ORIGINAL PAPER

Fibrous cellulose membrane mass produced via forcespinning® for lithium-ion battery separators

**Baicheng Weng · Fenghua Xu ·
Mataz Alcoutlabi · Yuanbing Mao ·
Karen Lozano**

Abstract In this study, fibrous cellulose membranes were successfully mass produced by forcespinning® cellulose acetate, followed by alkaline hydrolysis treatment. Its performance as lithium-ion battery separator was evaluated. The cellulose membrane exhibits a randomly-oriented, fully-interconnected and highly porous three-dimensional fibrous network structure with a high porosity of 76 %. The developed membranes show good electrolyte wettability and high electrolyte uptake capability. Differential scanning calorimetry and thermal treatment show a superior thermal stability of the cellulose nonwoven membrane. Compared to commercially available polypropylene based separators, the developed fibrous cellulose membrane displays higher ionic conductivity, lower interfacial resistance and better electrochemical stability. Given its outstanding thermal characteristics and excellent electrochemical performance, this fibrous cellulose membrane has potential to be used as high-performance lithium-ion battery separator. This study provides a novel and feasible pathway for developing promising separators for high-performance lithium ion batteries.

Baicheng Weng and Fenghua Xu have contributed equally to this work.

Disclaimer: Dr. Lozano and the University of Texas Pan American have research-related interests in Fiberio Technology Corporation.

B. Weng · F. Xu · M. Alcoutlabi (✉) · K. Lozano (✉)
Department of Mechanical Engineering, University of Texas–Pan American, Edinburg, TX 78539, USA
e-mail: alcoutlabimy@utpa.edu

K. Lozano
e-mail: lozanok@utpa.edu

Y. Mao
Department of Chemistry, University of Texas–Pan American, Edinburg, TX 78539, USA

Introduction

Lithium-ion batteries (LIBs) are the most employed power sources in electronic devices, such as cellular phones, laptop computers and digital cameras. LIBs possess high energy density, long cycle life and low self-discharge rate (Alcoutlabi et al.2011; Goodenough and Park 2013; Ji et al. 2011; Li et al. 2009; Tarascon and Armand 2001). One of the crucial components in a LIB is the separator, which provides a physical barrier to prevent electronic contact between the positive and negative electrodes, and at the same time serves as a medium to transport ions during the charging and discharging cycles (Arora and Zhang 2004; Zhang 2007). Presently, polyolefin microporous membranes are the most commonly used separators for commercial LIBs due to their good chemical stability, adequate mechanical strength and suitable

thickness. However, their low porosity, poor wettability with liquid electrolytes, low rate capability, and thermal dimensional instability at the high operational temperature may cause high cell resistance or internal short circuit (Alcoutlabi et al. 2013; Lee et al. 2013, 2014). Therefore, various approaches have been used to develop novel porous membrane separators to enhance their performance. Among them, spun nonwoven fibrous membranes with high porosity have shown the potential to hold a large amount of liquid electrolyte resulting in higher ionic conductivity. Spun membrane based separators of several polymeric systems have been developed such as PAN (Kim et al. 2013), PET (Orendorff et al. 2013), PVDF (Choi et al. 2003; Liang et al. 2013), nylon 6,6 (Yanilmaz et al. 2014), PVDF/PMMA (Cui et al. 2013) and PVDF/PEO (Prasanth et al. 2014).

In the last few decades, electrospinning has been the most commonly used method for preparing fibers for research related applications (Li and Xia 2004; Paneva et al. 2008). Recently, Forcespinning® (FS) has provided the opportunity to successfully transfer fiber related research into practical applications given its versatility to mass produce fine fibers from a wide variety of materials. In the FS process, the high-voltage electrostatic forces needed to draw fibers in the electrospinning process are replaced with centrifugal forces developed through high rotational speeds of spinnerets. A significant increase in yield, ease of production, and a broader spectrum of materials to be spun into fibers has been observed (Padron et al. 2013). Both conductive and nonconductive polymer solutions and polymer melts can be spun into fibers without the need of electric fields, given that the conductivity and/or electrostatic charges of the solution are not relevant parameters to prepare fibers (Raghavan et al. 2013; Sarkar et al. 2010; Weng et al. 2014a, b, 2015). The productivity of FS has been reported to be higher than 1 g min^{-1} per nozzle at the lab scale (industrial lines are believed to run at tens to hundreds of meters per minute) which is significantly higher than lab scale electrospinning (0.3 g h^{-1}; Lozano and Sarkar 2009; Ramakrishna et al. 2005; Sarkar et al. 2010).

Recently, cellulose, the most abundant, renewable, biodegradable and biocompatible natural polymer in nature has drawn considerable attention as a very promising material for a variety of applications, due to its excellent properties such as high dielectric

constant, good chemical stability, superior thermal stability (initial decomposition temperature >270 °C), biocompatibility, and environmental benignancy (Cherian et al. 2011; Jabbour et al. 2013; Reddy and Yang 2009). Given that cellulose is an abundant renewable biomaterial with superior thermal stability, several studies have been carried out to explore the potential applications as high-performance LIB separators (Jabbour et al. 2013; Kuribayashi 1996; Chun et al. 2012; Zhang et al. 2014).

In this study, cellulose nonwoven fibrous membranes were mass produced utilizing the FS method followed by hydrolysis of the membrane in an alkaline solution. The morphology, structure and thermophysical properties of the developed membranes were characterized. The potential application of the fibrous cellulose membrane as LIB separator was evaluated by investigating its electrolyte uptake capacity and electrochemical properties, such as ionic conductivity, interfacial resistance and electrochemical stability.

Experimental

Materials

Cellulose acetate (CA, M_n = 30,000, 39.8 wt% acetyl), dimethyl sulfoxide (DMSO), acetone, ethanol and potassium hydroxide (KOH) were purchased from Sigma-Aldrich. Anhydrous potassium bromide (KBr, >99 %) was purchased from Fisher Scientific, Inc. Lithium hexafluorophosphate (LiPF$_6$), ethylene carbonate, and diethyl carbonate were obtained from Alfa Aesar and used for liquid electrolyte uptake tests. Liquid electrolyte, 1 M LiPF$_6$ in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (EC + DMC +DEC, 1:1:1 in volume), was supplied from MTI Corporation. A Celgard® 2400 microporous polypropylene (PP) membrane separator was used for comparison. All chemicals were used as received without further purification. Deionized water (DI water, 18 MΩ cm) was produced from a Mill-Q filter (Millipore Ltd., UK).

Preparation of FS regenerated cellulose fiber membrane

A CA solution of 19 wt% was prepared by dissolving cellulose acetate in acetone/DMSO (6:4, v/v). This

concentration was selected based on a previous optimization study that considered cellulose concentration and angular velocity with fiber size, homogeneity, and yield. The solution was stirred overnight at ambient temperature until it became clear. FS was conducted on a lab scale Cyclone™ L-1000 M system (purchased from Fiberio Technology Corporation). The as-prepared polymer solution was injected into the spinneret. The fibers being elongated from the orifices of the spinneret were deposited on a substrate to obtain nonwoven fibrous membranes. The prepared CA membrane was detached from the collector and dried under vacuum for 24 h at 80 °C to remove traces of the solvent. To prepare regenerated cellulose membrane, hydrolysis of the collected CA membrane was performed in a 0.05 M KOH ethanol solution at ambient temperature for 1 h. After deacetylation, the membrane was thoroughly rinsed to neutral pH with DI water. The hydrolyzed membrane was then dried under vacuum at 80 °C for 24 h. The thickness of the obtained final fibrous cellulose membrane was around 50 μm.

Characterizations

The morphology of the fibrous CA and cellulose membranes was investigated using a field-emission scanning electron microscopy (FE-SEM; Sigma VP Carl Zeiss, Germany). The average diameter of the fibers was analyzed by measuring 300 randomly-selected fibers from SEM images using the image analysis software JMicroVision (V.1.2.7, University of Geneva, Geneva, Switzerland).

Fourier transform infrared (FTIR) spectra of native cellulose, fibrous CA and cellulose membranes were performed on a Bruker IFS 55 Equinox FTIR spectrophotometer. All samples were grinded and mixed with KBr and then pressed to form pellets. The samples were then scanned in the wave number range of 400–4,000 cm^{-1}.

The thermo-physical properties of the fibrous cellulose membrane and commercial Celgard® 2400 microporous PP membrane were analyzed by differential scanning calorimetry (DSC), which was carried out using a TA-Q series instrument, DSC-Q100 (TA Instruments Inc.). 10 mg samples were sealed in an aluminum pan and heated from room temperature to 220 °C at a heating rate of 10 °C min^{-1} under 30 mL min^{-1} air flow. The thermal shrinkage behavior

of these membranes was evaluated by heat treatment at 150 and 180 °C for 30 min, respectively.

The porosity of the fibrous cellulose membrane was determined using n-butanol uptake method. In the uptake test, the weight of the membrane was measured before and after soaking in n-butanol for 2 h at room temperature. The porosity was calculated by the following equation:

$$\text{Porosity } (\%) = [(W_\text{w} - W_\text{d}) / (\rho_b \times V)] \times 100\%$$

where W_w and W_d are the weights of n-butanol-soaked membrane and dry membrane, respectively, ρ_b the density of n-butanol, and V the geometric volume of the membrane.

Performance evaluation

For liquid electrode uptake (EU) measurements, the dry membranes were weighed and subsequently immersed in the liquid electrolyte of 1 M LiPF$_6$ in EC + DEC (1:1 in volume) for 2 h at room temperature, followed by being weighed after removing the surface liquid with filter paper. The EU was calculated using the following equation:

$$\text{EU } (\%) = [(W - W_0) / W_0] \times 100\%$$

where W_0 and W are the weights of the membranes before and after soaking in the electrolyte, respectively.

The ionic conductivity of the liquid electrolyte-soaked membrane was measured by electrochemical impedance spectroscopy (EIS) using Reference 600 Potentiostat/Galvanostat/ZRA (Gamry Instruments, Inc.). The liquid electrolyte-soaked membranes were sandwiched between two stainless steel blocking electrodes in coin cells, and the impedance measurement was conducted over a frequency range of 1 MHz to 1 Hz under AC amplitude of 10 mV at room temperature. The ionic conductivity was calculated by the following equation:

$$\sigma = d / (R_b \times S)$$

where d is thickness of the membrane, S is the contact area between the separator and stainless steel blocking electrode, and R_b is the bulk resistance obtained at the high frequency intercept of the Nyquist plot on the Z′ real axis.

The interfacial resistance between the liquid electrolyte-soaked membranes and lithium metal was investigated using EIS over the frequency range of

1 MHz to 1 Hz. The liquid electrolyte-soaked membranes were symmetrically sandwiched with two lithium non-blocking electrodes in coin cells.

The electrochemical stability of liquid electrolyte-soaked membranes was determined by linear sweep voltammetry with a scan rate of 10 mV s^{-1} and a potential range from 3.0 to 6.0 V at room temperature. For this test, coin cells consisting of stainless steel working electrode and lithium metal counter electrode were used.

Results and discussion

Morphology and structure

The use of centrifugal forces remarkably increases fiber production rate and provides a broader opportunity for a broad range of materials to be spun into fine fibers (Raghavan et al. 2013; Sarkar et al. 2010; Weng et al. 2014a, b, 2015). Figure 1 displays the schematic representation of the fabrication of fibrous cellulose membrane separators. A fine fibrous based membrane was successively mass produced by spinning CA solution in a mixture of acetone and DMSO.

Figure 2a, b show typical SEM images of the spun CA fibrous membrane. The CA membrane consists of loosely packed, smooth, long, beadless and continuous fibers with an average diameter of 1.18 μm. Hydrolysis in alkaline media of cellulose esters has been proved to fully regenerate cellulose by cleavage of the acetyl groups present in the polymer (Liu and Hsieh 2002). As such, the produced CA membrane was converted to fibrous cellulose membrane by alkaline hydrolysis. Figure 2c, d show SEM images for the obtained cellulose membrane after deacetylation. After alkaline hydrolysis, the changes in shape and morphology from CA membrane to cellulose membrane were negligible, although the cellulose fibers were packed more densely than the CA fibers. In particular, the nonwoven membrane structure with randomly-oriented, fully-interconnected and highly porous fibrous networks was maintained, which is consistent with other reports (Liu and Hsieh 2002; Ma et al. 2005; Vallejos et al. 2012).

Porosity of battery separators is an important factor that affects their ionic conductivity and electrochemical properties. Typically, the porosity of Celgard® separators is ∼41 %. In contrast, in this study, the developed fibrous cellulose membrane exhibits a
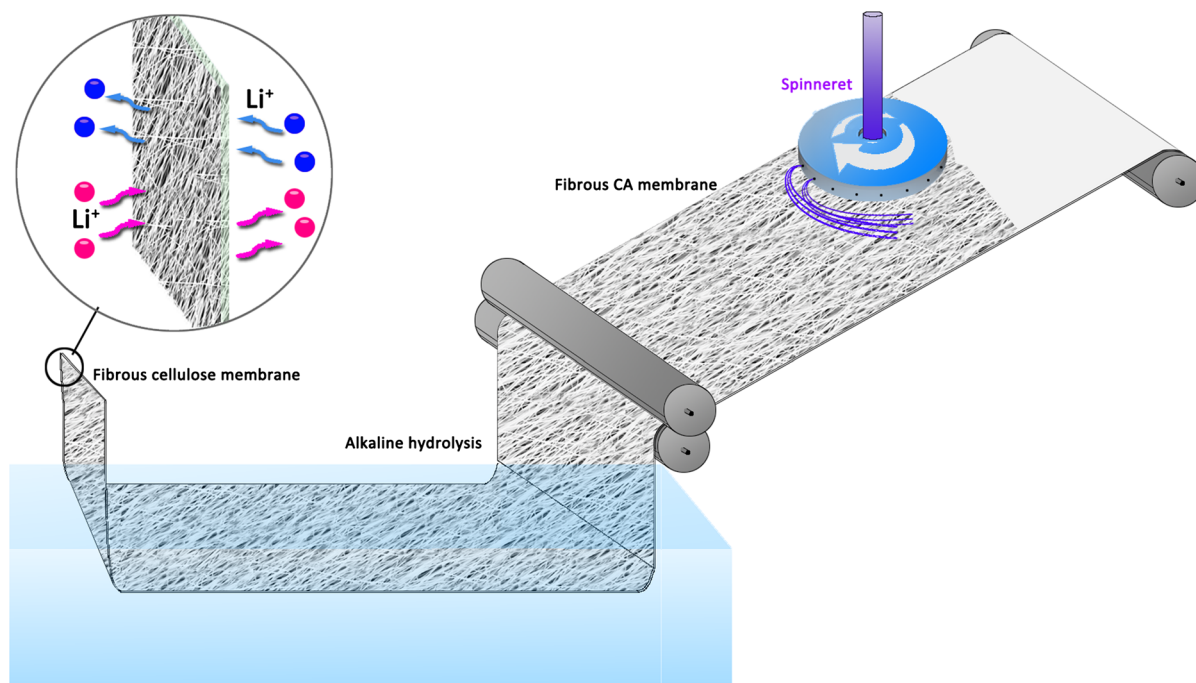

Fig. 1 Schematic representation of large-scale fabrication of fibrous cellulose membrane separator using the forcespinning® technique and subsequent alkaline hydrolysis treatment
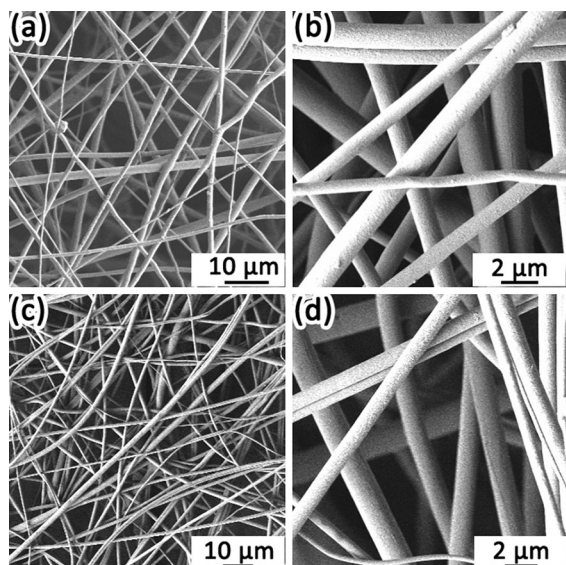
Fig. 2 SEM images of **a**, **b** FS CA and **c**, **d** fibrous cellulose membranes

higher porosity, 76 %. The higher porosity can be attributed to the intrinsic three-dimensional and fully-interconnected porous network structure. This type of structure endows high electrolyte uptake and consequently facilitates fast ionic transportation and ensures small internal resistance between two electrodes (Li et al. 2011; Wang et al. 2009; Yvonne et al. 2014; Zhai et al. 2014).

Fourier transform infrared spectroscopy was used to analyze the change in chemical structure of the spun CA fibers after deacetylation and confirm the complete hydrolysis of CA fibers into cellulose. Figure 3 shows the FTIR spectra of CA fibers before and after deacetylation. The spectrum of CA fibers shows the typical absorption features of CA polymer. The strong characteristic adsorption peaks at 1,745 ($\upsilon_{C=O}$), 1,375 (υ_{C-CH3}), and 1,235 cm^{-1} (υ_{C-O-C}), corresponding to the vibrations of acetate group were observed, and the wide stretching band at 3,500 cm^{-1} can be ascribed to the hydroxyl groups (υ_{O-H}) of CA polymer. After deacetylation, the peaks attributed to the vibrations of acetate group disappear, while the intensity of the absorption peak for υ_{O-H} increases and it shifts to 3,400 cm^{-1} (Deng et al. 2010; Ma et al. 2005; Son et al. 2004a, b; Vallejos et al. 2012). Moreover, the FTIR spectrum obtained after deacetylation is almost the same as that of native cellulose microcrystalline. Overall, these results suggest that acetyl groups in CA
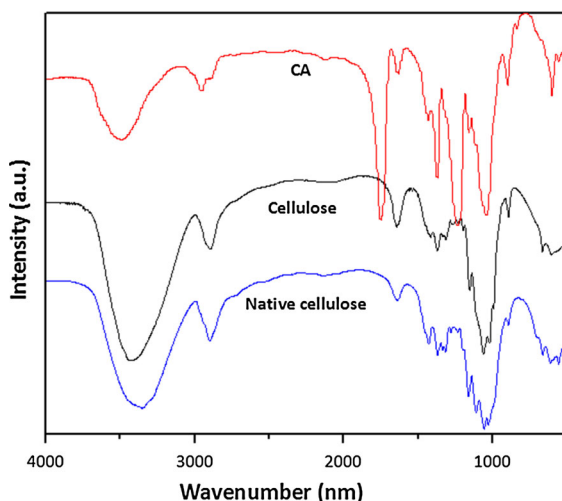

Fig. 3 FTIR spectra of FS CA fibers, cellulose fibers, and native microcrystalline cellulose

were fully converted to hydroxyl groups and thus cellulose was completely regenerated after alkaline hydrolysis.

Thermal stability

The thermal stability of separators plays an important role in the safe performance of LIBs (Zhang 2007). The thermal stability of the developed nonwoven fibrous cellulose membranes was compared with that of the PP membranes by DSC analysis (Fig. 4). It is observed that the PP separator shows an endothermic peak at 165 °C, corresponding to the typical melting
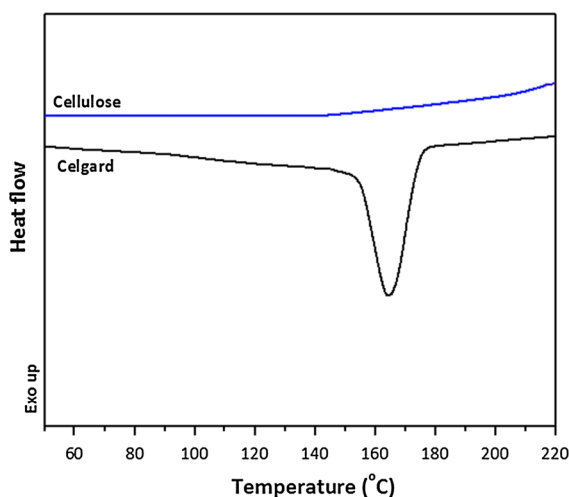

Fig. 4 DSC curves of fibrous cellulose membrane and PP separator
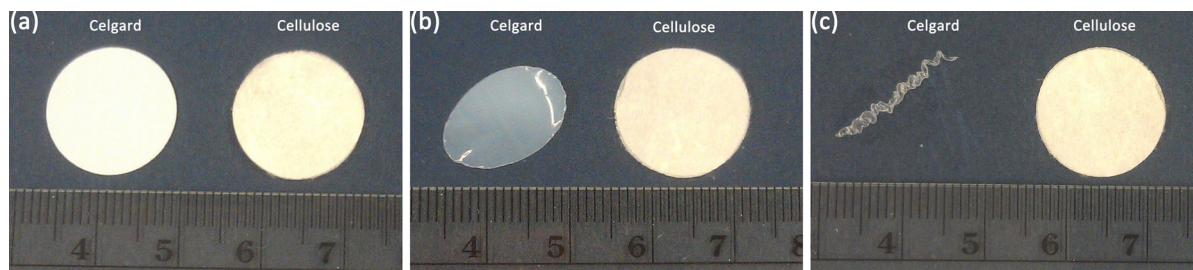
Fig. 5 Photographs of fibrous cellulose membrane and PP separator membrane (**a**) before and after thermal treatment at **b** 150 °C and **c** 180 °C for 30 min, respectively

temperature of PP, while no peaks were observed up to 220 °C from the cellulose fibrous membrane. This result suggests that fibrous cellulose membrane possesses better thermal stability. Figure 5 compares the photographs of fibrous cellulose membrane and the PP membrane before and after thermal treatment at 150 and 180 °C for 30 min, respectively. It can be seen that the PP membrane has shrunk remarkably after treatment at 150 °C (Fig. 5b), and has been completely damaged after exposure at 180 °C (Fig. 5c), resulting from the melting of PP, whereas FS fibrous cellulose membrane exhibits negligible dimensional change even after being exposed to 180 °C for 30 min (Fig. 5c). Therefore, fibrous cellulose membrane has outstanding thermal dimensional stability, which can effectively avoid internal short circuit caused by thermal shrinkage of the separators at elevated temperatures, and thus enhance the safety of LIBs.

Electrolyte uptake capacity

Lithium-ion batteries separators should possess good electrolyte wettability, easily absorb and effectively retain liquid electrolyte in order to achieve low internal resistance and good battery performance (Manthiram et al. 2008; Ryou et al. 2011; Song et al. 1999; Yang and Hou 2012). Here, the electrolyte wettability was evaluated and compared. As shown in Fig. 6, unlike the PP separator, the liquid electrolyte droplets easily spread and quickly wet the developed fibrous cellulose membrane, which indicates that FS nonwoven membrane exhibits better electrolyte wettability. Furthermore, electrolyte uptake capacity of the cellulose nonwoven membrane was determined. The uptake capacity of the FS nonwoven cellulose membrane is about 370 %, which is significantly higher than that of the microporous PP separator
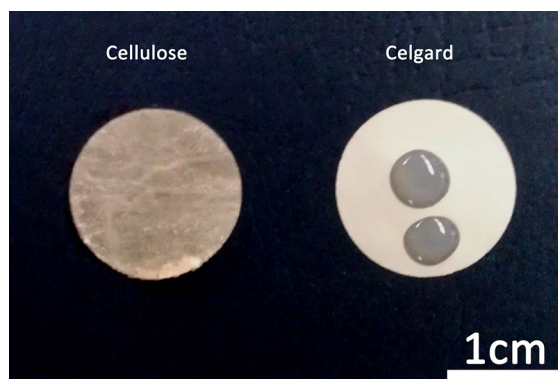

Fig. 6 Digital pictures indicating wettability toward the polar liquid electrolyte of FS fibrous cellulose membrane and PP separator, respectively

(110 %), indicating a high electrolyte retention ability of the fibrous cellulose membrane. This superior electrolyte wettability and remarkably high electrolyte uptake capability of the cellulose membrane may be attributed to its high porosity, well-interconnected microporous three-dimensional network structure and large specific surface area, as well as the intrinsically lyophilic nature of cellulose material, resulting in easier penetration and absorption of liquid electrolyte (Chun et al. 2012; Li et al. 2011; Zhang et al. 2014).

Electrochemical properties

It is crucial to have low ionic resistance between two electrodes for good performance of LIBs. The room-temperature ionic conductivity of fibrous cellulose membrane was compared with that of microporous PP separator after soaked in liquid electrolyte. The conductivity was calculated from the high-frequency intersection of the Nyquist curve with the Z′ axis. At room temperature, the ionic conductivity of the as-

prepared fibrous cellulose membrane saturated with liquid electrolyte can be up to 2.12 mS cm^{-1}, which is higher than that of the PP membrane (0.66 mS cm^{-1}). The relatively high ionic conductivity of the fibrous cellulose membrane can be attributed to its high electrolyte uptake capability and well-interconnected pore structure. Overall, the FS cellulose nonwoven membrane exhibits remarkably enhanced migration of lithium ions, which is favorable for the improvement of the battery performance.

The interfacial compatibility of a separator with lithium metal also plays an important role in the battery performance. The interfacial resistance between liquid electrolyte-soaked FS fibrous cellulose membrane with lithium electrode was evaluated through measuring EIS spectra of a symmetric Li/ liquid electrolyte-soaked membrane/Li cell. In the EIS spectra (Fig. 7), the diameter of the semicircle at the intermediate frequency region represents the interfacial resistance between the liquid electrolyte-soaked membrane and the lithium metal. It can be observed that the interfacial resistance of liquid electrolyte-soaked cellulose fibrous membrane is 200 Ω, while that of the PP separator is 400 Ω, which is consistent with the literature (Yanilmaz et al. 2014). Obviously, FS cellulose nonwoven fibrous membranes exhibit a lower interfacial resistance, indicating better interfacial characteristics when used as LIB separator. The higher electrolyte uptake capacity of FS fibrous cellulose nonwoven membrane is favorable for the penetration of electrolyte, and facilitates the migration
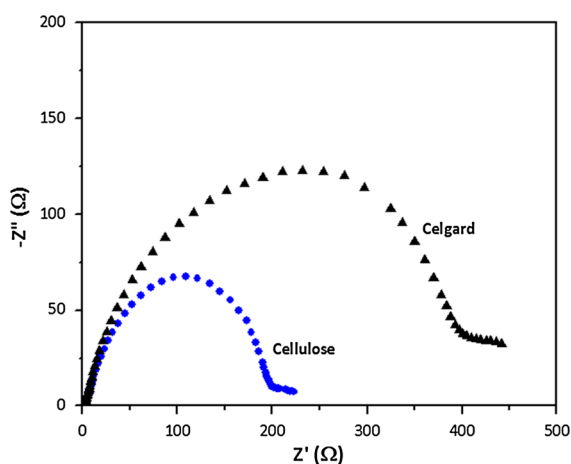
of lithium ions, resulting in the decrease of interfacial resistance.

The separator must be chemically and electrochemically stable towards the electrolyte, especially under the highly oxidative environments (Cai et al. 2012; Sirisopanaporn et al. 2009; Zhang 2007). Therefore, the electrochemical stability of separators within the operating voltage range of battery systems is another important aspect for high battery performance. Linear sweep voltammetry was used to evaluate the electrochemical stability window of liquid electrolyte-soaked membrane using stainless steel as the working electrode and lithium metal as the reference electrode. Figure 8 shows the linear sweep voltammogram of liquid electrolyte-soaked FS fibrous cellulose membrane and compares with that of liquid electrolyte-soaked PP separator. The voltage corresponding to the onset of a rapid increase in the current indicates the electrochemical stability limit of the electrolyte-soaked membranes (Cheruvally et al. 2007; Jung et al. 2009; Li et al. 2007). It can be seen that the electrolyte with the PP separator decomposes at about 4.3 V, which is in good accordance with a previous report (Yanilmaz et al. 2014), while FS cellulose nonwoven membrane exhibits anodic oxidation stability up to 4.7 V. This result indicates that the developed cellulose membrane possesses better compatibility with carbonate electrolyte and is expected to be more stable within the operating voltage range than PP separators. Therefore, the developed nonwoven cellulose membrane has promise for potential applications in high-power LIBs, given
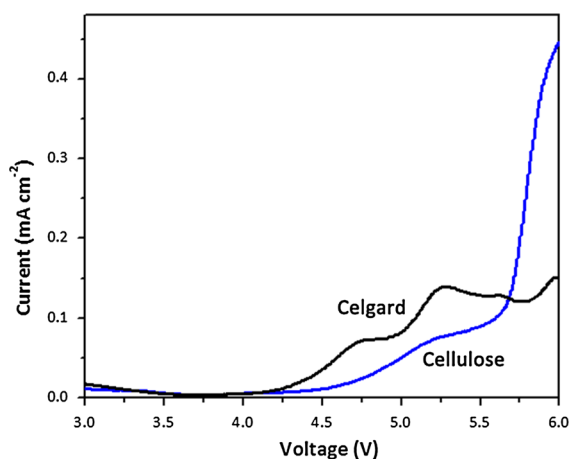

Fig. 7 Electrochemical impedance spectra of fibrous cellulose membrane and microporous PP membrane

Fig. 8 Linear sweep voltammograms of liquid electrolyte-soaked nonwoven fibrous cellulose membrane and PP separator at a voltage scan rate of 10 mV s^{-1}

that typical LIBs operate in working potential ranges of 2.5–4.2 V.

Conclusions

Fibrous cellulose membranes were successfully developed by alkaline hydrolysis of CA membranes, which were mass produced by the forcespinning® technique. The morphology, structure, thermo-physical properties, and electrochemical performance of the developed membranes were investigated for application as lithium-ion battery separator. The cellulose membrane with highly-interconnected fibers exhibits a nonwoven three-dimensional network structure, which favors penetration of liquid electrolyte while holding sufficient electrolyte to facilitate fast ionic transportation between two electrodes. Results indicate that the nonwoven cellulose membrane has a high porosity of 76 % and a high electrolyte uptake of 370 %, resulting in a high ionic conductivity of 2.12 S cm^{-1} at room temperature. Moreover, the fibrous cellulose membrane shows excellent thermal stability, lower interfacial resistance and better electrochemical stability when compared with PP separators. Overall, this FS cellulose nonwoven membrane is a promising candidate to be used as separator in high-power LIBs. The presented approach offers a new and feasible pathway to fabricate high-performance LIB separators.

References

Alcoutlabi M, Ji L, Guo B, Li S, Li Y, Zhang S, Toprakci O, Zhang X (2011) Electrospun nanofibers for energy storage. AATCC Rev 11:45–51

Alcoutlabi M, Lee H, Watson JV, Zhang X (2013) Preparation and properties of nanofiber-coated composite membranes as battery separators via electrospinning. J Mater Sci 48:2690–2700. doi:10.1007/s10853-012-7064-0

Arora P, Zhang Z (2004) Battery separators. Chem Rev 104:4419–4462. doi:10.1021/cr020738u

Cai Z, Liu Y, Liu S, Li L, Zhang Y (2012) High performance of lithium-ion polymer battery based on non-aqueous lithiated perfluorinated sulfonic ion-exchange membranes. Energy Environ Sci 5:5690–5693. doi:10.1039/C1EE02708E

Cherian BM, Leao AL, de Souza SF, Manzine Costa LM, de Oliveira GM, Kottaisamy M, Nagarajan ER, Thomas S (2011) Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibers for medical applications. Carbohydr Polym 86:1790–1798. doi:10.1016/j.carbpol.2011.07.009

Cheruvally G, Kim JK, Choi JW, Ahn JH, Shin YJ, Manuel J, Raghavan P, Kim KW, Ahn HJ, Choi DS, Song CE (2007) Electrospun polymer membrane activated with room temperature ionic liquid: novel polymer electrolytes for lithium batteries. J Power Sources 172:863–869. doi:10.1016/j.jpowsour.2007.07.057

Choi SW, Jo SM, Lee WS, Kim YR (2003) An electrospun poly(vinylidene fluoride) nanofibrous membrane and its battery applications. Adv Mater 15:2027–2032. doi:10.1002/adma.200304617

Chun SJ, Choi ES, Lee EH, Kim JH, Lee SY, Lee SY (2012) Eco-friendly cellulose nanofiber paper-derived separator membranes featuring tunable nanoporous network channels for lithium-ion batteries. J Mater Chem 22:16618–16626. doi:10.1039/C2JM32415F

Cui W, Tang D, Gong Z (2013) Electrospun poly(vinylidene fluoride)/poly(methyl methacrylate) grafted TiO$_2$ composite nanofibrous membrane as polymer electrolyte for lithium-ion batteries. J Power Sources 223:206–213. doi:10.1016/j.jpowsour.2012.09.049

Deng H, Zhou X, Wang X, Zhang C, Ding B, Zhang Q, Du Y (2010) Layer-by-layer structured polysaccharides film-coated cellulose nanofibrous mats for cell culture. Carbohydr Polym 80:474–479. doi:10.1016/j.carbpol.2009.12.004

Goodenough JB, Park KS (2013) The Li-ion rechargeable battery: a perspective. J Am Chem Soc 135:1167–1176. doi:10.1021/ja3091438

Jabbour L, Bongiovanni R, Chaussy D, Gerbaldi C, Beneventi D (2013) Cellulose-based Li-ion batteries: a review. Cellulose 20:1523–1545. doi:10.1007/s10570-013-9973-8

Ji L, Lin Z, Alcoutlabi M, Zhang X (2011) Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries. Energ Environ Sci 4:2682–2699. doi:10.1039/C0EE00699H

Jung HR, Ju DH, Lee WJ, Zhang X, Kotek R (2009) Electrospun hydrophilic fumed silica/polyacrylonitrile nanofiber-based composite electrolyte membranes. Electrochim Acta 54:3630–3637. doi:10.1016/j.electacta.2009.01.039

Kim YJ, Kim HS, Doh CH, Kim SH, Lee SM (2013) Technological potential and issues of polyacrylonitrile based nanofiber non-woven separator for Li-ion rechargeable batteries. J Power Sources 244:196–206. doi:10.1016/j.jpowsour.2013.01.166

Kuribayashi I (1996) Characterization of composite cellulosic separators for rechargeable lithium-ion batteries. J Power Sources 63:87–91. doi:10.1016/S0378-7753(96)02450-0

Lee H, Alcoutlabi M, Watson JV, Zhang X (2013) Electrospun nanofiber-coated separator membranes for lithium-ion rechargeable batteries. J Appl Polym Sci 129:1939–1951. doi:10.1002/app.38894

Lee H, Alcoutlabi M, Toprakci O, Xu G, Watson JV, Zhang X (2014) Preparation and characterization of electrospun nanofiber-coated membrane separators for lithium-ion batteries. J Solid State Electrochem 18:2451–2458. doi:10.1007/s10008-014-2501-4

Li D, Xia Y (2004) Electrospinning of nanofibers: reinventing the wheel? Adv Mater 16:1151–1170. doi:10.1002/adma.200400719

Li X, Cheruvally G, Kim JK, Choi JW, Ahn JH, Kim KW, Ahn HJ (2007) Polymer electrolytes based on an electrospun poly(vinylidene fluoride-*co*-hexafluoropropylene) membrane for lithium batteries. J Power Sources 167:491–498. doi:10.1016/j.jpowsour.2007.02.032

Li H, Wang Z, Chen L, Huang X (2009) Research on advanced materials for Li-ion batteries. Adv Mater 21:4593–4607. doi:10.1002/adma.200901710

Li X, Cao Q, Wang X, Jiang S, Deng H, Wu N (2011) Preparation of poly(vinylidene fluoride)/poly(methyl methacrylate) membranes by novel electrospinning system for lithium ion batteries. J Appl Polym Sci 122:2616–2620. doi:10.1002/app.34401

Liang Y, Cheng S, Zhao J, Zhang C, Sun S, Zhou N, Qiu Y, Zhang X (2013) Heat treatment of electrospun Polyvinylidene fluoride fibrous membrane separators for rechargeable lithium-ion batteries. J Power Sources 240:204–211. doi:10.1016/j.jpowsour.2013.04.019

Liu H, Hsieh YL (2002) Ultrafine fibrous cellulose membranes from electrospinning of cellulose acetate. J Polym Sci Part B: Polym Phys 40:2119–2129. doi:10.1002/polb.10261

Lozano K, Sarkar K (2009) Methods and apparatuses for making superfine fibers. Patent 20090280325 A1, USA

Ma Z, Kotaki M, Ramakrishna S (2005) Electrospun cellulose nanofiber as affinity membrane. J Membr Sci 265:115–123. doi:10.1016/j.memsci.2005.04.044

Manthiram A, Vadivel Murugan A, Sarkara A, Muraliganth T (2008) Nanostructured electrode materials for electrochemical energy storage and conversion. Energy Environ Sci 1:621–638. doi:10.1039/B811802G

Orendorff CJ, Lambert TN, Chavez CA, Bencomo M, Fenton KR (2013) Polyester separators for lithium-ion cells: improving thermal stability and abuse tolerance. Adv Energy Mater 3:314–320. doi:10.1002/aenm.201200292

Padron S, Fuentes AA, Caruntu DI, Lozano K (2013) Experimental study of nanofiber production through forcespinning. J Appl Phys 113:024318. doi:10.1063/1.4769886

Paneva D, Bougard F, Manolova N, Dubois P, Rashkov I (2008) Novel electrospun poly(ε-caprolactone)-based bicomponent nanofibers possessing surface enriched in tertiary amino groups. Eur Polym J 44:566–578. doi:10.1016/j.eurpolymj.2008.01.010

Prasanth R, Shubha N, Hng HH, Srinivasan M (2014) Effect of poly(ethylene oxide) on ionic conductivity and electrochemical properties of poly(vinylidenefluoride) based polymer gel electrolytes prepared by electrospinning for lithium ion batteries. J Power Sources 245:283–291. doi:10.1016/j.jpowsour.2013.05.178

Raghavan B, Soto H, Lozano K (2013) Fabrication of melt spun polypropylene nanofibers by forcespinning. J Eng Fibers Fabr 8(1):52–60

Ramakrishna S, Fujihara K, Teo WE, Lim TC, Ma Z (2005) An introduction to electrospinning and nanofibers technology. World Scientific Publishing Co., Singapore, p 130

Reddy N, Yang Y (2009) Properties and potential applications of natural cellulose fibers from the bark of cotton stalks. Bioresour Technol 100:3563–3569. doi:10.1016/j.biortech.2009.02.047

Ryou MH, Lee YM, Park JK, Choi JW (2011) Mussel-inspired polydopamine-treated polyethylene separators for high-power Li-ion batteries. Adv Mater 23:3066–3070. doi:10.1002/adma.201100303

Sarkar K, Gomez C, Zambrano S, Ramirez M, de Hoyos E, Vasquez H, Lozano K (2010) Electrospinning to forcespinning[TM]. Mater Today 13:12–14. doi:10.1016/S1369-7021(10)70199-1

Sirisopanaporn C, Fernicola A, Scrosati B (2009) New, ionic liquid-based membranes for lithium battery application. J Power Sources 186:490–495. doi:10.1016/j.jpowsour.2008.10.036

Son WK, Youk JH, Lee TS, Park WH (2004a) Electrospinning of ultrafine cellulose acetate fibers: studies of a new solvent system and deacetylation of ultrafine cellulose acetate fibers. J Polym Sci Part B: Polym Phys 42:5–11. doi:10.1002/polb.10668

Son WK, Youk JH, Park WH (2004b) Preparation of ultrafine oxidized cellulose mats via electrospinning. Biomacromolecules 5:197–201. doi:10.1021/bm034312g

Song JY, Wang YY, Wan CC (1999) Review of gel-type polymer electrolytes for lithium-ion batteries. J Power Sources 77:183–197. doi:10.1016/S0378-7753(98)00193-1

Tarascon JM, Armand M (2001) Issues and challenges facing rechargeable lithium batteries. Nature 414:359–367. doi:10.1038/35104644

Vallejos ME, Peresin MS, Rojas OJ (2012) All-cellulose composite fibers obtained by electrospinning dispersions of cellulose acetate and cellulose nanocrystals. J Polym Environ 20:1075–1083. doi:10.1007/s10924-012-0499-1

Wang Y, Zhan H, Hu J, Liang Y, Zeng S (2009) Wet-laid nonwoven fabric for separator of lithium-ion battery. J Power Sources 189:616–619. doi:10.1016/j.jpowsour.2008.09.078

Weng B, Xu F, Lozano K (2014a) Mass production of carbon nanotube-reinforced polyacrylonitrile fine composite fibers. J Appl Polym Sci 131(11):40302. doi:10.1002/app.40302

Weng B, Xu F, Salinas A, Lozano K (2014b) Mass production of carbon nanotube reinforced poly(methyl methacrylate) nonwoven nanofiber mats. Carbon 75:217–226. doi:10.1016/j.carbon.2014.03.056

Weng B, Xu F, Garza G, Alcoutlabi M, Salinas A, Lozano K (2015) The production of carbon nanotube reinforced poly(vinyl) butyral nanofibers by the forcespinning® method. Polym Eng Sci 55(1):81–87. doi:10.1002/pen.23872

Yang M, Hou J (2012) Membranes in lithium ion batteries. Membranes 2:367–383. doi:10.3390/membranes2030367

Yanilmaz M, Diricana M, Zhang X (2014) Evaluation of electrospun SiO₂/nylon 6,6 nanofiber membranes as athermally-stable separator for lithium-ion batteries. Electrochim Acta 133:501–508. doi:10.1016/j.electacta.2014.04.109

Yvonne T, Zhang C, Zhang C, Omollo E, Ncube S (2014) Properties of electrospun PVDF/PMMA/CA membrane as lithium based battery separator. Cellulose 21:2811–2818. doi:10.1007/s10570-014-0296-1

Zhai Y, Wang N, Mao X, Si Y, Yu J, Al-Deyab SS, El-Newehy M, Ding B (2014) Sandwich-structured PVdF/PMIA/PVdF nanofibrous separators with robust mechanical strength and thermal stability for lithium ion batteries. J Mater Chem A 2:14511–14518. doi:10.1039/C4TA02151G

Zhang SS (2007) A review on the separators of liquid electrolyte Li-ion batteries. J Power Sources 164:351–364. doi:10.1016/j.jpowsour.2006.10.065

Zhang J, Yue L, Kong Q, Liu Z, Zhou X, Zhang C, Xu Q, Zhang B, Ding G, Qin B, Duan Y, Wang Q, Yao J, Cui G, Chen L (2014) Sustainable, heat-resistant and flame-retardant cellulose-based composite separator for high-performance lithium ion battery. Sci Rep 4:3935. doi:10.1038/srep03935