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## Electrospun Membranes Based on PVdF-PEO Blends for Lithium Batteries

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Solid polymer electrolytes in lithium batteries have the dual function of electrolyte and separator to hinder lithium dendrite growth that causes hazardous short circuits during repeated charge/discharge cycles. Given the good compatibility between polyvinylidene difluoride (PVdF) and polyethylene oxide (PEO) and with the aim to merge the properties of these two polymers, we prepared and characterized PVdF/PEO membranes that act as separators and as hybrid gel polymer electrolytes when soaked in the liquid electrolyte with lithium salt. The membranes based on the polymer blends were prepared by electrospinning, a technique that yields micro-nanofibrous membranes with high porosity and, hence, huge values of electrolyte uptake. PEO 100,000 and PEO 1,000,000 were used to prepare two blends with PVdF:PEO 90:10 w/w composition. The electrochemical performance of the membranes, which were soaked in 1M LiPF<sub>6</sub> – ethylene carbonate:dimethyl carbonate (1:1 w/w), was evaluated in Li//LiFePO<sub>4</sub> and graphite//LiFePO<sub>4</sub> cells and discussed.

### Introduction

Solid polymer electrolytes (SPEs) in lithium batteries have the dual function of electrolyte and separator to hinder lithium dendrite growth that causes hazardous short circuits during repeated charge/discharge cycles [1-3]. Polyethylene oxide (PEO), together with a lithium salt, would be a promising candidate as SPE for its good electrochemical and mechanical properties, but the low ionic conductivity at room temperature limits its use. In the last years the attention has been focused on gel polymer electrolytes (GPEs), which consist of flexible polymeric matrix as supporting network and a liquid phase containing a lithium salt [2], for the high ionic conductivity at room temperature, good mechanical properties and safety improvements. Given that GPEs also act as separators by preventing physical and electrical contact between electrodes while allowing ions flow, they should be thin, porous and sufficiently strong to withstand the battery assembly process [4, 5]. Recently, research efforts have been devoted to the development of nano-architectures with large surface area to volume ratios and controllable morphologies as anodes, cathodes, separators and electrolytes by electrospinning technology [5-7]. This is a versatile and low-cost technique for fabricating micro or nanofibrous non-woven mats, characterized by high open porosity and high surface area. In separators or in GPEs these properties determine a huge electrolyte uptake [8] and an excellent ionic conductivity. Polyvinylidene difluoride (PVdF) is one of the most studied polymer in order to obtain electrospun membranes

suitable as separators [9], both for its good electrochemical stability and high dielectric constant that allows a great amount of charge carriers. One of PVdF drawbacks is its high melting point, which does not guarantee the shutdown function, namely the ability to shut the battery down when overheating occurs [10, 11]. In this work, a novel strategy is proposed to overcome this limitation by making use of a blend of PVdF with a lower-melting temperature polymer, such as polyethylene oxide (PEO). PEO is also able to coordinate and transport  $\text{Li}^+$  through local relaxation and segmental motion of its chains and, thus, it could improve ionic conductivity. The novelty of this approach is testified by the fact that only two very recent papers dealing with PVdF/PEO blends have been published [12, 13].

We prepared and characterized PVdF/PEO membranes that can act as separators and as hybrid gel polymer electrolytes (HGPEs) when soaked in the liquid electrolyte with lithium salt. The membranes based on PVdF:PEO 90:10 w/w blends were prepared by electrospinning using PEO 100,000 and PEO 1,000,000. Such membranes were soaked in 1M  $\text{LiPF}_6$  – ethylene carbonate : dimethyl carbonate (1:1 w/w) and the electrochemical performance of these HGPEs were investigated in  $\text{Li//LiFePO}_4$  and  $\text{graphite//LiFePO}_4$  cells and discussed on the basis of their physical, mechanical, thermal and morphological properties.

## Experimental

Polyvinylidene difluoride (PVdF, Solvay, Solef 6020,  $M_w$  690'000  $\text{g mol}^{-1}$ ), polyethylene oxide (PEO, Sigma-Aldrich  $M_v$  100'000  $\text{g mol}^{-1}$  and  $M_w$  1'000'000  $\text{g mol}^{-1}$ ) and *N,N*-dimethylformamide (DMF, Sigma-Aldrich) were used as received. A solution of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 w/w) (LP30 Selectilyte, Merck KGaA) was used for electrolyte uptake and electrochemical tests.

The two blends of PVdF:PEO with a 90:10 w/w composition and with PEO with low and high molecular weight are hereinafter named B100 and B1000, respectively. PVdF and PEO were dissolved in DMF at a total concentration of 15% and 10% w/v, for B100 and B1000 and stirred overnight. The electrospinning apparatus was composed of a syringe pump (KDSscientific), a glass syringe, a stainless-steel blunt-ended needle (0.5 mm inner diameter), connected to a high voltage power supply (Spellman, SL 50 P 10/CE/230) and a grounded cylindrical rotating collector (12 cm length, 5 cm diameter, 50 rpm rotation angular speed). The polymer solution was dispensed from the needle, fixed to a support rod and placed 22 cm apart from the collector. The electrospinning process was carried out in a glove box, at room temperature and relative humidity of 40-45%, with 0.4 mL/h solution flow-rate and 20 kV applied voltage. Membranes with thickness in the range of 70-100  $\mu\text{m}$  were obtained. A PVdF membrane was also prepared for comparison by dissolving the polymer in DMF at a concentration of 16% w/v with the same electrospinning parameters but 0.3 mL/h flow rate. Circular membranes (0.785  $\text{cm}^2$ ) were cut by a puncher and some were pressed with a hydraulic E-Z Press (ICL) at 500 psi for 15 min at room temperature. The pressed membranes are indicated as B100p and B1000p. The membranes were dried at 80°C under vacuum for 4h in a Büchi B-585 Kugelrohr in order to remove any trace of residual solvent and humidity. Then, they were transferred in an argon filled MBraun Labmaster SP dry box (< 0.1 ppm  $\text{H}_2\text{O}$ , < 0.1 ppm  $\text{O}_2$ ) for further use.

Fiber morphology was investigated using a Philips 515 Scanning Electron Microscope (SEM) at an accelerating voltage of 15kV. Before SEM analysis, the samples were sputter-coated with gold. Differential Scanning Calorimetry (DSC) measurements

were performed using a calorimeter (TA Instruments Q100 DSC) equipped with the Liquid Nitrogen Cooling System (LNCS) accessory. DSC measurements were conducted in helium atmosphere from -100°C to 250°C with a heating scan rate of 20°C/min. The evaluation of the electrolyte uptake of the membranes was carried out as described in ref. [8]. The resistivity of the electrolyte-soaked membranes was measured by electrochemical impedance spectroscopy (EIS), using a Solartron SI 1255 frequency response analyzer coupled with an EG&G Model 273A PAR potentiostat/galvanostat.

For EIS analysis, symmetrical T-shaped Teflon cells with stainless steel blocking electrodes were assembled with the soaked membranes. The EIS measurements were carried out at different temperatures in a Memmert IPP 200 incubator by applying an AC perturbation of 5 mV with a variable frequency, from 100 kHz to 1 Hz, collecting 10 points per decade. The MacMullin number and the shutdown temperature were evaluated as described in ref. [14].

Electrochemical tests were performed by a VMP multichannel potentiostat/galvanostat (Bio-logic Science Instruments) on Li//LiFePO<sub>4</sub>, Li//Li and graphite//LiFePO<sub>4</sub> cells; metallic lithium was also used as reference electrode. LiFePO<sub>4</sub>-based cathodes contained 90 wt.% LiFePO<sub>4</sub> (Advanced Lithium Electrochemistry Co. Ltd.), 5 wt.% Super P (Erachem) and 5 wt.% PVdF (Kynar HSV 900, Arkema). The commercial graphite electrode (MTI Corporation) had 94.5% active material.

## Results and Discussion

The B100 membranes display fibers having a diameter broad distribution in the range of ca. 300-800 nm (Figure 1a). On the contrary, B1000 membranes exhibit a homogeneous distribution of fiber diameters (~800 nm) (Figure 1b) quite similar to that of PVdF (Figure 1c). The rough surface of the B100 and B1000 fibers could be associated to the hygroscopic nature of PEO, which is responsible for moisture absorption during fiber formation and, being probably connected to a fiber porosity, is beneficial for wettability and electrolyte uptake. Moreover, it could improve the adhesion with electrode surface and the interfacial properties of the separators.

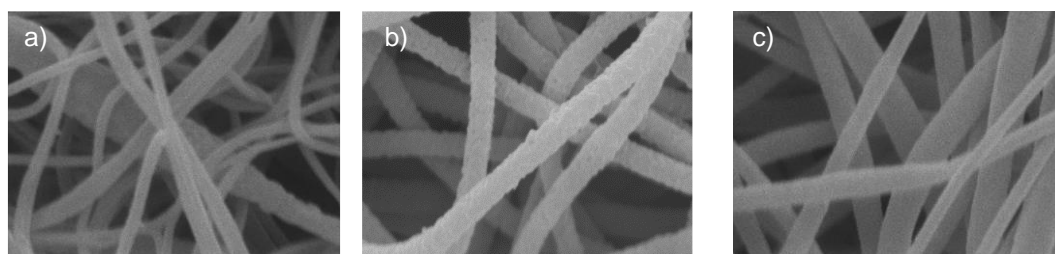


Figure 1. SEM images (9000x) of a) B100, b) B1000 and c) PVdF membranes.

Figure 2 shows the DSC thermograms of B100 and B1000. The two independent melting processes attributable to PEO (~60°C) and PVdF (~170°C) demonstrate that the crystallization processes of PEO and PVdF are independent as well. Indeed, the corresponding melting temperature of PEO100, PEO1000 and PVdF homopolymers are 64°C, 69°C, 168°C, respectively. This result indicates that during the electrospinning co-crystallization processes do not occur, in agreement with previous results [12]. The small melting temperature shift of PVdF and PEO components in the blends, compared to homopolymers, might be attributed to the interactions between ether oxygen of PEO and

fluoride of PVdF. These shifts are more evident in the B1000 DSC curve, probably due to the longer PEO1000 chains, which increase the number of interactions with PVdF.

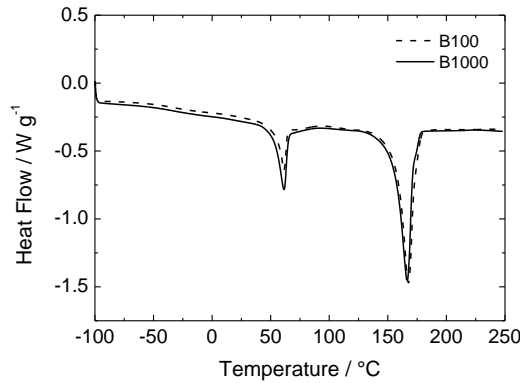


Figure 2. DSC analysis of B1000 and B1000.

Figures 3a and 3b show the behavior of the blends vs. temperature. The presence of PEO in the blends leads to an increase of the ionic conductivity between 30°C and 100°C as evinced by the conductivity plots of the blends compared to that of PVdF reported in Figure 3a. Figure 3b display the results of the shutdown tests on B100 and B1000, where the real part of the impedance ( $Z_{re}$ ) at 1 kHz is plotted vs. temperature. The shutdown process is a safety measure against abnormal rise of temperature, effective only if occurring before thermal runaway, and the U.S. Advanced Battery Consortium (USABC) shutdown temperature requirement for conventional separators is 135°C. The B100 curve shows that the shutdown process, i.e. polymer softening and pore closure, starts at 110°C and ends at about 140°C, with  $Z_{re}$  value increased of two orders of magnitude. By contrast, B1000 shutdown process occurs between 100°C and 140°C, with a growth of resistance of three orders of magnitude. These temperatures are in good agreement with the USABC requirements. Hence, the presence of PEO, blended with PVdF, leads to an improvement in terms of safety, as can be seen by comparing B100 and B1000 to plain PVdF that displays a shutdown temperature of 160°C-180°C. The presence of PVdF in the blend is anyhow important to assure mechanical integrity when shutdown occurs.

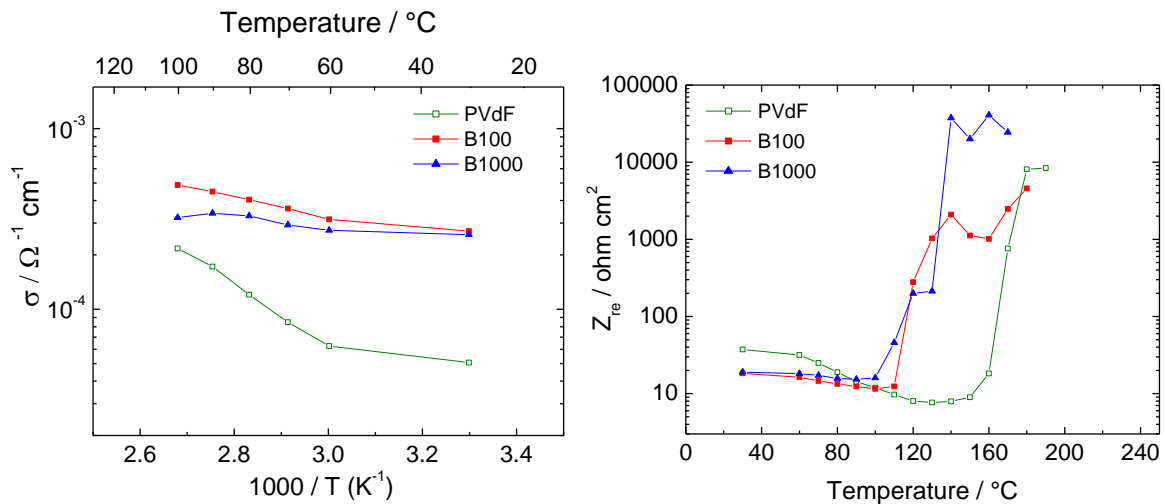


Figure 3. a) Ionic conductivity Arrhenius plot and b)  $Z_{re}$  vs T for shutdown test.

The electrolyte uptake percentages of B100 and B1000 are similar to that of PVdF (530%, 300% and 440%, respectively) and also are the MacMullin numbers (10, 6 and 8, respectively). These data are discussed in ref. [15] where also the mechanical characterization of the blends is reported.

The electrochemical tests, shown in Figures 4a and 4b, were performed on T-type cells with  $\text{LiFePO}_4$  and metal Li by repeated galvanostatic charge/discharge cycles at C/10 and at 1C. Pressed membranes (B100p, 15min at 500psi) have higher initial capacity and a better stability over cycling despite their lower electrolyte uptake and decreased porosity. However, with all the samples we observed a higher capacity fading after the 50th cycle that occurs in parallel to a decrease of coulombic efficiency (from near 100% of the first cycles to 50% at 100th cycle).

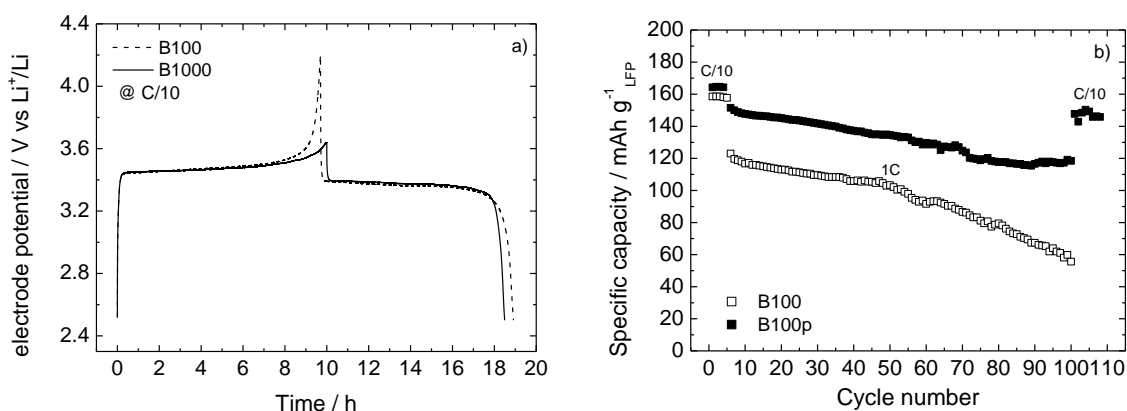


Figure 4. a) Charge/discharge potential profiles at C/10 of the Li// $\text{LiFePO}_4$  cell with B100 and B1000 membranes and b) specific capacity values over cycling at 1C of Li// $\text{LiFePO}_4$  cell with B100 and B100p membranes.

The low coulombic efficiency is due to the occurrence of unwanted chemical and electrochemical reactions of the electrolyte. Given that  $\text{LiFePO}_4$  works inside the stability window of the electrolyte, we argued that the reactivity of Li metal may affect the cell performance. Li anode sustains plating/stripping processes during the charge/discharge of the cell. We proved the uneven electrodeposition of lithium and resulting dendrites growth by applying galvanostatic charge/discharge cycles at different currents (0.050, 0.100, 0.165, 0.500 and 1.000 mA) to a symmetric Li//Li cell. Figure 5 displays the plots of the Li working electrode potential and of the applied current vs. time. It is evident that after two tenths of cycles the solid electrolyte interface (SEI) layer on the Li surface is broken. This determines a lower overpotential (due to the area increase following dendrite formation) and the possibility of the electrolyte to react continuously, provoking Li and electrolyte consumption, gas evolution and other unwanted products formation. Although these membranes are vulnerable to the dendrites because of their high open porosity, dendrites seem not the main problem. Reactive species produced at the electrode surface may retro diffuse through the highly porous separator and react on the opposite electrode. This could also justify the better discharge capacity values of cells with B100p compared to those of cells with B100, both for its lower thickness and for the lower porosity that can hinder the shuttle movement of side products.

A full cell with a graphite anode was assembled to show the effectiveness of these membranes in a Li-ion cell, i.e. in absence of Li metal.

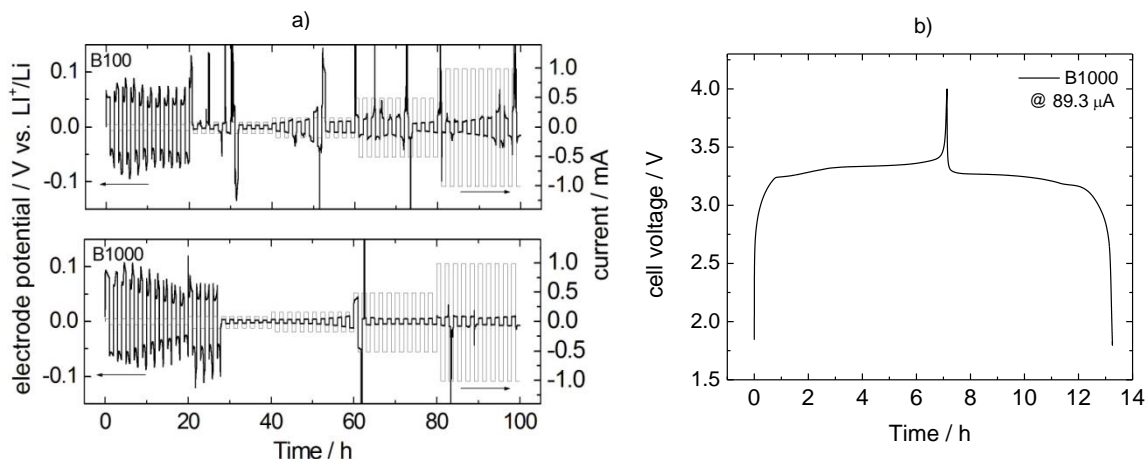


Figure 5. a) Lithium plating/stripping cycles in a Li//Li cell and b) voltage profile of the 2nd cycle of charge/discharge at C/10 of a graphite//LiFePO<sub>4</sub> cell with B1000.

The full cell performs charge/discharge cycles at C/10 in two electrode mode with a good coulombic efficiency as displayed by the cycle in Figure 5b. However, after few cycles, its specific capacity decreases. The reaction of the electrolyte at the negative potentials of the graphite insertion and the related products can be deleterious even in absence of Li metal. Indeed, the occurrence of side reactions may unbalance the cell up to its complete failure. The reason of this high reactivity can reside in the greater amounts of water and moisture that these PEO-based membranes may retain, although they were dried before use. A deeper insight of this aspect is given in ref. [15].

## Conclusions

PVdF/PEO blend membranes were prepared by electrospinning starting from their homopolymers. They ensure increased conductivities, greater electrolyte uptake and higher porosity than polyolefines, all factors that may improve cell performance. Moreover, they are safer than PVdF separators, thanks to the lower shutdown temperature. These separators are promising candidates for Li-ion batteries applications although they need to be further optimized in terms of mechanical properties and purity.

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