, C. T. Hsieh, P. A. Chen and Y. F. Chen, *J. Power Sources*, 2015, **286**, 526–533.
62 X. Li, J. He, D. Wu, M. Zhang, J. Meng and P. Ni, *Electrochim. Acta*, 2015, **167**, 396–403.
63 T.H. Cho, M. Tanaka, H. Onishi, Y. Kondo, T. Nakamura, H. Yamazaki, S. Tanase and T. Sakai, *J. Electrochem. Soc.*, 2008, **155**, A699–A703.
64 S. M. Eo, E. Cha and D. W. Kim, *J. Power Sources*, 2009, **189**, 766–770.
65 M. Kim, G. Y. Han, K. J. Yoon and J. H. Park, *J. Power Sources*, 2010, **195**, 8302–8305.
66 Y. Zhai, K. Xiao, J. Yu and B. Ding, *Electrochim. Acta*, 2015, **154**, 219–226.
67 D. Takemura, S. Aihara, K. Hamano, M. Kise, T. Nishimura, H. Urushibata and H.Yoshiyasu, *J. Power Sources*, 2005, **146**, 779–783.
68 D. W. Kim, *J. Power Sources*, 2000, 87, 78–83.
69 P. P. Prosini, P. Villano and M. Carewska, *Electrochim. Acta*, 2002, **48**, 227–233.

70 P. Yan, Z. Huang, Y. Lin, X. Wu, Y. Yang, D. Wang, F. Chen, C. Zhang and D. He, *Ionics*, 2015, **21**, 593–599.
71 K. M. Kim, N. G. Park, K. S. Ryu and S. H. Chang, *Electrochim. Acta*, 2006, **51**, 5636–5644.
72 A. D. Pasquier, P. C. Warren, D. Culver, A. S. Gozdz, G. G. Amatucci and J. M. Tarascon, *Solid State Ionics*, 2000, **135**, 249–257.
73 A. Subramania, N. T. Kalyana Sundaram, A. R. Sathiya Priya and G. Vijaya Kumar, *J. Membrane Sci*., 2007, **294**, 8–15.
74 R. Miao, B. Liu, Z. Zhu, Y. Liu, J. Li, X. Wang and Q. Li, *J. Power Sources*, 2008, **184**, 420–426.
75 Z. Li, G. Su, X. Wang and D. Gao, *Solid State Ionics*, 2005, **176**, 1903–1908.
76 Y. Xia, Y. Zhou and M. Yoshio, *J. Electrochem. Soc*., 1997, **144**, 2593–2600.
77 D. H. Jang, Y. J. Shin and S. M. Oh, *J. Electrochem. Soc*., 1996, **143**, 2204–2211.
78 S. S. Zhang, K. Xu and T. R. Jow, *J. Power Sources*, 2005, **140**, 361–364.
79 C. H. Kim, H. T. Kim, J. K. Park, S. I. Moon and M. S. Yoon, *J. Polym. Sci.: Polym. Phys*., 1996, **34**, 2709–2714.
80 Z. Y. Cui, Y. Y. Xu, L. P. Zhu, J. Y. Wang, Z. Y. Xi and B. K. Zhu, *J. Membrane Sci*., 2008, **325**, 957–963.
81 S Rajendran, R Kannan and O Mahendran, *J. Power Sources*, 2001, **96**, 406–410.
82 N. S. Choi, Y. G. Lee , J. K. Park and J. M. Ko, *Electrochim. Acta*, 2001, **46**, 1581–1586.
83 N. T. K. Sundaram and A. Subramania, *Electrochim. Acta*, 2007, **52**, 4987–4993.
84 H. Huang and S. L. Wunder, *J. Power Sources*, 2001, **97-98,** 649–653.
85 W. Wieczorek, K. Such and J. R. Steven, *Electrochim. Acta*, 1995, **40**, 2251–2258.
86 B. Kumar, S. J. Rodrigues and S. Koka, *Electrochim. Acta*, 2002, **47**, 4125–4131.
87 F. Croce, L. Persi, B. Scrosati, F. Serraino-Fiory, E. Plichta and M. A. Hendrickson, *Electrochim. Acta*, 2001, **46**, 2457–2461.
88 W. Wieczorek, P. Lipka, G. Zukowska and H. Wycislik, *J. Phys. Chem. B*, 1998, **102**, 6968–6974.
89 C. Yang, Z. Jia, Z. Guan and L. Wang, *J. Power Sources*, 2009, **189**, 716–720.
90 L. Zhao, H. Zhang, X. Li, J. Zhao, C. Zhao and X. Yuan, *J. Appl. Polym. Sci*., 2009, **111**, 3104–3112.
91 P. Raghavan, X. Zhao, J. K. Kim, J. Manuel, G. S. Chauhan, J. H. Ahn and C. Nah, *Electrochim. Acta*, 2008, **54**, 228–234.
92 F. Croce, S. Sacchetti and B. Scrosati, *J. Power Sources*, 2006, **162**, 685–689.
93 M. Yanilmaz, F. Kalaoglu and H. Karakas, *Fibres Text. East. Eur*., 2013, **21**, 19–21.
94 M. Yanilmaz, F. Kalaoglu and H. Karakas, *Res. J. Text. Apparel*, 2012, **22**, 212–217.
95 M. Yanilmaz, F. Kalaoglu, H. Karakas and A.S. Sarac, *J. Appl. Polym. Sci*., 2012, **125**, 4100–4108.
96 M. Yanilmaz and A. S. Sarac, *Text. Res. J*., 2014, **84**, 1325-1342.
97 H. R. Jung, D. H. Ju, W. J. Lee, X. Zhang and R. Kotek, *Electrochim. Acta*, 2009, **54**, 3630–3637.
98 Y. Liang, Z. Lin, Y. Qiu and X. Zhang, *Electrochim. Acta*, 2011, **56**, 6474–6480.
99 X. Zhang, L. Ji, O. Toprakci, Y. Liang and M. Alcoutlabi, *Polym. Rev*., 2011, **51**, 239–264.
100 S. H. Chung, Y. Wang, L. Persi, F. Croce, S. G. Greenbaum, B. Scrosati and E. Plichta, *J. Power Sources*, 2001, **97-98**, 644–648.
101 F. Croce, G.B. Appetecchi, L. Persi and B. Scrosati, *Nature (London)*, 1998, **394**, 456–458.
102 G. Jiang, S. Maeda, H. Yang, Y. Saito, S. Tanase and T. Sakai, *J. Power Sources*, 2005, **141**, 143–148.
103 M. Wachtler, D. Ostrovskii, P. Jacobsson and B. Scrosati, *Electrochim. Acta*, 2004, 50, 357–361.
104 Y. Ding, P. Zhang, Z. Long, Y. Jiang, F. Xu and W. Di, *Sci. Technol. Adv. Mater*., 2008, **9**, 015005.
105 M. Yanilmaz, Y. Lu, M. Dirican, K. Fu and X. Zhang, *J. Membrane Sci*., 2014, **456**, 57–65.
106 P. Raghavan, J. W. Choi, J. H. Ahn, G. Cheruvally, G. S. Chauhan, H. J. Ahn and C. Nah, *J. Power Sources*, 2008, **184**, 437–443.
107 J. K. Kim, G. Cheruvally, X. Li, J. H. Ahn, K. W. Kim and H. J. Ahn, *J. Power Sources*, 2008, **178**, 815–820.
108 P. Raghavan, X. Zhao, J. K. Kim, J. Manuel, G. S. Chauhan, J. H. Ahn and C. Nah, *Electrochim. Acta*, 2008, **54**, 228–234.
109 G. B. Appetecchi, P. Romagnoli and B. Scrosati, *Electrochem. Commun*., 2001, **3**, 281–284.
110 P. P. Chu and Z. P. He, *Polymer*, 2001, **42**, 4743–4749.
111 T. H. Cho, T. Sakai, S.Tanase, K. Kimura, Y. Kondo, T. Tarao and M. Tanaka, *Electrochem. Solid St*., 2007, **10**, A159–A162.
112 Y. Liang, L. Ji, B. Guo, Z. Lin, Y. Yao, Y. Li, M. Alcoutlabi, Y. Qiu and X. Zhang, *J. Power Sources*, 2011, **196**, 436–441.
113 Y. Lu, Y. Li, S. Zhang, G. Xu, K. Fu, H. Lee and X. Zhang, *Eur. Polym. J*., 2013, **49**, 3834–3845.
114 L. A. Mary, T. Senthilram, S. Suganya, L. Nagarajan, J. Venugopal, S. Ramakrishna and V. Dev, *Express Polym. Lett*., 2013, **7**, 238–248.
115 M. Yanilmaz, Y. Lu, Y. Li and X. Zhang, *J. Power Sources*, 2015, **273**, 1114–1119.
116 M. Yanilmaz, C. Chen and X. Zhang, *J. Polym. Sci. Po. Phys*., 2013, **51**, 1719–1726.
117 F. Croce and B. Scrosati, *Ann. N. Y. Acad. Sci*., 2003, **984**, 194–207.
118 J. Xi, X. Qiu, M. Cui, X. Tang, W. Zhu and L. Chen, *J. Power Sources*, 2006, **156**, 581–588.
119 D. Shanmukaraj and R. Murugan, *J. Power Sources*, 2005, **149**, 90–95.
120 M. Sethupathy, V. Sethuraman and P. Manisankar, *Soft Nanoscience Letters*, 2013, **3**, 37–43.
121 J. Zhang, H. Han, S. Wu, S. Xu, Y. Yang, C. Zhou and X. Zhao, *Solid State Ionics*, 2007, **178**, 1595–1605.
122 S. Y. Xiao , Y. Q. Yang , M. X. Li , F. X. Wang , Z. Chang , Y. P. Wu and X. Liu, *J. Power Sources*, 2014, **270**, 53–58.
123 G. Ding, B. Qin, Z. Liu, J. Zhang, B. Zhang, P. Hu,C. Zhang, G. Xu, J. Yao, and G. Cui, *J. Electrochem. Soc.*, 2015, **162**, A834–A838.
124 C. Cao, L. Tan, W. Liu, J. Ma and L. Li, *J. Power Sources*, 2014, **248**, 224–229.

Table 1. Summarization of composite membranes

Substrate	Inorganic Particle	Binder	Preparation Method	Membrane Thickness	Liquid Electrolyte	Ionic Conductivity	Cathode, Anode	Electrochemical Performance	References
PE	SiO_2	PMMA	Dip coating	28 µm	1M $LiPF_6$-EC/DEC	7.4×10^{-4} S cm^{-1}	$LiCoO_2$, Li	In 3.0–4.3 V, the initial discharge capacity of 158, 140, 122 and 70 mAh g^{-1} at 0.2 C, 0.5 C, 1.0 C and 2.0	53

								C ,respectively.	
PE	SiO_2	SBR, CMC	Coating by automatic machine	29 µm	1M $LiPF_6$-EC/DEC/DMC	0.82 mS cm^{-1}	$LiMn_2O_4$, Li	In 3.0─4.3 V, the discharge capacity of 102.5 mAh g^{-1} after 100 cycles at 0.5 C.	57
PE	SiO_2	PVDF-HFP	dip coating	30 µm	1M $LiPF_6$-EC/DEC	0.53-0.61s	$LiCoO_2$, graphite	In 3.0─4.4 V, the initial discharge capacity of 153 , 150 and 111 mAh g^{-1} at 0.2 C, 0.5 C and 1.0 C, respectively, the discharge capacity of 112 mAh g^{-1} after 200 cycles at 0.5C.	54
PE	Al_2O_3	PVDF-HFP	Dip coating	30 µm	1M $LiPF_6$-EC/DEC	0.34-0.53 mS cm^{-1}	$LiCoO_2$, Li	In 3.0─4.3 V, the initial discharge capacity of 155, 149 and 90 mAh g^{-1} at 0.2 C, 1.0 C and 2.0 C, respectively.	58
PE	Al_2O_3	PVDF-HFP	Dip coating,	30-43 µm	1M $LiPF_6$-EC/DEC	0.495-0.719 mS cm^{-1}	$LiCoO_2$, Li	In 3.0─4.3 V, the initial discharge capacity of 154, 148, and 88 mAh g^{-1} at 0.2 C, 1.0 C and 2.0 C, respectively (composite membrane with the system of acetone-water)	59
PE	SiO_2	—	Chemical vapor deposition	19 µm	1M $LiPF_6$-EC/DEC/EMC	7.60×10^{-4}-1.00×10^{-3} S cm^{-1}	$LiCoO_2$, mesocarbon microbeads	In 3.0─4.2 V, the initial discharge capacity of 128, 126, 120.5 and 60 mAh g^{-1} at 0.2 C, 0.5 C, 1.0 C, 1.5 C and 3C, respectively.	60
PP/PE/PP	TiO_2	—	Microwave	—	1M $LiPF_6$-EC/PC/DMC	0.4O-0.80 mS cm^{-1}	$Li_4Ti_5O_{12}$, Li	In 1.0─3.0 V, the initial discharge capacity of 173 and 167mAh g^{-1} at 0.1 C and 0.2 C, respectively.	61
PMMA	Al_2O_3	PVDF-HFP	Dip coating	30 µm	1M $LiPF_6$-EC/DEC/DMC	5.35×10^{-4} S cm^{-1}	$LiCoO_2$, mesocarbon microbeads	In 3.0─4.2 V, the initial discharge capacity of 8.0, 7.2, 6 and 4 mAh at 0.2 C, 1.0 C, 2.0 C and 3 C, respectively.	65
PEI-PU	SiO_2	PVDF-HFP	Dip coating	35 µm	1M $LiPF_6$-EC/DMC/EMC	2.3 mS cm^{-1}	$LiFePO_4$, Li	In 2.5─4.0 V, the initial discharge capacity of 164.68, 163.98 , 159.87 and 142.57 mAh g^{-1} at 0.1 C, 0.2 C, 0.5 C and 1.0 C, respectively, and discharge capacity of 163.25 mAh g^{-1} after 50 cycles at 0.2 C.	66
PET	SiO_2	PVDF-HFP	Dip coating	30 µm	1M $LiPF_6$-EC/DEC	0.91 mS cm^{-1}	$LiCoO_2$, graphite	In 3.0─4.2V, the initial discharge capacity of 135, 130, 125 and 68 mAh g^{-1} at 0.2 C, 0.5 C, 1.0 C and 2.0 C, respectively, and the discharge capacity of 101 mAh g^{-1} after 100 cycles at 0.1 C.	55
PVDF-HFP	TiO_2	—	None-solvent evaporate	—	1M $LiPF_6$-EC/DEC	1.5×10^{-3} S cm^{-1}	$LiFePO_4$, Li	In 2.5─4.2 V, the initial discharge capacity of 164, 157, 143, and 122 mAh g^{-1} at 0.1C, 0.5 C, 1.0 C, and 3.0 C, respectively.	70
PVDF-HFP	SiO_2	—	Phase inversion	50-75 µm	1M $LiPF_6$-EC/DMC	0.9-3.1 mS cm^{-1}	$LiMn_2O_4$, C	Good discharge rate capability	72
PVDF-HFP	ZrO_2	—	Phase inversion	50-80 µm	1 M $LiClO_4$-EC/DEC	1.1×10^{-2} S cm^{-1}	$LiMg_{0.10}Mn_{1.90}O_4$, C	In 3.0─4.5 V, the initial discharge capacity of 135.0 mAh g^{-1} at 0.1 C, and the capacity fading of 2.7% at the 25th cycle.	73
PVDF-HFP	Al_2O_3	—	Phase inversion	—	1 M $LiClO_4$-EC/DEC	2.11×10^{-3} S cm^{-1}	—	Good ion transport	75
PVDF-HFP/PVA blend	$LiAlO_2$	—	Phase inversion	50-80 µm	1 M $LiClO_4$-EC/DEC	8.12×10^{-3} S cm^{-1}	$LiCoO_2$, C	In 3.0─-4.2 V, the discharge capacity of 148.0 and 142.5 on the first and 25th cycle at 0.25 mA cm^{-2}, respectively.	83

PVDF-HFP/PS Blend	SiO_2	—	Casting	—	1M $LiPF_6$-EC/DEC/DMC	4 mS cm^{-1}	—	Increased porosity and better ionic conductivity	84
PVDF	TiO_2	—	Electrospin-ning	30 µm	1M $LiPF_6$-EC/DMC	1.4×10^{-3} S cm^{-1}	$LiFePO_4$, Li	In 2.4–4.1 V, the initial discharge capacity of 148 mAh g^{-1} at 0.1 C.	104
PVDF	SiO_2	—	Electrospin-ning	—	1M $LiPF_6$-EC/EMC	1.7-2.6 mS cm^{-1}	$LiFePO_4$, Li	In 2.5–4.2 V, the discharge capacity of initial and 100th cycle of 162 mAh g^{-1} and 132 mAh g^{-1} at 0.2 C and 1.0 C, respectively.	105
PVDF-HFP	SiO_2	—	Electrospin-ning	100-120 µm	LIFSFI-BMITFSI	2.3×10^{-3}-4.3×10^{-3} S cm^{-1}	$LiFePO_4$, Li	In 2.5–4.0 V, the initial discharge capacity of 169 mAh g^{-1} at 0.1 C, and better cycling capability.	107
PVDF-HFP	SiO_2, Al_2O_3, $BaCO_3$	—	Electrospin-ning	150 µm	1M $LiPF_6$-EC/DMC	5.9×10^{-3}-7.2×10^{-3} S cm^{-1}	$LiFePO_4$, Li	In 2.5–4.0V, the discharge capacity of initial and 30th cycle of 164 mAh g^{-1} and 156 mAh g^{-1} at 0.1 C, respectively.	108
PAN	LLTO	—	Electrospin-ning	—	1M $LiPF_6$-EC/EMC	2.0×10^{-3} S cm^{-1}	$LiFePO_4$, Li	In 2.5–4.2 V, the discharge capacity of initial and 50th cycle of 162 mAh g^{-1}, and 156 mAh g^{-1} at 0.2 C, respectively.	112
PAN	SiO_2	—	Electrospin-ning	—	1M $LiPF_6$-EC/DMC	1.1×10^{-2} S cm^{-1}	$LiCoO_2$, graphite	In 2.7–4.2 V, the discharge capacity of initial and 150th cycle of 139 mAh g^{-1} and 127 mAh g^{-1} at 0.1 C ,respectively.	97
PAN	SiO_2	—	Centrifugal spinning	—	1M $LiPF_6$-EC/EMC	3.0×10^{-3}-3.6×10^{-3} S cm^{-1}	$LiFePO_4$, Li	In 2.5–4.2 V, the initial discharge capacity of 163 mAh g^{-1}, and 85 mAh g^{-1} at 0.2 C and 8 C, respectively, and better cycling capacity.	115

TABLE OF CONTENT (TOC). Various composite membranes with inorganic particles for lithium ion batteries are summarized and discussed.