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A simple method to prepare a polydopamine modified core-shell structure composite separator for application in high-safety lithiumion batteries

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ABSTRACT

In this work, we report a simple dip coating method to grow a thin polydopamine (PDA) layer on the surface of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) nano-fibers as the composite separator for application in high-safety lithium-ion batteries. A thin adherent PDA film uniformly distributed on the surface of PVDF-HFP nano-fibers, formed a unique core-shell structure. Compared with pure PVDF-HFP nonwoven membrane, the PDA coating PVDF-HFP composite membrane (PVDF-HFP-PDA) not only exhibits much higher thermal stability, but also shows enhanced mechanical strength and tensile strength, which are very important for the assemble and long-term performance of the batteries. The ionic conductivity of the PVDF-HFP-PDA composite membrane is 1.40 mS cm⁻¹ which is much higher than 0.80 mS cm⁻¹ of the polypropylene (PP) separator. The lithium-ion batteries with PVDF-HFP-PDA composite membrane show excellent cyclic stability and good rate performance. The PVDF-HFP-PDA composite membrane is suitable for applications in secondary lithium-ion batteries due to its advantages mentioned above.

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1. Introduction

Large-scale lithium-ion batteries are developed to meet the requirement of energy storage systems and hybrid electric vehicles (HEVs) [1,2]. The potential safety hazard of the batteries was exacerbated with the increase of the battery capacity. Separators as one main parts of the batteries were designed to avoid the direct contact of the cathode and anode, meanwhile sustains the free transport of the lithium-ions when absorbed liquid electrolyte [3]. Polypropylene (PP), polyethylene (PE) separator with excellent mechanical strength and chemical stability were applied as

¹ Both authors contribute equally to this work.

http://dx.doi.org/10.1016/j.memsci.2016.06.046 0376-7388/© 2016 Elsevier B.V. All rights reserved. lithium-ion batteries separator. However, they also lead to serious concerns such as weak thermal stability and poor wettability in liquid electrolytes [3,4]. Compared with the conventional PE and PP separators, the nonwoven membranes [5,6] have been widely studied in the past decades since they exhibit better wettability for the polar electrolytes, lower resistance and the batteries assembled with the nonwoven separator show higher retention capacity and rate performance. Also, the thermal stability of the nonwoven membrane could be well controlled by the selection of manufacture materials.

Among these polymers used for preparing nonwoven membranes, polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) [6–9], polyvinylidene fluoride (PVDF) [10–14], polyacrylonitrile (PAN) [15–19] have drawn considerable attention due to theirs good process ability, good chemical stability, lightweight, high ionic conductivity (dielectric constant), excellently wettability with electrolyte and easy swelling or gelation in liquid electrolyte. It must be noted that the gel polymer electrolytes are consisted of a polymer matrix and a liquid electrolyte. Therefore, the gel polymer electrolytes can use such advantages as the safety of the





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polymer matrix and high ionic conductivity of the liquid electrolyte. However, the polymer matrix of the gel polymer electrolytes will be softened by the liquid electrolyte uptake which will lead to poor mechanical properties of the membrane and further result in winding and internal shorts of the cells prepared with this membrane during the assembly processes. The weak thermo-stability and mechanical strength of nonwoven membrane limit their further application as separator for lithium-ion batteries.

Poly-dopamine (PDA) [20–28], as a small-molecule compound, contains catechol (DPA) and amine (lysine) groups. The two groups, mimic of Mytilus edulis foot protein 5 (Mefp-5), can establish covalent and non-covalent interactions with surfaces of organic and inorganic materials, makes it possible for PDA to deposit a thin layer with a wide variety of functional uses on the surfaces of virtually any bulk material [21,29]. Based on this finding, lots of works were carried out in the field of surface modification. Ryou et al. [20,25] have reported surface modification method for PE separators using PDA. The PDA-coated separators showed good electrochemical properties, and performed well in Lithium-ion batteries (LIBs). Works on the PDA coating nonwoven membrane were carried out for the improvement of interface and electrochemical properties [24]. From the above researches, we know that PDA has a melting temperature of about 230 °C. The PDA coating method should be beneficial, not only to the electrochemical performance improvement, but also to the thermo-stability and mechanical strength enhancement of the nonwoven membrane. However, there still lack of detailed research on the improvements of nonwoven membrane after PDA modified.

In this work, PVDF-HFP nonwoven membrane were coated with a thin adherent PDA film (PVDF-HFP-PDA) formed a coreshell structure. The thermo-stability, mechanical strength and electrochemical performance of the PVDF-HFP-PDA were carefully studied. Compared with pure PVDF-HFP nonwoven membrane. the PDA coating PVDF-HFP composite membrane (PVDF-HFP-PDA) not only exhibits much higher thermal stability, but also shows enhanced mechanical strength and tensile strength, which are very important for the assemble and long-term performance of the batteries. The ionic conductivity of PVDF-HFP-PDA composite membrane is 1.40 mS cm^{-1} which is much higher than 0.80 mS cm^{-1} of the PP separator. The lithium-ion batteries with PVDF-HFP-PDA composite membrane show excellent cyclic stability and good rate performance. Moreover, the whole react process is induced in an aqueous solution which is environmental friendly. The PVDF-HFP-PDA composite membrane could meet the safety requirements of large-scale lithium-ion batteries due to its advantages mentioned above.

2. Experiment

2.1. Fabrication of PVDF-HFP-PDA composite membrane

PVDF-HFP (Mw~3000,000, Aldrich, Shanghai) was dissolved into a binary solvent system with acetone and N. N-dimethylformamide (DMF) at equal volume ratio to get the solution of 16 wt% concentration, and the solution was vigorously mixed by magnetic stirring for 10 h resulting in a slurry. PVDF-HFP nonwoven membrane was fabricated by the electrospinning process with the slurry. The setup for preparing the PVDF-HFP nonwoven membrane included a high voltage source (Gamma, USA), copper collector, a pump (Harvard, USA) and syringe. The ground collector placed on top of an X-Y motion stage (Googletech, Shenzhen, China) was connected to the cathode of the high voltage source while the conductive spinneret was connected to anode. The electrospinning process of PVDF-HFP was conducted under an applied bias of 10 kV with a flow rate of 125 μ l h⁻¹. The spinneretto-collector distance is 10 cm. The collector moved forth and back in the X-axial direction at a speed of 40 cm min⁻¹ with a moving displacement of 12 cm while moved intermittently in the Y-axial direction with a moving displacement of 40 µm after a loop movement in the X-axial direction for better distribution and uniformity of nano-fibers. Then as-prepared PVDF-HFP nonwoven membrane was dried at 110 °C overnight for the further modification.

The manufacture procedure of PVDF-HFP-PDA composite membrane is shown in Fig. 1. Simple immersion of the PVDF-HFP nonwoven membrane in a aqueous/ethanol (equal volume) solution for 48 h, per milliliter consists 2 mg dopamine hydrochloride and 10 mM tris(hydroxymethyl)aminomethane with a pH of 8.5, results in spontaneous deposition of a thin PDA layer on the surface of PVDF-HFP nonwoven membrane. As-prepared PVDF-HFP-PDA composite membrane was flushed off by deionized water and then dried overnight at 80 °C in a vacuum drying oven. Characterization of the PVDF-HFP-PDA composite membrane was investigated with PP separator (Nantong Tianfeng New Electronic Materials Co., Ltd.) and PVDF-HFP nonwoven membrane as references.

2.2. Electrode preparation and cell assembly

The 2016-type coin cells assembled with PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane were used for the measurement of batteries performance. The cathode included 5 wt% of PVDF, 90 wt% of LiMn₂O₄ (Qingdao Xinzheng Material Co., Ltd, China), 5 wt% of super-P was coated on



Fig. 1. The manufacture procedure scheme-demonstration figure of PVDF-HFP-PDA composite membrane.

the aluminum foil after blending with N-methyl pyrrolidine (NMP)-based. The result cathode was used in the further tests and experiment after dried at 80 °C for 24 h in a vacuum drying oven. As-prepared PVDF-HFP-PDA composite membrane, PVDF-HFP nonwoven membrane and the PP separator, respectively, were used as separators for the cells, but the PVDF-HFP nonwoven membrane and the PP separator were used as references. The weights of electrolytes (EC:DEC:DMC=1 V:1 V:1 V, LiPF₆ 1 mol L⁻¹) injected into the cells were the same. A glove box (Mbraun, Germany) filled with argon gas were used for the manufacture of the batteries.

2.3. Characterization of the membranes

The surfaces and cross-sectional morphologies of the PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane were investigated using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). The PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane were broken mechanically after a cooling process in liquid nitrogen in order to obtain the smooth cross-sectional morphologies of the separators. Nanofiber diameter and pore size distributions of PVDF-HFP and PVDF-HFP-PDA were determined using an image analysis software (ImageJ software, National Institutes of Health, USA) and the results were plotted as histograms [30]. The porosity changes of the nonwoven membrane before and after PDA coating can be calculated as the following equation with the *n*-butanol uptake method [31]:

$$P(\%) = M_{BuOH} / (\rho_{BuOH} \times M_{BuOH} / \rho_{BuOH} + (M_m / \rho_p)) \times 100\%$$

where ρ_P and ρ_{BuOH} represent the densities of polymer and n-butanol, while M_m and M_{BuOH} represent the mass of membrane before and after absorbed n-butanol, respectively. The Fourier transform infrared (FT-IR) spectra of the nonwoven membrane before and after PDA coating were measured to further support the existence of the PDA. Round separators with diameter of 1.85 cm were subjected to high temperatures from 130 °C to 200 °C for 30 min for the heat treatment. To calculate the thermal shrinkage percent of the membrane, the following equation was used:

Shrinkage (%) =
$$\frac{S_0 - S}{S_0} \times 100\%$$

where S_0 and S present the areas of membranes before and after subjected to high temperatures, respectively. Mechanical strengths of the PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane in dry and wet state were measured using a universal testing machine (UTM-4000, SUNS, Shenzhen) with a stretching speed of 1.66 mm s⁻¹. The sample for mechanical strengths tests is about 1 cm in width, 5 cm in length and 40 µm in thickness. A commercial drop shape analysis system (Powereach JC2000C1, Shanghai Zhongchen Digital Technique Equipment Co. Ltd., China) were used for the contact angle measurement to ascertain the effect of the PDA layer on the electrolyte wettability of the separator. The electrolyte uptake of the membrane was obtained by measure the weight change before and after absorbing liquid electrolyte and the result was calculated as the following equation:

$$Uptake (\%) = \frac{W - W_0}{W_0} \times 100\%$$

where W_0 , W are the weights of the membrane before and after absorbing the liquid electrolyte.

2.4. Electrochemical measurements

Electrochemical workstation (Solartron, SI-1260, England) with a frequency range of 1 Hz to 100 kHz was used to investigate the ionic conductivity of separator which were soaked in liquid electrolyte in advance and blocked between two copper metal plate. The cells with PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane were assembled to investigate the influence of the separator on the repeat cycling and rate performance with a battery test equipment (LAND-V34, Land Electronic, China). To investigate the repeat cycling performance, the cells were charged to 4.2 V and discharged to 3 V at rate of 1 C and for the rate performances, the cells were charged to 4.2 V and discharged to 3 V at current rates of 0.5 C, 1 C, 2 C and 5 C.

3. Results and discussions

The surface scanning electron micrographs of the PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane are shown in Fig. 2a, b and c. The PP separator with a uniformly submicron elliptic pores structure was manufactured through a dry process (Fig. 2a). The short axis of about 50 nm and the long axis of the pore was 100-200 nm. The fibers of PVDF-HFP nonwoven membrane exhibited homogeneous diameters and there are no observable beads on the fibers as shown in Fig. 2b. The average diameter of the PVDF-HFP nano-fiber, as shown in Fig. 1s, is about 217.4 nm and the average diameter of pores in the membrane is about 429.8 nm. This well-interconnected microporous structure and highly tortuous pores formed by the smooth nano-fibers could increase the trapped ability of the membrane with the liquid electrolyte and allow more lithium ions transport in inner the membrane freely. But the mechanical strength of PVDF-HFP nonwoven membrane very likely decreased significantly when soaked in the electrolyte which might cause problems, such as winding tension and internal shorts during the cell assembly processes. Compared with the PVDF-HFP nonwoven membrane, the PVDF-HFP-PDA composite membrane shown in Fig. 2c maintains the same PVDF-HFP network structure with highly tortuous pores, meanwhile, a thin PDA film was deposited on the surface of PVDF-HFP nano-fibers. Compared with the pure PVDF-HFP nonwoven, the average diameter of the PVDF-HFP-PDA nano-fiber increased from 217.4 nm to 257.4 nm and the average diameter of micro-pores decreased from 429.8 nm to 387.7 nm (shown in Fig. 1s). The change in the nano-fiber diameter and pore size of the nonwoven membrane indirect proved that a PDA film successfully deposited on the surface of nano-fibers. This thin PDA film (about 40 nm) is favorable to prevent the separator from distortion or cracking in the electrolyte and being thermally shrunk under the environment of high temperature, which is especially important to the large-scale lithium-ion batteries be designed to meet the requirements of energy storage systems and electric vehicles.

The cross section morphologies of the PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane with uniformity thickness of 40 μ m are shown in Fig. 2d and e. It can be seen from the Fig. 2e that the PDA grew not only on the surface nano-fibers of the PVDF-HFP nonwoven membrane, but also on the inner nano-fibers uniformly. The core-shell structure of the PVDF-HFP-PDA can be seen clearly from the insert images of the Fig. 2e. The PDA shell layer uniformly distributed on the surface of PVDF-HFP nano-fibers. The uniformity of PVDF-HFP-PDA composite membrane can guarantee the uniformly distribution of electric current inside the batteries and further suppress the formation of metal Li [32,33].

The weight and porosity of the membrane before and after PDA







Fig. 2. Surface morphology: (a) PP separator, (b) PVDF-HFP, (c) PVDF-HFP-PDA. Cross section morphology: (d) PVDF-HFP, (e) PVDF-HFP-PDA.

modification were measured and shown in the Table 1. The weight of PVDF-HFP nonwoven membrane increased from 3 mg to 3.4 mg, meanwhile, the porosity of the membrane decreased from 77.7% to 72.8% after PDA coating. Both changes mentioned above further corroborated that the PDA deposited on the surface of PVDF-HFP nano-fibers successfully.

The above mentioned result is also supported by the Fourier transform infrared (FT-IR) spectra shown in Fig. 3. In the case of dopamine modified membrane, a broad peak between 3100 cm⁻¹ and 3600 cm⁻¹ ascribed to N–H/O–H stretching vibration, that's means lots of O–H were retained during the polydopamine formation process. The overlap of C=C resonance vibration in aromatic ring and N–H bending is observed at 1602 cm⁻¹. The adsorption peak at 1519 cm⁻¹ is the N–H shearing vibration of the amide group [21]. Result of FTIR combined the results of changes

Table 1

Thickness, weight, porosity, electrolyte uptake and ionic conductivity of PP separator, PVDF-HFP and PVDF-HFP-PDA.

	PP separator	PVDF-HFP membrane	PVDF-HFP-PDA membrane
Thickness (µm) Weight (mg) Porosity (%) Electrolyte uptake (%) ionic conductivity (ms cm ⁻¹)	$\begin{array}{c} 40 \\ 5.90 \\ 43.6 \\ 62.9 \pm 6 \\ 0.80 \end{array}$	$\begin{array}{c} 40 \pm 1.0 \\ 3.0 \\ 77.7 \pm 1.0 \\ 206 \pm 10 \\ 1.87 \pm 0.10 \end{array}$	$\begin{array}{c} 40\pm 1.0\\ 3.4\pm 0.1\\ 72.8\pm 1.0\\ 254\pm 10\\ 1.40\pm 0.10\end{array}$

in the morphologies and the weight addition of the separator should be reasonable to indicate that the amine and phenolic hydroxyl groups are adhered to the membrane surface via the



simple coating process.

As is well known, the separators play a major role in preventing cathode and anode from contacting each other, meanwhile, guarantee lithium ions transport inner the membrane freely. For the large-scale lithium-ion batteries, the separators must be thermal stable in the batteries even the batteries are exposed to high temperature [34,35]. Otherwise, thermal runaway may happen in the batteries and further lead to combustion or explosion if the separators suffer obvious dimensional loss. In order to investigate the thermal-resistant characterizations of the membranes, the membranes were treated at a series of high temperature from 130 °C to 200 °C for 30 min to observe the area-based dimensional change (the normal graph paper was used to calculating the areabased shrinkage of the separator) and the results are shown in Fig. 4. The color of the PP and PVDF-HFP is white. The color of the PVDF-HFP-PDA separator changes from white to grey after the coating process [21,29]. The melting temperature of PP is a little higher than PVDF-HFP, but the PP separator exhibits dimensional shrinkage of more than 10% at 140 °C while there are no area changes for both PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane. This was caused by the fact that productive process of the PP separator had to undergo a uniaxial stretching method. So the thermal shrinkage of the PP separator occurred below the melting temperature of PP and almost focused on one dimensional of the separator. The thermal shrinkage of the PP separator and PVDF-HFP nonwoven membrane increase as increasing temperature and, over 160 °C, an obvious thermal shrinkage with the color change from white to transparent (the color change is caused by the fact that pristine porous PP membrane form a dense structure at high temperatures) will be observed. As a comparison, the PVDF-HFP-PDA only suffers less than 15% of thermal shrinkage at 200 °C and without color change. The PVDF-HFP-PDA composite membrane shows less thermal shrinkage than PP separator and PVDF-HFP membrane at wider range of temperatures. This improvement in thermal stability of the PVDF-HFP-PDA composite membrane can be attributed to the application of PDA coating layer. The melting temperature of the PDA coating layer is above 230 °C (the DSC curve of PDA is shown in Fig. 2s), resulting in its good ability to suppress the shrinkage of the PVDF-HFP-PDA at elevated high temperatures [29]. Thus, it can be supposed that the thermo-stability of the lithium-ion batteries will be improved significantly if the PVDF-HFP-PDA composite membrane is applied as battery separator.



Fig. 4. Optical photographs of PP separator, PVDF-HFP and PVDF-HFP-PDA after annealing treatments for 30 min.

To further study the causal factors for the thermal shrinkage, the SEM images of the PVDF-HFP nonwoven and PVDF-HFP-PDA composite membrane after annealing treatment were observed and shown in Fig. 5. It can be seen from the Fig. 5a and b, the thermal shrinkage of the PVDF-HFP nonwoven membrane were mainly caused by the bending and deformation of the pristine straight nano-fibers at temperature of below 160 °C. However, the nano-fibers of the PVDF-HFP-PDA composite membrane almost did not present bending or deformation at 160 °C, which implied that the PVDF-HFP-PDA composite membrane did not suffer dimensional change. Form Fig. 5c, it was found that the nano-fibers of PVDF-HFP nonwoven membrane melted and formed a dense layer resulting in obvious shrinkage of the membrane at 170 °C. As a comparison, there was no very obvious bending or deformation observed for the nano-fibers of PVDF-HFP-PDA composite membrane (Fig. 5d), hence, the PVDF-HFP-PDA composite membrane only presented thermal shrinkage of less than 15% at 170 °C. Though the holes of PVDF-HFP-PDA membrane were gradually shut (Fig. 5e, f and g) due to the melt of nano-fibers at the temperature rise from 180 °C to 200 °C, the thermal shrinkage of the PVDF-HFP-PDA composite membrane almost did not show increase. To make clear this phenomenon, the cross section of the PVDF-HFP-PDA composite membrane after annealing treatments at 200 °C for 30 min was measured and shown in Fig. 5h. The Fig. 5h clearly shows that the volume decreases caused by shut of the holes of the PVDF-HFP-PDA composite membrane resulted in only thickness decrease from 40 μ m to 15 μ m (Fig. 5h) as exist of the PDA coating layer rather than dimensional change. Thus, it can be expected that the mechanical strength of the PVDF-HFP-PDA membrane will be significantly improved too.

The poor mechanical strength of nonwoven membrane due to the porous nature is one of the critical obstacles for the application of nonwoven membrane. The polymers like PVDF-HFP further reduced the mechanical strength of the nonwoven membranes as they formed gel polymer electrolyte. The photographs and SEM images of the PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membranes after absorbed electrolyte were shown in Fig. 6. From Fig. 6a and c, it was found that the PVDF-HFP nonwoven membrane formed a gel droplet as a result of the distance reduction between the PVDF-HFP nano-fibers caused by the gelation (the reduction of mechanical strength) of the nonwoven membrane after absorbed electrolyte. Compared with the PVDF-HFP nonwoven membrane, the PVDF-HFP-PDA (Fig. 6b and d) did not suffer dimensional change, which implied that the doping of a PDA layer onto the surface of PVDF-HFP nano-fibers should play a



Fig. 5. Surface SEM images: (a) PVDF-HFP at 160 °C, (b) PVDF-HFP-PDA at 160 °C, (c) PVDF-HFP at 170 °C, (d) PVDF-HFP-PDA at 170 °C, (e) PVDF-HFP-PDA at 180 °C, (f) PVDF-HFP-PDA at 190 °C, (g) PVDF-HFP-PDA at 200 °C. (h) Cross section SEM image of PVDF-HFP-PDA at 200 °C for 30 min.



Fig. 6. Photographs after absorbed electrolyte: (a) the PVDF-HFP, (b) PVDF-HFP-PDA. SEM images after absorbed electrolyte: (c) PVDF-HFP, (d) PVDF-HFP-PDA. (e) Tensile strengths of PVDF-HFP and PVDF-HFP-PDA in dry and wet states.

role in increasing the mechanical strength, tensile strength and toughness.

The tensile strength of the PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membranes in dry and wet states were measured and shown in Fig. 6e. Tensile properties of PVDF- HFP-PDA composite membrane were significantly improved from 7.1 MPa to 11.2 MPa in dry state and 3.5 MPa to 7.1 MPa in wet state, respectively, with additional thin PDA coating layer. The enhanced mechanical strength of the PVDF-HFP-PDA was mainly ascribed to polydopamine bonding between PVDF-HFP nano-



Fig. 7. Contact angles: (a) PP separator, (b) PVDF-HFP, (c) PVDF-HFP-PDA.

fibers from the mussel-inspired dopamine [28]. Such mechanical performances could meet the technical requirements for most conventional winding machines used in cylindrical battery fabrication. It was deduced that PVDF-HFP-PDA composite membrane with high mechanical strength and tensile strength could reduce the threats to safety of the lithium-ion batteries caused by the mechanical rupture of the membrane.

The good wettability of a membrane with electrolyte is very necessary for the manufacture and long-running performance of batteries as the electrolyte filling time of the batteries during the assemble process could be effectively reduced and the ability of retain electrolyte solution and facilitate ion transport between electrodes during running process could be improve. The contact angles of liquid electrolyte on the surfaces of membranes as one of the indicators for the wettability of separator were measured and shown in Fig. 7. The contact angles of PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane decrease more rapidly than that of the PP membrane during the dynamic process. As shown in Fig. 7, the contact angle for PP separator was measured as 43.0°. However, the contact angles significantly decreased to 0° for PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane in same contact time with same volume of electrolyte, which indicated significant increases in the wettability of membranes with electrolyte [36]. This can be due to the porous structure of nonwoven and close polarity between the polar PVDF-HFP nano-fiber and the highly polar liquid electrolyte.

The electrolyte uptake as one of the other indicators for the wettability of the separator were measured and summarized in Table 1. The electrolyte uptake of PP separator, PVDF-HFP non-woven membrane and PVDF-HFP-PDA composite membrane are 62.9%, 206% and 254%, respectively. The electrolyte uptake capacity of PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane is almost 2 times and 3 times higher than that of the PP separator. This indicates that the porous structures of PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membranes play a major role in guarantee the high electrolyte uptake percentage. Though the porosity of PVDF-HFP-PDA composite membrane decreased from 77.7% to 72.8%, the electrolyte uptake capacity of PVDF-HFP-PDA composite membrane was still higher

than the PVDF-HFP nonwoven membrane, which could be caused by the fact that the PDA layer could help to hold more liquid electrolyte and the ability retaining electrolyte solution of the PVDF-HFP nonwoven membrane was reduced by the distance reduction between the PVDF-HFP nano-fibers after absorbed electrolyte. The PVDF-HFP-PDA composite membrane with excellent wettability is expected to improve the battery performance.

The effects of the PDA coating layer on the ionic conductivities of membranes also be studied and the results are shown in Table 1. The ionic conductivities of PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane after soaking in electrolyte solution are 0.80 mS cm⁻¹, 1.87 mS cm⁻¹ and $1.40\ \text{mS}\ \text{cm}^{-1}$ at 20 °C, respectively. The ionic conductivity of PVDF-HFP-PDA nonwoven membrane is lower than the PVDF-HFP nonwoven membrane, but much higher than the PP separator due to the porous structure of nonwoven membrane. This result is caused by the fact that the well-interconnected micro-porous structure and highly tortuous pores of the PVDF-HFP and PVDF-HFP-PDA can guarantee more free transportation of lithium ions in inner the membrane. The porosity decrease of PDA coating is the main reason for the ionic conductivities decrease of PVDF-HFP-PDA. Batteries assembly with nonwoven membranes are expected to have excellent rate performance.

Fig. 8a shows the discharge capacities as a function of cycle numbers for the PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane. At charge/discharge conditions of 1 C/1 C under 3.0–4.2 V, the cycling performances of cells all are stable. After 100 cycles, the discharge capacities of the coin cells using PP separators, PVDF-HFP nonwoven membranes and PVDF-HFP-PDA composite membranes remain 96.5%, 98.8% and 99.1% of their initial capacities, respectively. This indicates that performances of lithium-ion batteries using PVDF-HFP nonwoven membrane and PVDF-HFP-PDA nonwoven membrane are improved. Furthermore, the capacity retention of cell with PVDF-HFP-PDA nonwoven membrane is a little higher than that of PVDF-HFP nonwoven membrane. It means that the ability retaining electrolyte solution of the PVDF-HFP-PDA nonwoven membrane is higher than that in PVDF-HFP nonwoven membrane without PDA layer, which thus favorable to prevent a leak or lack of electrolyte



Fig. 8. (a) Cycle performances of cells with PP separator, PVDF-HFP and PVDF-HFP-PDA. (b) Rate performances of cells with PP separator, PVDF-HFP and PVDF-HFP-PDA.

during repeated cycling. Therefore, the repeated cycling performance of the cells is improved by introducing the PDA coating layer.

The rate performances were tested when the coin cells were charged to 4.2 V and discharged to 3.0 V at current rates of 0.5 C, 1 C, 2 C and 5 C, respectively. Fig. 8b shows the rate capabilities of the cells with PP separator, PVDF-HFP nonwoven membrane and PVDF-HFP-PDA composite membrane. Batteries with different separators showed similar capacity retentions at 0.5 C and 1 C rate and their discharge capacities decreased gradually with the rate increase. It was evident that when increasing the rate to 5 C, the cells with PP separator showed an abrupt capacity retention decrease. Its capacity retention ratio at 5 C was about 86.9%. Compared with the cells with the PP separator, the PVDF-HFP-PDA composite membrane showed a capacity retention ratio of 88.8% at 5 C, which was a little lower than that of the PVDF-HFP nonwoven membrane (91.2% at 5 C rate) but higher than the PP separator. The rate capacities showed above are agreed with previous results about ionic conductivities.

4. Conclusion

In conclusion, compared with the PVDF-HFP nonwoven membrane, the PVDF-HFP-PDA not only exhibits much higher thermal stability (thermal shrinkage of less than 15% at 200 °C for 30 min) and higher electrolyte uptake (254%), but also shows enhanced mechanical strength and tensile strength, which is very important for the assemble and long times performance of the batteries. The ionic conductivity of PVDF-HFP-PDA composite membrane is 1.40 mS cm⁻¹ which is much higher than the PP separator's (0.80 mS cm⁻¹). The lithium-ion batteries with the PVDF-HFP-PDA composite membranes exhibit excellent cyclic stability and good rate performance. Moreover, the whole react process is induced in an aqueous solution which is environmental friendly. With such advantages mentioned above, the PVDF-HFP-PDA composite membrane is suitable to meet the requirements of large-scale secondary lithium-ion batteries.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2016.06. 046.

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