Silk fibroin separators: a step towards lithium ion batteries with enhanced sustainability

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ABSTRACT: Battery separators based on silk fibroin (SF) have been prepared aiming at improving the environmental issues of lithium-ion batteries. SF materials with three different morphologies were produced: membrane films (SF-F), sponges prepared by lyophilization (SF-L) and electrospun membranes (SF-E). The latter materials presented a suitable porous three-dimensional microstructure and were soaked with 1 M LiPF_6 electrolyte. The ionic conductivity for SF-L and SF-E were 1.00 and 0.32 $\text{mS}\cdot\text{cm}^{-1}$ at 20 °C, respectively. A correlation between the fraction of β -sheet conformations and the ionic conductivity was observed. The electrochemical performance of the SF-based materials was evaluated by incorporating them in cathodic half-cells with C-LiFePO_4 . The discharge capacity of SF-L and SF-E were 126 and 108 $\text{mAh}\cdot\text{g}^{-1}$, respectively, at C/2-rate, and 99 and 54 $\text{mAh}\cdot\text{g}^{-1}$, respectively, at 2C-rate. Furthermore, the capacity retention and capacity fade of the SF-L membrane after 50 cycles at the 2C-rate were 72 and 5 %, respectively. These electrochemical results show that a high percentage of β -sheet conformations was of prime importance to guarantee excellent cycling performance. This work demonstrates that SF-based membranes are appropriate separators for the production of environmentally friendlier lithium ion batteries.

1. INTRODUCTION

Lithium-ion batteries (LIBs) are one of the most relevant existent energy-storage technologies, commonly used in portable electronic devices, such as laptops and mobile phones, among others. Moreover, they are strongly being improved targeting their use in terrestrial transportation applications, including passenger vehicles, such as electric vehicles ¹⁻³.

These batteries offer a number of very attractive features. Apart from being light and cheap, they exhibit high energy density as other post-LIBs systems (including lithium metal batteries and lithium-sulphur batteries, among others) and power, long cycle life and no memory effect ⁴⁻⁵. One of the major concerns in the area of energy storage is to produce sustainable and secure systems. Several technical issues of lithium-ion batteries still need further progress to further reduce their environmental impact and improve safety. With respect to those issues, the separator membrane with traditional organic liquid electrolytes plays a key role considering security and environmental concerns, including its potential risk of explosion caused by short circuit ⁶⁻⁷.

The separator is the component placed between the two battery electrodes and its main function is to serve as a medium for the transfer of ions. It should exhibit good mechanical and thermal stability and be an electrical insulator with good ionic conductivity ⁸. Typically, the separator comprises a polymer membrane soaked in the electrolyte solution, i.e., a liquid electrolyte, a solvent or mixture of solvents where the lithium salts are dissolved in ⁹⁻¹⁰. The properties of the separator membrane are influenced by different parameters, the most important being the degree of porosity, the average pore size, the tortuosity and the thickness ⁸. The most widely used polymers for the development of separator membranes are poly(propylene) (PP) ¹¹, poly(ethylene oxide) (PEO) ¹² and poly(vinylidene fluoride) (PVDF) ¹³⁻¹⁵ and their copolymers. Natural polymers, such as cellulose ¹⁶ and lignin ¹⁷, are also beginning to be explored in this context.

Considering the beneficial environmental impact that will result from the suppression of the use of synthetic polymers in the composition of separator membranes, it is highly desirable to replace them by natural polymers, while maintaining the excellent battery performance provided by the synthetic counterparts.

Silk is considered to be one of the four most important available natural fibers ¹⁸. It is produced by arthropods, such as silkworms or spiders, scorpions, mites, bees and flies. The most extensively produced silk is that spun from the silkworm of the domesticated *Bombyx mori* moth ¹⁹. The thread core of silkworm silk fibers is composed of a fibrous protein named fibroin which is surrounded by a glue-like protein named sericin that maintains the fibers together. Silk fibroin (SF) is an aqueous insoluble protein with more than 5000 amino acids and large molecular weight (200 – 350 kDa or more). SF possess intrinsic features, including excellent mechanical properties, self-assembly, non-toxicity or biodegradability, that largely exceed those of many polymers, either natural or synthetic ¹⁹. This unique biopolymer is largely known for its use in the textile and healthcare sectors (e.g., as suture). In the last decade, silk has been successfully processed in innovative ways, and explored its application biomedical field, explaining why silk research is at present essentially focused on this domain application ²⁰. However, it has been recognized in the last few years that reconstituted SF is extremely attractive for other technological areas, such as of optics, photonics, and electronics ²¹⁻²³. In the field of solid state electrochemistry, the potential of SF for electrochemical devices has begun to be explored and a few successful examples of devices including SF have been introduced in the last three years. Romero et al ²⁴ incorporated interpenetrating networks made of SF and poly(pyrrole) (PPy) in the design of electrochemical actuators able to operate in a biologically environment and generate forces comparable to those of natural muscles (> 0.1 MPa), and stable to repeated actuation. Hou et al.²⁵ reported hierarchical porous

nitrogen-doped carbon nanosheets derived from biomass-derived natural silk with excellent characteristics for applications in the hybrid energy storage sector and in the area of renewable delivery devices with high power and energy density. Some of us ²³ developed green SF-based electrolytes exhibiting exceptional filmogenic properties, very high transparency, and suitable adhesion to glass substrates, which were employed in the fabrication of electrochromic devices (ECDs) with particularly good performance in terms of switching speed, cycling stability and coloration efficiency. The produced EC's were stable up to 5160 cycles, with a switching speed of about 15 s, a coloration efficiency up to 53.1 m²C⁻¹, and an optical modulation up to 5.5%. Jia et al. ²⁶ synthesized a partially biodegradable SF-PPy film cathode for a Mg-air bioelectric battery (biobattery) displaying a discharge capacity of 3.79 mAhcm⁻² at a current of 10 mAcm⁻² at room temperature, and delivering a specific energy density of about 4.70 mWhcm⁻². Very recently Jia et al. ²⁷ fabricated a transient (biodegradable) thin-film Mg battery, encapsulated in SF and containing an electrolyte composed of SF and the choline nitrate ionic liquid. The battery offered a specific capacity of 0.06 mAh cm⁻² and its enzymatic degradation occurred over 45 days in the buffered protease XIV solution.

In the present work we demonstrate for the first time the potential of SF as environmental friendly separator for lithium ion batteries, thus enlarging the number of applications of SF in energy storage devices. SF was processed as a film membrane by solvent casting, as a sponge by lyophilization and a fibrous membrane by electrospinning. The cycling performance of the as-produced battery separators was analyzed in depth, and their physical-chemical properties were characterized in parallel.

2. EXPERIMENTAL

2.1. Materials

Bombyx mori cocoons were supplied by APPACDM from Castelo Branco (Portugal). Sodium carbonate (Na_2CO_3 , $\geq 99.5\%$), lithium bromide (LiBr , $\geq 99\%$), formic acid and calcium chloride (CaCl_2) were supplied by Sigma-Aldrich and used as received. Cellulose dialysis membranes (molecular-weight cut-off of 12.000–14.000 Da) were purchased from Medicell, International Ltd. All aqueous solutions were prepared using Millipore-Q water. Poly(vinylidene fluoride) (PVDF, Solef 5130, Solvay), C-LiFePO₄ (LFP, Phostech Lithium), carbon black (Super P-C45, Timcal Graphite & Carbon), N,N'-dimethylpropyleneurea (DMPU, LaborSpirit), and 1M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC)-dimethyl carbonate (DMC) 1:1 vol/vol solution (Solvionic) were used as received.

2.2. SF degumming

Degumming is the process of removing sericin from silk fibers to obtain pure SF. *Bombyx mori* cocoons were cut into small pieces and degummed by boiling them for 30 min in a 0.02 M Na_2CO_3 solution. After that, the fibers were rinsed several times with distilled water, squeezed out to remove the excess water, and finally dried overnight in a fume hood. The obtained fibers were used in the following procedures.

2.3. Preparation of the SF aqueous solution

The SF aqueous solution was prepared according to the procedure reported elsewhere²⁸ with some minor modifications. Briefly, fibers were dissolved in a 9.3 M LiBr solution at 60 °C for 4 h. The solution was subsequently dialyzed against ultrapure water until complete salt removal using cellulose dialysis tubing. The efficiency of the dialysis process was monitored by conductivity measurements. In order to remove impurities, SF aqueous solution was centrifuged twice at 8000 r. p. m., at 4 °C for 20 min. The final

concentration of SF (6.0 % w/v) was determined by measuring the dry weight of the solution. The as-prepared SF solution was stored at 4 °C until further use.

2.4.SF samples

To prepare the SF samples three different techniques were adopted: solvent-casting, lyophilization (L) and electrospinning (E). The resulting materials were produced as a film (SF-F), a three-dimensional (3D) sponge scaffold (SF-L) and a 3D fibrous scaffold (SF-E), respectively.

SF-F: The SF aqueous solution was cast onto poly(propylene) petri dishes and then drying it in a fume cupboard at room temperature during 72 h. The average thickness of the prepared films was $200 \pm 30 \mu\text{m}$.

SF-E: Degummed SF fibers were first dissolved in a 0.2 M CaCl_2 formic acid solution at room temperature for 1 h. A film was prepared by casting this solution onto PP petri dishes and then drying it in a fume cupboard at room temperature during 24 h. CaCl_2 was removed from the film by immersion in water for 2 days. Water was changed four times per day. The complete removal of the salt was monitored by conductivity measurements. The as-prepared SF films were then dried in a fume cupboard at room temperature during 24 h and used to prepare a 8 wt.% SF formic acid solution. This solution was drawn into a plastic syringe connected to a flux regulator. After an optimization process, a high voltage (15 kV) was applied between the syringe needle (0.5 mm inner diameter) and an aluminum foil, where the electrospun fibres were collected, in the form of membranes with an average thickness of $13 \pm 3 \mu\text{m}$. A flow rate of 0.5 mL.h^{-1} and a 15 cm needle-collector distance were used.

SF-L: The SF aqueous solution was poured into a cylindrically shaped container and frozen at $-20 \text{ }^\circ\text{C}$ (overnight) and $-80 \text{ }^\circ\text{C}$ (6 h) prior to the lyophilization ($-1.0 \times 10^{-3} \text{ mbar}$,

−86 °C). Lyophilization was performed in a Christ Alpha 2-4 LD Plus freeze dryer. Slices with an average thickness of $206 \pm 25 \mu\text{m}$ were cut with a scalpel.

2.5.Characterization techniques

Samples morphology were studied by scanning electron microscopy (SEM) using a FEI Nova 200 (FEG/SEM).

Attenuated total reflection Fourier Transform infrared spectroscopy (ATR/FTIR) spectra were obtained with a Raffinity-IS Fourier Transform Infrared Spectrophotometer (Shimadzu, Izasa Scientific), resorting to an ATR accessory with a diamond crystal. The spectra were collected in the $4000\text{--}400 \text{ cm}^{-1}$ range by averaging 64 scans at a resolution of 2 cm^{-1} . Band deconvolution was performed using the residuals procedure offered by the PeakFit software ⁶. More details about this procedure can be found in ²³ in which Gaussian shapes were assumed and band frequency, bandwidth and intensity were varied.

Thermal properties of the samples were determined by differential scanning calorimetry, DSC, (Mettler Toledo DSC 821e). The thermograms were acquired from 0 to 350 °C, at a heating rate of 10 °C/min under argon purge in aluminum crucibles of 40 mL.

The ionic conductivity (σ_i) of the SF separators (film, 3D sponge scaffold and 3D fibrous scaffold) was measured using an Autolab PGSTAT-12 (Eco Chemie). The three SF samples filled with the liquid electrolyte (1 M LiPF₆ in EC/DMC solution) were placed between two gold blocking electrodes and complex impedance spectroscopy measurements were carried out at frequencies between 500 mHz and 65 kHz with an amplitude of 10 mV at room temperature. The ionic conductivity of the samples was determined by:

$$\sigma_i = \frac{d}{R_b \times A} \quad (1)$$

where d is the thickness, R_b is the bulk resistance and A is the area of the sample.

2.6. Degree of porosity

The degree of porosity of the SF separators was measured by the pycnometer method and calculated using the following relation:

$$porosity = \frac{W_2 - W_3 - W_s}{W_1 - W_3} \quad (2)$$

where W_s is the mass of the sample, and W_1 , W_2 and W_3 are the weight of the pycnometer filled with ethanol, the weight after placing the sample in the pycnometer with additional ethanol to complete the volume and the weight after removing the sample from the pycnometer, respectively. The value of the degree of porosity of each SF separator was obtained as the average of the measurements performed in three different samples.

2.7. Electrolyte uptake value

The uptake value was obtained by immersing the SF separators into the liquid electrolyte, and evaluated using the following expression:

$$uptake = \frac{m_i - m_0}{m_0} \times 100 \quad (3)$$

where m_0 is the mass of the dry SF separator and m_i is the mass of the SF separator after immersion in the liquid electrolyte.

2.8. Preparation and testing of cathode electrode and half-cell

The preparation of the LFP electrode is described in ³⁰ based on the mixing of C-LiFePO₄ (LFP), carbon black (Super P) and the PVDF binder in DMPU solvent.

Li/LFP half-cells into a Swagelok type were fabricated and assembled in a home-made Ar-filled glove box. The half-cells contained lithium metallic as counter/reference

electrode, LFP electrode film as working electrode and the different SF separators or a commercial separator (Glass fiber membrane) soaked with the electrolyte (1M LiPF₆ in EC-DMC) as separator. Galvanostatic measurements from 2.5 to 4.2 V at different scan rates (C/5 to 5C, C = 170 mA g⁻¹) were carried out in the Li/LFP half-cell with a Landt CT2001A Instrument. Electrochemical impedance spectroscopy was performed in the Li/LFP half-cells before and after cycling with an Autolab PGSTAT12 instrument at 10 mV between 1 MHz to 10 mHz.

3. RESULTS AND DISCUSSION

3.1. Morphology, polymer phase and thermal properties of the SF separators

The SF-F sample prepared by solvent casting exhibited a non-porous texture (see Fig. S1 in the supporting information). The lack of porosity demonstrated that SF-F could not adsorb and retain the liquid electrolyte and thus play the role of battery separator. As a consequence, this material was discarded from subsequent studies. In contrast, the SEM images of the surface and cross-section of the SF-E and SF-L samples reveal the presence of highly interconnected porous structures with distinct morphology. As expected, SF-E was produced as a 3D scaffold composed of thin fibers with an average diameter of 256 ± 50 nm (Figures 1a) and 1b)). This sort of 3D structure, characterized by high surface area to volume ratios and high porosity, is very attractive for application as battery separator, as it enables fast penetration of a significant amount of the guest electrolyte, an essential requirement to guarantee high ionic conductivity³¹.

Figure 1. SEM images of the SF-E ((a) surface and b) cross-section) and SF-L ((c) surface and d) cross-section) separators.

Figures 1c) and 1d) show that SF-L has a sponge-like 3D structure made of interconnected pores with average size of $\sim 150 \mu\text{m}$ uniformly distributed along the surface (Figure 1c) and cross-section (Figure 1d). The higher magnification image of Figure 1c) allows inferring that two types of open pores coexist in this scaffold: pores with irregular shape and a diameter of $\sim 100 \mu\text{m}$, and smaller pores (diameter of $\sim 50 \mu\text{m}$) circularly shaped. The various conformational arrangements present in the SF chains of the prepared materials were evaluated through the analysis of the ATR/FTIR spectra (Figure S2 of the Supporting Information). The results of the curve-fitting performed in the amide I region and the integrated area fraction of the resolved components are represented in Figures 2a) and 2b), respectively, for each sample.

SF contains three crystalline polymorphs, so-called silk I, II, and III, which are usually considered as the main protein secondary structures³²⁻³³. Silk I represents a metastable state between a partially ordered α -helix and the β -sheet structures, silk II is an antiparallel β -sheet structure and silk III is formed at air-liquid interfaces³³⁻³⁴. The ordered β -sheets of silk II, the most stable structures³³, are typically found in the silk fibers as raw material. In the case of regenerated SF, the polymer chains typically assume random conformations, which can be transformed into highly stable conformations through physical or chemical treatments³⁵. The secondary structure of SF is usually determined by an in-depth inspection of the amide I band, a characteristic absorption mode of the peptide backbone (Figure 2a)). This mode is essentially associated with the carbonyl (C=O) stretching vibration and is particularly sensitive to the specificity and magnitude of the hydrogen bonds. It is the most conformation-sensitive band to changes of the SF chains^{23, 33, 36}. To deduce the fraction of the various conformations present in the SF-F, SF-E and SF-L samples, the amide I band of the ATR/FTIR spectra were deconvoluted based on the attribution proposed by Hu et al.³³. Absorption bands in the frequency range from 1615 to 1605 cm^{-1} are assigned to side chains, those from 1637 to 1616 cm^{-1} and 1705 to 1695 cm^{-1} are ascribed to ordered β -sheets, those in the 1655-1638 cm^{-1} range correspond to random coils, those in the 1662-1656 cm^{-1} range are assigned to α -helices, and those between 1696 and 1663 cm^{-1} are attributed to turns^{23, 33}.

Figure 2. a) Results of the curve-fitting performed in the amide I region of the ATR/FTIR spectra of the separators. b) Integral area fraction of the spectral components resolved in spectral region. The different contributions to the amide I envelope are marked as random coil (R), β -sheets (B), α -helices (A), turns (T), and side chains (SC).

The profile of the amide I band of SF-F displays an intensity maximum at 1639 cm^{-1} (random coil range) and a shoulder at 1622 cm^{-1} (β -sheet range) (Figure 2a)). Figure 2b) reveals that in this material the proportion of random coil and ordered β -sheet conformations is practically the same (32 versus 29 %, respectively). The amide I band of SF-E has an intensity maximum at 1648 cm^{-1} (random coil range). Figure 2b) demonstrates that the dominant conformations of this sample are the random coils and turns. In the case of SF-L, the intensity maximum of the amide I band is downshifted to 1627 cm^{-1} (β -sheet range) and a shoulder is seen at 1643 cm^{-1} (random coil range). In

this sample 37 % of the SF chains adopt β -sheet conformations and 26 % occur as random coils. The ATR/FTIR results unequivocally confirm that the processing method adopted to produce the three SF-based materials affected substantially the relative proportion of the chain conformations. Also, the ATR/FT-IR spectrum of SF-L after immersion in the electrolyte solution indicate that the relative proportion of this conformation (β -sheet) increases in ~7% (see figure S2 (b) of supplementary information)

The thermal properties of the SF-based samples were determined by DSC. The DSC thermograms of the SF-based materials shown in Figure 3 demonstrate that all the samples exhibit similar thermal behavior. The broad endothermic peak, centered at 64, 67 and 76 °C in the DSC curves of SF-F, SF-E and SF-L, respectively, is associated with the release of water and/or solvent, since water molecules strongly bind to silks and remain after thermal treatment³⁷. The glass transition, as well as crystallization and degradation peaks, are observed at characteristic temperatures of the SF-based materials³⁷⁻⁴¹. The glass transition temperature (T_g) occurs around 180, 169 and 180 °C for SF-F, SF-E and SF-L, respectively. In addition, an exothermic peak attributed to β -sheet crystallization is evident at 214 °C (crystallization enthalpy (ΔH) = 10.9 J g⁻¹) for SF-F, at 197 °C (ΔH = 9.5 J g⁻¹) for SF-E and, at 215 °C (ΔH = 21.4 J g⁻¹) SF-L. These values are in good agreement with previous reports^{37, 40-41}. The enthalpy value associated with this thermal event increases with the increase of the fraction of β -sheet conformations pointed out by FTIR/ATR (Figure 2). Beyond this event all the SF-based materials immediately started to degrade, as substantiated by the presence of endotherms peaking at roughly the same temperature: 283, 282 and 286 °C for SF-F, SF-E, SF-L, respectively. Considering the FTIR/ATR (Figure 2) and DSC (Figure 3) data, it is concluded that the content of ordered regions follows the order SF-E < SF-F < SF-L.

Figure 3. DSC curves of SF-F (black line), SF-L (red line) and SF-E (blue line) separators.

3.2. Degree of porosity, electrolyte uptake and ionic conductivity of the membranes

The degree of porosity and the electrolyte uptake values determined for the 3D porous scaffolds, i.e., SF-E and SF-L, may be deduced from Figure 4a). The differences observed can only be explained in terms of morphological arguments (Figure 1). The degree of porosity of SF-E (68 %) is slightly higher than that of SF-L (60%) but lower when compared to commercial separators (see table S1 of supplementary information). This trend is correlated with that of the uptake value (1738 and 1111 %, respectively, after 15 s of immersion in the electrolyte).

It must be noted that these values are associated, not only with the extent/type of the micropores, but also with the SF/electrolyte interactions. In this respect, the accessibility and interconnectivity of the pores in the SF-E sample allows accommodating a larger amount of electrolyte for a similar degree of porosity due to its larger swelling

ability/capacity. It is known that the dissolution of SF-based materials in organic and mixed aqueous-organic salt systems depends on the salt concentration and on the relative fraction of α -helices and β -sheets formed ⁴². The prevalence of one or another SF conformation depends on the organic solvent used ⁴². It was demonstrated that the swelling behavior of SF is influenced by restriction of β -sheet networks ⁴³. The uptake process is illustrated in Figure 4b) for SF-E. This behavior is similar to that of the SF-L sample. After the adsorption of the electrolyte, the color of the sample changed from white to transparent as a result of gelation. The process took place without mechanical fragmentation and consequently the sample remained mechanically stable (Figure 4b)).

Figure 4. a) Degree of porosity and uptake value of SF-E and SF-L separators after immersion in the electrolyte. b) Swelling process of SF-E after electrolyte uptake.

The room temperature ionic conductivity of the SF-E and SF-L separators was evaluated by complex impedance spectroscopy (Figure 5).

Figure 5. Nyquist plots at 25 °C for the SF-L (red symbols) and SF-E (black symbols) separators. The lines drawn are guides for the eyes.

The Nyquist plot of Figure 5 for both SF-based membranes is characterized by a straight line in the whole frequency range ⁴⁴, which is attributed to the high uptake value and represents the electrode/electrolyte double layer capacitance behavior ⁴⁵. The ionic conductivity value was calculated using equation 1 and the resistance of both samples was obtained from the intercept with the Z' axis. The ionic conductivity values measured for SF-E and SF-L were 0.32 and 1.00 mS.cm⁻¹, respectively, which is lower when compared to commercial separators (see figure S3 of supplementary information). As the degree of porosity is similar in both cases and the electrolyte uptake is larger for the SF-E sample, we believe that the higher ionic conductivity of SF-L can only be related to different β -sheet conformation content, which is higher for SF-L. Thus, the planar conformations of the polymer β -sheets apparently promotes higher ionic conductivity due to the interaction established between the lithium ions and the dipole moments formed in the crystalline regions as a result of the extensive hydrogen bonding interactions the

peptide chains of SF are involved in ⁴⁶. This issue will be discussed in more detail below. It must be emphasized that both samples display ionic conductivities higher than 0.1 mS.cm⁻¹ which is the minimum ionic conductivity value required for lithium ion battery separator applications ⁴⁷.

Two other important parameters to characterize battery separators are the tortuosity (τ) value, that represents the ratio of the mean effective capillary length to separator thickness, and describes the average pore connectivity of the separator ³¹, and the MacMullin number (N_M). These parameters are calculated, respectively, using the following equations ⁴⁸⁻⁴⁹:

$$N_M = \frac{\sigma_0}{\sigma_{eff}} \quad (4)$$

$$\text{where } \sigma_{eff} = \sigma_0 \frac{\phi}{\tau^2} \quad (5)$$

where σ_{eff} is the ionic conductivity of the separator and electrolyte pair, σ_0 is the ionic conductivity of the pure liquid electrolyte and ϕ is the porosity of the separator.

The values found were 5 and 3 for SF-E and SF-L, respectively, thus very similar, indicating high pore connectivity that results in faster ion transport properties. The N_m values are 36 for SF-E and 12 for SF-L, indicating that SF-L shows a relatively lower resistivity with respect to SF-E and therefore that it should exhibit a better battery cycling performance.

3.3. Battery performance

The electrochemical performance of SF-E and SF-L as battery separators was investigated in Li/C-LiFePO₄ half cells fabricated using C-LiFePO₄ as a cathode and lithium foil as counter and reference electrodes.

Figure 6 shows the electrochemical performance of the different half cells for scan rates from C/5 to 5C. Figure 6a reproduces the charge–discharge profile of the half-cell with the SF-L separator in the 5th cycle, which is characterized by two voltage pseudoplateaus that represent the reversible charge (lithium removal)/discharge (lithium insertion) process, i.e., the Fe²⁺/Fe³⁺ redox reaction of the C–LiFePO₄ spinel, independently of the C-rate⁵⁰. Figure 6a also reveals that the cycling profiles decrease with increasing C-rates except for the C/5-rate.

This behavior is ascribed to the ohmic polarization effect and the lower discharge value at C/5 is due to the formation of the solid electrolyte interface (SEI) during the first cycles^{45, 51}. For the SF-L separator (Figure 6a)), the discharge capacity value is 107, 126, 114, 98 and 38 mAh.g⁻¹ at rates of C/5, C/2, C, 2C and 5C, respectively, indicating excellent electrochemical values at C-rates above C.

Figure 6b) shows the 5th charge–discharge curves at C/2 and 2C-rates for SF-E and SF-L. The voltage profile is very similar for both materials, the discharge capacity of SF-E and SF-L being 108 and 126 mAh.g⁻¹ at C/2-rate and 54 and 99 mAh.g⁻¹ at 2C-rate, respectively. Further, the rate performance for both SF separators is depicted in Figure 6c, demonstrating a better rate capability for the SF-L separator membrane, due to the higher discharge capacity at the various C-rates. In addition, Figure 6c) also shows that in terms of cycling performance, it is very stable as a function of the cycling number, independently of the C-rate. The excellent rate capacity of the SF-L separator is attributed to its higher ionic conductivity value, which is correlated in turn with a high fraction of β -sheet conformations, as shown in Figure 8, and also to a decrease in the interfacial

resistance between separator and electrodes related to the compact morphology of this sample ⁵².

Figure 6. Charge/discharge profiles for the SF-L separator (a). C/2 and 2C rate (b), rate performance as a function of cycle number (c) and capacity retention (d) during the discharge process for SF-E and SF-L separators.

The capacity retention in the discharge process (capacity normalized with respect to the C/5 rate), as a function of C-rate for both separator membranes is represented in Figure 6d). A progressive decrease of the capacity retention value with increasing C-rate is observed except for SF-L at C-rates below C, this behavior being attributed to a diffusion phenomenon taking place within the cathode electrode and separator ⁵³. Moreover, the stable SEI layer of SF-L results in good cycling performance due steady ionic transportation for high C-rate ⁵⁴.

The degree of porosity, electrolyte absorption and degree of crystallinity of the two separators are practically the same, being nevertheless the ionic conductivity the main parameters with relevant variations.

Typically, in polymer electrolytes the ionic conductivity (migration and transport of ions) is determined by large-scale segmental movements of the polymer chains in the amorphous regions ⁵⁵. In the present case, the presence of crystalline regions in the separator scaffold was beneficial, as it enhanced ion movement mobility as a result of the efficient interaction established between the lithium ions and the dipole moments of the anti-parallel β -sheet structure (Figure 7), explaining the higher ionic conductivity exhibited by the SF-L with respect to SF-E.

Figure 7. Schematic representation of the interaction between lithium ions and the dipole moments (red arrows) of the β -sheet structure of the SF-based materials.

As already pointed out, SF has a semi-crystalline fibrillar character. Its ordered regions correspond to an anti-parallel β -sheet structure with a monoclinic unit cell, as illustrated in Figure 7⁵⁶. This β -sheet structure gives rise to an internal polarization which is responsible for the piezoelectric effect of SF⁵⁷. In fact, it was demonstrated that β -sheet crystallinity is one of the pre-requisites that must be fulfilled to guarantee a strong piezoelectric effect in silk⁵⁷. Clearly, in the present case this local electric field facilitated motion of the lithium ions⁵⁸ via the interaction of the charge carriers with the dipole moments of the β -sheets. This efficient β -sheet assisted hopping mechanism enhanced ion migration through the separator, leading to the increase of ionic conductivity⁵⁹.

Figure 8a) shows the cycling performance and coulombic efficiency for SF-L at C and 2C-rate during 50 cycles, in which good cycling stability is observed for all cycles. Furthermore, the discharge capacity value after 50 cycles at 2C is 81 mAh.g⁻¹, corresponding to 72% of the capacity retention. Also for this sample, Figure 8a shows that the coulombic efficiency (CE) is about 100 % and remained stable upon cycling,

related to the reversibility of the process, i.e, the movement of active species through the separator.

Figure 8b) shows the cycling performance of the SF-E and SF-L membranes at 2C for over 50 cycles and its comparison with a glass microfibre separator. After 50 cycles, the discharge capacity values were 81, 53 and 18 mAh.g⁻¹ for SF-L, glass microfibre and SF-E, respectively, indicating the excellent electrochemical performance of the SF-L sample due to its high ionic conductivity.

Figure 8. a) Capacity and coulombic efficiency for the half-cells incorporating SF-L separator when cycled at C and 2C-rates and b) discharge capacity value for over 50 cycles at 2C for SF-E, SF-L and glass fiber commercial membranes.

Table 1 summarizes the electrochemical results of the SF separator membranes after 50 cycles at C and 2C-rate.

Table 1 - Discharge capacity values, capacity fade and capacity retention for the SF membranes at C and 2C-rates.

	SF-L		SF-E	
	C	2C	C	2C
First discharge capacity (± 3) mAh.g ⁻¹	117	85	91	32
50 th cycle discharge capacity (± 3) mAh.g ⁻¹	107	81	80	19
Capacity fade: 2-50 cycles (%)	9	5	12	40
Capacity retention after 50 cycles (%)	95	72	68	16

The SF separator with the best electrochemical performance was SF-L. At 2C-rate (charge and/or discharge process in half an hour) its capacity retention and capacity fade are 72 and 5%, respectively, demonstrating high rate capability. Considering the results of Table 1, we may state that a lithium-ion battery containing SF as separator can cycle at high rates with a very controlled capacity decay with low resistance value (Figure 9).

It is of interest to refer that battery performance for the SF-L separator is similar or even better than those of green polymer membranes, such as lignin ¹⁷, aramid ⁶⁰ and cellulose ⁶¹, used as battery separators, but presents several additional advantages with respect to these polymers, such as piezoelectricity, biocompatibility and degradability effect, exceptional mechanical properties, multiple variety of material formats, etc.

Finally, in order to evaluate the resistance changes of the cathodic half-cells based on the both separators, the ac impedance spectra were obtained before cycling in a freshly assembled cell, (Figure 9a)) and after (Figure 9b)) cycling.

Figure 9. Impedance spectroscopy of the cathodic half-cell incorporating SF-E and SF-L separators: before a) and after b) cycling.

Figure 9 shows the Nyquist spectra with a semicircle in the high frequency region that represents the total resistance (sum of solid electrolyte interface (SEI) resistance and the charge-transfer resistances process) corresponding to the migration of lithium ions between the electrode and electrolyte interface and a straight line in the low frequency regions that represents the diffusion of lithium ions in the active material of the cathode electrode ³⁰.

Figure 9a) shows that the total resistance value of SF-E before cycling was 2000 Ω , a value which is slightly lower than that of SF-L (3375 Ω). After cycling, the resistance value of SF-E and SF-L were 6679 and 3313 Ω , respectively (figure 9b). Thus, the resistance increased after cycling for SF-E as a result of a significant increase of the interfacial resistance leading to reduced lithium ion diffusion. For SF-L, its resistance value remained practically constant, indicating better interface stability which is at the basis of the excellent cycling performance.

4. CONCLUSIONS

New environmentally friendly separators based on SF were prepared by solvent casting, electrospinning and lyophilization.

Porous 3D scaffolds with different porous morphologies, high degree of porosity, excellent thermal stability, and good electrolyte uptake were produced by electrospinning and lyophilization. The ionic conductivity value measured after electrolyte uptake was higher for the SF-based membrane produced by lyophilization (SF-L) than for that fabricated by electrospinning (SF-E). As the degree of porosity is similar and the uptake is higher for the SF-E sample, the higher ionic conductivity exhibited by SF-L is attributed to the higher β -sheet conformation content.

Cathodic half-cells with the SF-L samples exhibited a higher capacity value and enhanced cycling performance than a battery incorporating a commercial separator. After 50 cycles at 2C, the SF-L separator showed a discharge capacity value of 81 mAh.g⁻¹, corresponding to a capacity retention of 72 %. The electrochemical results suggest that the SF-based separators with a high fraction of β -sheet conformations have excellent cycling performance, thus offering excellent prospects for the fabrication of separators of environmentally friendlier and more sustainable lithium-ion batteries.

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Notes

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