Preparation and Electrochemical Performance of PVdF Ultrafine Porous Fiber-Separator-Cum-Electrolyte for Supercapacitor

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Poly (vinylidene fluoride) (PVdF) ultrafine porous fiber membranes with a three-dimensional network structure, high porosity and electrolyte uptake are prepared via a blend electrospinning and phase separation process under ultrasonic-assisted vibration. The structure and morphology of PVdF fiber membranes are investigated by the scanning electron microscope and porous structure parameter analyzer. The electrochemical performances of supercapacitor constructed with PVdF ultrafine porous fiber membrane as separator-cum-electrolyte are investigated. PVdF ultrafine porous fiber membranes possess high electrolyte uptake (360 wt%) and wide electrochemical stability windows (0.0 to 3.3 V). The activated electrode supercapacitor constructed by PVdF ultrafine porous fiber separator-cum-electrolyte exhibits superior specific capacity (39.5 F g−1) even under high current density (100 mA g−1).

Supercapacitors serving as a kind of rechargeable energy source have been widely applied in electric vehicles, power tools and other devices owing to its high power density, rapid charging/discharging capability, and long cycle life.1 Separator acts as a physical barrier between the cathode and anode to avoid short circuit when they are direct contact, and meanwhile allows the liquid electrolyte ions to transport rapidly.7 Nowadays, micro-porous membranes such as polyethylene, polypropylene and composite separators are commercially available in electrode separator due to their superior chemical stability, significant mechanical property and thermal shut-down performance.7 However, these polyolefin-based separators possess inherent hydrophobicity, low porosity and weak ionic conductivity and poor electrolyte wettability.8 Separators with nano-structured morphologies play a crucial role in the development of such high performance supercapacitor packs for power source applications due to their high specific surface, facile ion mobility and highly exposed electrode-separator-electrolyte interface compared to bulk materials.9 Numerous procedures have been adopted for the synthesis of nano-structured separator materials with various morphological features.8 Among them, electrospinning is appealing due to its simple procedure and scalability in which ultra-long one-dimensional nano-fibers can be easily prepared in the form of single component fibers or composite fibers.7 Electrospun fiber membranes have been applied as electrode separators due to their high porosity, large specific surface and excellent electrochemical performance compared with commercialized separators.9 Both mono-component membrane and composite membrane fabricated using electrospinning process have been used as separators,2 particularly fluoropolymer, such as poly (vinylidene fluoride) (PVdF) which has been investigated in native form, along with nano-size ceramic particles and as a blend with other polymer. Generally, electrospun membranes are gelled with conventional carbonate-based electrolytes during the supercapacitor assembly.10 Irrespective of the combinations, overall PVdF-based membranes exhibit an ionic conductivity of over 1 mS cm−1 at ambient conditions, since porous electrospun membranes provide higher liquid uptake, lower interfacial resistance, higher ion diffusion rate and exhibit liquid-like conductivity over conventional separator prepared by either solution casting or phase inversion process.11 PVdF electrospun fibers with micro-porous structure prepared via blend electrospinning and phase separation method exhibit good electrochemical performance in solution electrolyte.10 However, organic electrolyte with high velocity and large ionic size, such as quaternary ammonium salts in organic solvent, is necessary for supercapacitors with high energy and power capacity for use as dynamic power source in such applications as electric vehicles. PVdF electrospun fiber membranes with large pore size and electrolyte permeability could provide an attractive solution to the challenges.

In the present work, PVdF ultrafine meso/macro-porous fiber membranes as separator-cum-electrolyte were investigated and characterized for the first time (Schematic. 1). PVdF ultrafine meso/macro-porous fibers are created via an electrospinning and phase separation process. First, polymer solutions of PVdF and polyvinylpyrrolidone (PVP) blends dissolved in a co-solvent were electrospun to make electrospun fibers. The incompatibility of PVdF and PVP induces phase separation to form micro-domains of PVP in the polymer blend electrospun fibers. Then, PVP micro-domains in the blend fibers were leached out in water under ultrasonic-assisted vibrating condition, and ultrafine PVdF fibers with meso/macro-porous structure were obtained. Lastly, the relationship between structure and electrochemical performance constructed with separator-cum-electrolyte was investigated by the scanning electron microscope, BET specific surface area analysis and electrochemical measurement.

Experimental
Preparation and characterization of ultrafine fibers separator—All the chemicals such as N, N-Dimethylformamide (DMF), acetone and methanol in analytical reagent grade were purchased from Shanghai Chemicals Ltd., and used as received unless otherwise specified. The 15 wt% polymer precursor for electrospinning were prepared by mixing PVdF and PVP (PVdF: PVP mass ratio = 10:0, 10:1, 10:2, 10:5 and 10:10, respectively) in a mixture solvent of DMF and acetone with a mass ratio = 7:3. PVdF/PVP electrospun fibers were prepared using a typical electrospinning process.12 The polymer precursor of PVdF/PVP were drawn with 18 kV positive voltage, 15 cm working distance between the needle tip (0.61 mm in diameter) and the target, and 0.5 mL h−1 flow rate. Electrospinning was carried out at room temperature for 3.0 h. As-spun electrospun fibers were immersed into the deionized water under ultrasonic-assisted vibration (500 W) for 20 minutes in order to extract PVP from the PVdF/PVP electrospun fibers. The deionized water was renewed and the above treatment process was repeated until the weight of the ultrafine fibers reached a constant value.

Optical microscopy was performed using a microscope (Nikon HS50L) to investigate the phase behavior of the PVdF/PVP blends. PVdF/PVP precursor was cast on a glass cover slip at room temperature until the weight of the ultrafine fibers reached a constant value.
temperature. After allowing the solvent to evaporate slowly in air, the samples were dried under vacuum for 12 h to remove all traces of the solvent before observation by optical microscopy. The morphologies of electrospun fibers membranes were observed by field emission scanning electron microscopy (SEM, Hitachi S-4800). The functional groups of polymer fibers were analyzed by Fourier transform infrared (FTIR) spectrometer (Varian 640) from 4000 cm⁻¹ to 400 cm⁻¹ with 0.5 cm⁻¹ resolution. The thermal stability of the polymer was measured by thermal gravimetric analysis (TGA) with 5°C·min⁻¹ scanning rate from room temperature to 700°C under N₂ atmosphere (Diamond TG/DTA, USA). The surface area and pore-size distribution of ultrafine fibers were tested by the nitrogen adsorption at 77 K (SSA-4500, Builder Corporation) and calculated using the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods, respectively. The thermal properties of the separators were measured by thermal gravimetric analyzer (Diamond TG/DTA) at a heating rate of 10°C·min⁻¹. Thickness of electrospun membranes was determined by thickness measurement (CHY-C2). Contact angle device (JC2000-D1) was used for measuring the liquid electrolyte contact angles with the separator. To measure the electrolyte uptake, 1.0 M tetraethylammonium tetrafluoroborate (Et₄N·BF₄) in propylene carbonate (PC) was employed to soak separators for 6 h. The masses of separator before and after swelling in liquid electrolyte were measured to obtain the electrolyte uptake which were based on: $Uptake = (W - W₀)/W₀ × 100\%$, where $W₀$ and $W$ are the weights of separator before and after immersed in electrolyte, respectively.

**Electrochemical performance of separator-cum-elecrolytes.**—The bulk resistance and the interfacial resistance of separator-cum-electrolytes were evaluated by electrochemical impedance spectroscopy (EIS) using an electrochemical work station (VMC, Princeton), with frequency ranging from 0.1 Hz to 100 kHz and 5.0 mV of alternative current amplitude at room temperature. Stainless-steel plate electrodes were used for the bulk resistance and interfacial resistance measurement. The electrochemical stability window of the separator-cum-electrolytes was determined by linear sweep voltammetry method conducted on a working electrode of stainless-steel electrode within 0.0−5.0 V versus Ag wire at a 2.0 mV s⁻¹ scan rate. The ionic conductive ($K$) of separator-cum-electrolytes was calculated based on $K = d(Rₑ, S)$, where $d$, $S$, $Rₑ$ are the thick, surface area and intrinsic resistance, respectively.

**Preparation and characterization of supercapacitor.**—Activated carbon (YP50 Kuraray Chemical) was chosen as the electrode material for the supercapacitors. The electrode was prepared as follows: Activated carbon, 40 wt% polytetrafluoroethylene emulsion and conductive carbon black were mixed at a mass ratio of 90:40:6, and stirred 12 h at room temperature. The slurry was then cast onto the surface of Al foil current collector to 50 μm thickness using an applicator. The AC-coated Al foil was subsequently vacuum-dried 12 h at 120°C, hot-pressed for 10 min under 18 MPa at 120°C. The apparent surface area of the electrode had a 1.0 cm diameter, and its thickness was approximately 150 μm.}

Electrochemical measurements of supercapacitor were performed using a two-electrode disc-type capacitor, in which a separator was soaked in liquid electrolyte of 1.0 M Et₄N·BF₄ in PC. The experiments were performed in a two-electrode arrangement with the assembled capacitor dried at 120°C for 24 h and then filled and hermetically sealed in an Ar-filled glove box ($H₂O<10 ppm$). All electrochemical performances of separator-cum-elecrolytes were determined using an electrochemical work station (VMC, Princeton) and supercapacitor testing system (SCTS, Arbin). The capacitance measured was expressed as the charge stored per total mass of activated materials and separator (F/g). The preparation and fabrication of separator-cum-electrolyte supercapacitor were shown in Scheme 1.

**Scheme 1.** Schematic diagrams.
Figure 1. SEM images of ultrafine fibers. Electrospun fibers (a) PVdF, (b) PVdF/PVP (10/10), PUPF derived from mass ratio of PVdF: PVP (c) 10:1, (d) 10:2, (e) 10:5, (f) 10:10.

Figure 2. Optical microscopy of PVdF/PVP blends. Mass ratio of PVdF: PVP (a) 10:1, (b) 10:2, (c) 10:5, (d) 10:10.

Optical microscopes images of PVdF/PVP blends before phase separation were shown in Figure 2. PVdF and PVP were phase-separated because the difference of the solubility parameters between PVdF ($R_{ij}^2 = 26.0$ MPa$^{1/2}$) and PVP ($R_{ij}^2 = 22.7$ MPa$^{1/2}$) was considerable. When the content of PVP in PVdF/PVP electrospun fibers was less, PVP formed small droplets that dispersed within PVdF continuous phase (Figures 2a and 2b). As the content of PVP increased, PVdF and PVP became more immiscible because of the additional entropic penalty, which increased the size of the dispersed PVP domains (Figures 2c and 2d). As a result the PVP droplets became elongated, deformed and fragmented during the electrospinning process, distributed rather uniformly in the PVdF/PVP blend electrospun fibers. PVdF has lower surface tension (36 dyne·cm$^{-1}$) than PVP (42 dyne·cm$^{-1}$). Most PVP was encapsulated by PVdF when PVP content was low, and the pore size and quantity of the pores obtained were small after removal of PVP using water treatment under ultrasonic vibration (Figures 1f). However, higher content of PVP in the PVdF/PVP blend precursor can partly lead to phase inversion, resulting in discontinuous macro and super-macro pore structures (Figure 1f).

The PVP contents in various PUPF after the removal of PVP from PVdF/PVP blend fibers under ultrasonic wave treatment were analyzed via the characteristic C=O vibrational band of PVP, as shown in Figure 3. The strength of the characteristic peak of C=O vibrational band (around 1678 cm$^{-1}$) of PVP in PUPF decreased with the increasing content of PVP in the PVdF/PVP blend electrospun fibers compare to the same strength of the characteristic peaks of C-F vibrational band (around 873 cm$^{-1}$) in PVdF (Figures 3c–3f). When the mass ratio of PVdF: PVP was high (10:1 and 10:2), the PVP was encapsulated in the PVdF phase completely and it was hard to permeate the PVP encapsulation in PVdF under ultrasonic-assisted vibration.
specific surface area of PUPF increases as the PVP content is increased that can also be observed in the SEM images (Figures 1c–1f). BET the porous structure formed in PUPF fibers after PVP being removed weight loss of PUPE is from 309

PVdF lead to the weak crystallization property of PVdF. The thermal

amorphous polymer, however PVdF belongs to crystalline polymer, and therefore there is an obvious characteristic peak of C=O in PUPE (Figures 3c and 3d). However, PVP was able to permeate the encapsulation of PVdF and dissolve into the water when the mass ratio of PVdF: PVP was low (10:5 and 10:10), which lead to less PVP residue in PUPE, so the weak characteristic peak of C=O was observed in PUPE (Figures 3e and 3f).

The thermal stability of PUPF was evaluated by TGA, as shown in Figure 4. Electrospun PVP fibers have two thermal weight losses: the first step (room temperature to 77°C) is the volatilization of water and the solvent retained in the PVP because of its high hydrophilicity. The second step (from 368°C to 452°C) is the decomposition and carbonization of PVP (Figure 4a). Electrospun PVdF fibers exhibit noticeable thermal weight loss from 442°C to 487°C (Figure 4b). PVP content in PVdF seriously decrease the thermal stability of PUPF. PVP is amorphous polymer, however PVdF belongs to crystalline polymer, so the high content and well distribution (Figures 2a and 2b) of PVP in PVdF lead to the weak crystallization property of PVdF. The thermal weight loss of PUPE is from 309°C to 439°C (Figures 4c and 4d). The thermal stability of PUPE with low PVP content in PVdF possesses better thermal stability and their thermal weight loss is from 364°C to 476°C (Figures 4e and 4f).

The pore structure parameters of ultrafine fibers were measured by nitrogen adsorption method, as shown in Figure 5 and Table I. With the increase in PVP pore-forming agent in PVdF/PVP electrospun fibers, the specific surface area of the ultrafine fibers increases. As can be seen, BET specific surface of PUPF is about 4 to 10 times higher than that of the virgin PVdF electrospun fibers (Table I), which is due to the porous structure formed in PUF fibers after PVP being removed that can also be observed in the SEM images (Figures 1c–1f). BET specific surface area of PUPF increases as the PVP content is increased in PVdF/PVP blend electrospun fibers, because more porosity can be obtained after more PVP is leached out of the PVdF/PVP blend electrospun fibers. The specific surface area of PUPF derived from mass ratio of PVdF: PVP = 10:5 is more than 110 m²·g⁻¹ (Table I) due to the large quantity of micro-meso pores and large pore volume (Figure 5). However, the BET specific area surface decreases with excessive PVP in the PVdF/PVP blend electrospun fibers. This is because more macro and super-macro pores are formed in PUF fibers as can be seen in the SEM images (Figure 1f).

The wettability behavior of PUPF membranes were investigated by measuring the contact angles of liquid electrolyte of 1.0 M Et₄N-BF₄ in PC, as shown in Figure 6. The contact angle of PUPF membranes is smaller than virgin PVdF electrospun fiber membranes, because the micro/meso pore structure of porous ultrafine fibers can lower the surface tension of electrolyte (Figures 6b–6d). PUPF with macro/super macro-pores structure shows stronger reduction effect on the surface tension of electrolyte, and show better wettability, and thus a smaller contact angle (Figure 6c).

The electrolyte solution uptake properties of PUPF membranes reaching equilibrium state are shown in Figure 7. The electrolyte solution uptake of PUPF membranes were significantly higher than virgin PVdF electrospun fiber membranes, which is due to PUPF exhibiting higher porosity and specific surface area (Figures 5 and Table I). The electrolyte can be absorbed by both the outside surface of PUPF and the inside of pores of PUPF. The electrolyte uptake of PUPF increased with the content of PVP in PVdF/PVP electrospun fiber, since more PVP sacrificial pore-forming agent could lead to much more pores and higher surface area (Table I), providing more room for the storage of electrolyte. PUPF membrane shows the highest electrolyte uptake of (360 wt% at PVdF:PVP ratio = 10:5). Further increase PVP sacrificial pore-forming agent resulted in forming a spare pore structure with decreased specific surface area of PUF, and therefore electrolyte leakage increased (Figure 7).

Electrochemical feature of capacitor.—Alternating current impedance spectroscopy was used to measure the ionic conductivities of PUPF separators, performed on a symmetric two stainless steel electrode capacitor, as shown in Figure 8. The intercept of the impedance spectrum at the real axis represents the bulk resistance of the electrolyte solution in the pores of the separator. PUPF separators have lower ionic resistance than virgin PVdF electrospun fiber separator (Figure 8). PUPF separator has a hierarchical porous structure, as shown in Figure 9, with high electrolyte uptake (Figure 7) and small electrolyte concentration difference between electrolyte and separator,

![Figure 4](image_url)

Figure 4. Thermogravimetric analysis. Electrospun fibers (a) PVP, (b) PVdF; PUPF derived from mass ratio of PVdF: PVP (c) 10:1, (d) 10:2, (e) 10:5, (f) 10:10.

| Table I. Pore structure parameter of PUPF ultrafine fibers. |
|-----------------------------|-----------------------------|-----------------------------|
| PVPdF: PVP (mass ratio)     | 10: 0 | 10: 1 | 10: 5 | 10: 10 | 10: 20 |
| Specific surface area (m²·g⁻¹) | 24.2 | 41.3 | 63.4 | 111.5 | 76.7 |
| Pore Volume (cm³·g⁻¹)       | 0.0377 | 0.0624 | 0.1147 | 0.1952 | 0.0932 |
| Pore Size (Å)               | 3.5 | 12.8 | 21.4 | 23.1 | 77.9 |

![Figure 5](image_url)

Figure 5. Parameters of pore structure. PUPF derived from mass ratio of PVdF/PVP = 10:5. (a) nitrogen adsorption/desorption isotherms, (b) pore size distributions, (c) pore volume distributions.
resulting in fast ion diffusion rate and low concentration polarization resistance. PUPF separator derived from PVdF/PVP (10/5) exhibits the highest bulk conductivity (1.8 mS·cm⁻¹) (Figure 7) due to its good porosity (Figure 5 and Table 1) and high electrolyte uptake (Figure 7).

The electrochemical stability of PUPF separators was determined by linear sweep voltammetry performed on the stainless steel (SS)/separator/SS system cells at a scan rate of 10 mV s⁻¹ ranging from 0.0 to 4.0 V in liquid electrolyte of 1.0 M Et₄N-BF₄ in PC, as shown in Figure 10. The electrochemical oxidation limit was identified from the sharp increase in current when the electrolyte decomposed. There were no apparent increases in anodic currents below 3.3 V for all the separators (Figure 10), which indicated that PUPF separators were compatible with the quaternary ammonium salt organic electrolyte and had sufficient electrochemical stability to be charged or discharged against the anodic potential applied in this work (2.5 V). Furthermore, PUPF separator-cum-electrolyte exhibited better current response character than virgin PVdF non-porous fibers separator (Figure 10). The reason is that PUPF separators possess high electrolyte uptake and porosity, ensuring a fast ion diffusion rate and low electrolyte contact resistance between separator and electrolyte.
exhibited the best current response character because of its highest electrolyte uptake (Figure 7) and optimum porosity structure (Figures 1e and Figure 5 and Table I).

The charge/discharge performance analysis of PUPF separators-cum-electrolyte was performed at different galvanostatic modes (5.0 mA·g⁻¹ to 100.0 mA·g⁻¹) within 0.0–2.5 V are shown in Figure 11. The voltage changes linearly over time, indicating that only ion adsorption and desorption are involved among the electrode/separator/electrolyte interface without other chemical reactions. Supercapacitors based on PUPF separators-cum-electrolyte show smaller voltage drops and symmetric charge/discharge plots (Figures 11b–11e) than those based on virgin PVdF non-porous fiber separator, and therefore less heat loss and higher charge/discharge efficiency can be obtained during the charge/discharge process.

Conclusions

Ultrafine PVdF fibers with meso/macro pore structure were fabricated via a blend electrospinning and phase separation process. The relationship between morphology and electrochemical performance was investigated. Ultrafine PVdF fibers with meso/macro-pore structure can be achieved from PVdF/PVP (10:5) blend electrospun fibers and it exhibits high specific surface (111.5 m²·g⁻¹), suitable meso/macro pore structure and good electrolyte uptake (360 wt%). Furthermore, PVdF ultrafine porous fiber membrane also shows low ionic conductivity (1.8 mS·cm⁻¹), good electrochemical stability (0.0–3.3 V) and good power density (39.5 F·g⁻¹) under high charge/discharge current density (100 mA·g⁻¹) for AC electrode supercapacitors.

Acknowledgments

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