Mesoporous poly(vinylidene fluoride-co-trifluoroethylene) membranes for lithium-ion battery separators

C. M. Costa^{1,2,#,*}, M. Kundu^{3,4,#}, J. C. Dias^{1,2}, J. Nunes-Pereira^{1,5}, G. Botelho²,
M. M. Silva², S. Lanceros-Méndez^{6,7,*}

#equal contribution

¹Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

²Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

³Department of Chemistry, SRM University, Kattankulathur, 603203 Tamil Nadu, India

⁴Department of Material Science and Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

⁵C-MAST – Centre for Mechanical and Aerospace Science and Technologies, Universidade da Beira Interior, Rua Marquês d'Ávila e Bolama 6200-001 Covilhã, Portugal

⁶BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain

⁷IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

***Corresponding Authors** Email: C. M. Costa (cmscosta@fisica.uminho.pt); S. Lanceros-Méndez (senentxu.lanceros@bcmaterials.net)

Abstract: Mesoporous separator membranes based on poly(vinylidene fluoride-co-trifluoroethylene), PVDF-TrFE, were prepared through the removal of ZnO nanoparticles from the polymer matrix composite. Different filler concentrations were used, and the evaluation of the morphology, mechanical properties, uptake and ionic conductivity of the membranes were demonstrated that they depend on initial ZnO content in the composite. On the other hand, the vibration peaks characteristics of PVDF-TrFE and the thermal properties are independent on initial filler content. The membrane with the best ionic conductivity, 1.6 mS/cm, is the one prepared after 70wt.% ZnO removal. The separator membranes were assembled in Li/C-LiFePO₄ half-cells exhibiting good rate capability and cycling performance, the best battery performance being obtained for the PVDF-TrFE after 70wt.% ZnO removal. The good performance of the developed separators was also demonstrated in full battery cells. Thus, a way to tailor membrane mesoporosity is presented and it is shown that the obtained membranes represent suitable separators for lithium-ion battery applications.

Graphical abstract

Keywords: Porosity; membranes; PVDF-TrFE; ZnO; battery separator

1. Introduction

An increasingly technological society resulting from the growth of electronic miniaturization and the appearance of new gadgets has led to a growing demand for smaller and lighter energy storage systems with improved safety, energy and power characteristics [1, 2]. These energy storage systems are not just used for portable consumer devices but are becoming relevant in transportation, such as electric vehicles (EVs), leading to a society highly dependent on energy storage systems [3, 4].

One of the most efficient technologies for energy storage are lithium-ion batteries, which are expected to become increasingly relevant for the next-generation rechargeable batteries [5-7].

Lithium-ion batteries present some advantages as power sources, as they are lighter, cheaper, show higher energy density (290 Wh.kg^{-1}), less charge loss, no memory effect, prolonged service-life, and higher number of charge/discharge cycles, when compared to other battery technologies [8, 9].

Lithium-ion batteries are fabricated from three key components: anode, cathode and a separator membrane, which is typically soaked by a electrolyte solution (liquid electrolyte where salts are dissolved in aqueous or organic solvents) [10]. The main functions of the separator membrane is to become the medium for ions transfer between the electrodes, prevent contact between the anode and the cathode, regulate cell kinetics and promote safety in the charge and discharge mechanisms [11]. The incorporation of the lithium solution into the separator membrane is usually achieved by uptake, i.e. the immersion of the polymer membrane directly into the lithium solution until the weight remains unchanged [12]. The properties of the separator membrane are dependent on the polymer membrane characteristics, including thickness, permeability, overall porosity, pore size and interconnectivity, wettability, electrolyte absorption and retention, chemical, thermal and mechanical stability [13].

Different processing techniques have been used to obtain porous membranes for battery applications, including template synthesis [14], dry and wet processes [15, 16], electrospinning [17], preirradiation grafting [18] and solvent casting techniques with thermally induced phase separation (TIPS) [19, 20] or non-solvent induced phase separation [21], among others. The most used host polymer types are poly(ethylene) (PE) [22], poly(propylene) (PP) [23], poly(ethylene oxide) (PEO) [24, 25], poly(acrylonitrile)

(PAN) [24, 26], poly(vinylidene fluoride) and its copolymers (PVDF-TrFE and PVDF-co-hexafluoropropene, PVDF-HFP) [27-30]. In order to improve the thermal and mechanical properties of porous polypropylene separators (PP) for lithium-ion batteries, a SiO₂ layer has been placed in both sides of the separator, these layers improving the capacity and performance of this separator when compared to pristine PP separator [31]. The effect of temperature on the performance for macroporous separators based on polyethylene and polypropylene were investigated and these separators presented performance degradation when submitted to an aging treatment [32]. Further, electrospun nanofiber separators of organic F-doped poly-m-phenyleneisophthalamide have been proposed for lithium-ion batteries. This separator is characterized by lower electronic conductivity and higher electrochemical stability window when compared to commercial polyethylene membranes [33]. A new multifunctional separator based on poly(ethylenealternate-maleic acid) dilithium salt into a poly(vinylidene fluoride-hexafluoropropylene) copolymer matrix has been developed showing improved battery performance due to Mn chelate ions [34]. PVDF and its copolymers belong to the fluorinated class and are characterized by exceptional properties for battery separator applications such as high polarity, excellent thermal and mechanical properties, wettability by organic solvents, being chemically inert and stable in cathodic environment and controllable porosity in binary and ternary systems [35, 36].

The advantages of the co-polymer PVDF-TrFE for battery separator applications with respect to PVDF and other copolymers are that the porous PVDF-TrFE membranes exhibit low degree of crystallinity, high contents of polar phase (β -phase) and the possibility of controlling its porosity in binary systems at room temperature [37].

Microporous membranes based on PVDF-TrFE as battery separators have been prepared by thermal induced phase separation (TIPS) [30] and composite membranes have been developed with lithium salts [29] and fillers such as zeolite (NaY) [38], barium titanate (BaTiO₃) [39], carbon nanotube (CNT) [40], montmorillonite (MMT) [41]. It has been reported that the membrane structure of PVDF-TrFE prepared by TIPS strongly depends on the solvent evaporation temperature on the polymer/solvent ratio. The porosity of membranes, ranging from 70 to 80%, determines the electrolyte solution uptake, being larger (up to 600%) for the samples with larger porosity. The electrolyte solution improves the ionic conductivity of the microporous membranes with the ionic conductivity decreasing with increasing degree of porosity of the membranes [28, 30]. For PVDF-TrFE composites, the optimized filler contents leading to membranes with

better electrochemical performance have been shown to be 4 wt% of MMT, 16 wt% of NaY, 16 wt% of BaTiO₃ with 500 nm average size and 0.1 wt% of MWCNT. Further, filler type deeply affects membrane separator performance in lithium-ion batteries [42]. Recently, it has been demonstrated that the best fluoropolymer-based separator membrane with degree of porosity larger than 50% is PVDF-TrFE due to the higher β -phase content that facilitates faster lithium ion migration due to its higher polarity and electromechanical response with respect to other polymer phases [43]. On the other hand, typically obtained pore size obtained in PVDF-TrFE ranges from 2.5 to 4 μm , whereas the ideal pore size is below 1 μm in order to avoid the trend for particle penetration within the separator and the formation of dendrites during excessive loading [44]. In order to improve those issues, the goal of the present work is to prepare porous membranes of PVDF-TrFE with pore size below 1 μm with different degrees of porosity through a simple, reproducible and scalable method. For a given average pore size, the effect of degrees of porosity (ranging from 30 % to 70 %) on the lithium ion battery cycling performance was evaluated. Based on the experimental results and theoretical simulations, the ideal degree of porosity should be above 50% [45].

The porosity within PVDF-TrFE was obtained by using ZnO nanoparticles with sizes between 90-210 nm. Moreover, the ZnO nanoparticles are low-cost, non-toxic and simple to remove from the polymer in acidic solution. Further, the fabrication method of this separator allows a suitable control of the degree of porosity and pore size and can be easily up-scaled for industrial production. Moreover, impressive electrochemical performance of the Li/C-LiFePO₄ half-cells, make such mesoporous separator membranes a promising alternative to commercial LIBs separators.

2. Experimental details

2.1. Materials

Poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) (70/30) and poly(vinylidene fluoride) (PVDF, Solef 5130) were purchased from Solvay.

Zinc oxide nanoparticles (ZnO, average particle size (APS): 90-210 nm) were acquired from Iolitec. C-LiFePO₄ (LFP) and carbon black (Super P-C45) were supplied by Phostech Lithium and Timcal Graphite & Carbon, respectively.

The solvents N,N'-dimethylpropyleneurea (DMPU), N,N-dimethylformamide (DMF), the conventional electrolyte 1M LiPF₆ in ethylene carbonate-dimethyl carbonate (EC-DMC, 1:1 vol) and the hydrochloric acid solution (HCl) (37%) were purchased from LaborSpirit, Merck, Iolitec and Sigma-Aldrich, respectively

2.2. Membrane preparation

PVDF-TrFE composites were prepared following the general guidelines presented in [46]. First ZnO powder was dispersed in a solution of N,N-dimethylformamide (DMF) at a polymer plus ZnO concentration of 15% (w/w) of the total solution with concentrations of ZnO relative to the polymer of 10%, 30%, 50% and 70% (w/w). The processing steps and corresponding sequence are illustrated in Figure 1.

Figure 1 - Main experimental steps for the processing of PVDF-TrFE membranes.

The ZnO particles were dispersed in DMF with the help of an ultrasonic bath (Ultrasons Selecta P) during 2 hours. After complete dispersion of the ZnO particles, PVDF-TrFE powder was added and dissolved under magnetic agitation during 4 h at 25 °C. After dissolution of the polymer, the solution was casted uniformly on clean glass substrates by doctor blade and placed in an air oven (Binder, ED23) at 210 °C during 15 minutes [46]. For the preparation of the membranes, the films were then immersed in a 37% HCl

solution for ZnO removal. After completely removal of ZnO particles, the films were washed with deionized water for several times and mesoporous PVDF-TrFE membranes were obtained with average thickness of $\sim 75 \mu\text{m}$. Finally, PVDF-TrFE membranes will be identified henceforth by the initial amount of ZnO in the composites, which was later removed.

2.3. Characterization techniques and procedures

UV–visible spectra of the HCl solution after removal of the ZnO particles was obtained using a UV–vis spectrophotometer (Jasco V-670 spectrophotometer) in the spectral range of 300 to 700 nm.

Surface morphology of the membranes was evaluated by Scanning Electron Microscopy (SEM) using a FEI Nova 200 with an accelerating voltage of 5kV. The membranes were previously coated with gold for 120 s under $<10^{-4}$ bar pressure and 10 mA current (Sputter coater SC7620, Quorum Technologies Ltd, UK).

The polymer phase of the obtained membranes was determined by Fourier transformed infrared spectroscopy (FTIR) using a Spectrum 100 set up, Perkin-Elmer, in the ATR mode over a range of $650\text{--}1750 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . 64 scans were performed for each sample

The thermal properties of the membranes were determined by Differential scanning calorimetry (DSC). DSC was carried out in a Perkin-Elmer Pyris 1 DSC instrument in nitrogen atmosphere at the temperature range between 25 and 200 °C with a heating rate of $10 \text{ }^{\circ}\text{C}.\text{min}^{-1}$. All samples were measured in 40 μL aluminium pans with perforated lids to allow the release and removal of decomposition products.

The degree of crystallinity (ΔX_{cryst}) of the samples was calculated from the DSC scans using following equation:

$$\Delta X_c = \frac{\Delta H_f}{\Delta H_{100}} \quad (1)$$

where ΔH_f is the melting enthalpy of the sample and ΔH_{100} (103.4 J.g^{-1}) is the melting enthalpy for a 100% crystalline sample [47].

The stress-strain mechanical measurements were carried out in the tensile mode with a TST350 Linkam Scientific Instruments at room temperature and a strain rate of 15mm/s.

2.4. Degree of porosity, electrolyte uptake and ionic conductivity

The porosity of the PVDF-TrFE membranes was calculated as:

$$Porosity (\%) = \left(1 - \frac{\rho_a}{\rho_c}\right) \times 100\% \quad (2)$$

where ρ_c stands for bulk density of PVDF-TrFE/ZnO films calculated with $1.78 \text{ g}\cdot\text{cm}^{-3}$ as the density of PVDF [48] and $5.61 \text{ g}\cdot\text{cm}^{-3}$ as the density of ZnO [49]. ρ_a is the membrane apparent density.

The uptake value was obtained by immersing the membranes into the electrolyte solution and applying the following equation:

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

where m_0 is the weight of the dry membrane and m_i is the weight of the membrane after immersion in the electrolyte solution.

Impedance spectroscopy measurements were carried out for the different membranes after immersion in the electrolyte solution for 15 minutes. Measurements were performed in the frequency range between 500 mHz and 65 kHz in an AutolabPGSTAT-12 (Eco Chemie) equipment in the temperature range from 20 to 60 °C. A constant volume support equipped with gold blocking electrodes located within a Büchi TO 50 oven was used for the measurements. The ionic conductivity (σ_i), tortuosity (τ) and MacMullin number (N_M) of the membranes were calculated after the following equations, respectively:

$$\sigma_i = \frac{d}{R_b \cdot A} \quad (4)$$

$$\sigma_i = \sigma_0 \frac{\varepsilon}{\tau^2} \quad (5)$$

$$N_M = \frac{\sigma_0}{\sigma_i} \quad (6)$$

where R_b is the bulk resistance, d is the thickness, A is the area of the sample, σ_0 is the conductivity of the pure liquid electrolyte, σ_i is the room temperature conductivity of the membrane plus the liquid electrolyte and ε is the degree of porosity of the membrane.

2.5. Electrode fabrication and electrochemical performance evaluation

2.5.1. Cathode preparation

The cathode was prepared using 80wt.% C-LiFePO₄, 10wt.% carbon black and 10wt.% PVDF in 2.25 mL of DMPU for 1 g of solid material, following the procedure reported in [50]. The resulting slurry was then casted on aluminum foil by doctor-blade technique and dried at 100°C for 2 h. The active mass loading was $\sim 1 \text{ mg.cm}^{-2}$.

2.5.2. Half-cell preparation and electrochemical testing

Li/C-LiFePO₄ 2016 coin-type half-cells were assembled in an argon-filled glove box where O₂ and H₂O levels were kept below 0.1 ppm. The half-cells were prepared using the different PVDF-TrFE membranes as separators (14 mm diameter) soaked in the electrolyte solution. Metallic lithium (10 mm diameter) was used as anode and the C-LiFePO₄ based electrode as cathode (10 mm diameter). Charge-discharge tests were performed at room temperature in the voltage range 2.5 V to 4.2 V at current rates from C/5 to 2C (C = 170 mA_g⁻¹) using a multichannel Maccor 4200 potentiostat. For each PVDF-TrFE separator, a minimum of 6 half cells were fabricated and tested.

3. Results and discussions

3.1. ZnO removal

ZnO particles were used as sacrificial additives for the preparation of the PVDF-TrFE membranes after considering their advantages: low cost, non-toxicity and easy removal by acidic solution, whereas PVDF-TrFE shows excellent chemical stability against acid solutions [51, 52]. After the membranes are formed, the ZnO particles are removed from the PVDF-TrFE membrane to give rise to a porous membrane structure and improve electrolyte uptake, ionic conductivity and electrochemical performance. In order to remove ZnO from the as-prepared PVDF-TrFE membranes, an HCl solution of 37% at room temperature was used and upon immersion into the HCl solution, the color of the membranes begins changed from slightly yellow to white.

In order to evaluate ZnO removal, the variations in membrane's weight were recorded as a function of time, as shown in Figure 2a). Figure 2a) shows that pristine PVDF-TrFE does not undergo any weight loss, proving that the HCl solution does not affect the weight and, therefore, PVDF-TrFE is chemically stable in HCl solution. For the PVDF-TrFE/ZnO composite membranes, the weight loss increases with increasing ZnO particle concentration and effectively demonstrates the removal of the ZnO filler from the composite.

Figure 2 – Weight loss as a function of time for the PVDF-TrFE membranes with different wt% of ZnO (a). UV–visible spectra of the HCl solution after ZnO particle removal from the composite (b).

Figure 2a also shows that for the PVDF-TrFE membranes with ZnO concentration above of 30% wt, the membrane weight is reduced by more than half of the expected weight loss (original ZnO concentration) after 15 min in the solution and the weight reaches a steady state after 2 h, indicating the complete removal of the ZnO.

After ZnO particles dissolution, the color of the HCl solution changes to yellow. The UV–Visible spectra of the HCl solution is presented in figure 2b, where the two vibration peaks at 320 – 380 nm, characteristic of the UV – Vis spectrum of ZnO particles [53], demonstrate the presence of the dissolved ZnO in the solution. Further, the vibration peaks wavelength is independent of the ZnO concentration but are more intense for higher ZnO concentration (figure 2b)). Thus, the present method shows to be efficient in the development of mesoporous membranes with controlled porosity, as it will be shown in the following section.

3.2. Membrane morphology, polymer phase, thermal, mechanical properties and degree of porosity

ZnO removal from the composite leads to porous membranes as demonstrated by the surface SEM presented in Figure 3.

The SEM images of figure 3a and 3b represent the morphology of pristine PVDF-TrFE and PVDF-TrFE composite with 50wt.% of ZnO, respectively. The images in figure 3c and 3d illustrate the morphology of the PVDF-TrFE membranes after the removal of ZnO in the samples with 50 wt.% and 70 wt.% filler content, respectively. The presented images are representative for the rest of the samples. Figure 3a and b show that the samples show the characteristic compact fibrillary microstructure of PVDF-TrFE [54], independently on the filler content. Further, figure 3b also shows that the ZnO particles are well dispersed and distributed in the PVDF-TrFE polymer matrix.

Figure 3 – Surface SEM images of pristine PVDF-TrFE a); PVDF-TrFE with 50wt.% of ZnO b); PVDF-TrFE after 50%wt ZnO particles removal (c); and PVDF-TrFE after 70%wt ZnO particles removal (d).

After ZnO removal (figures 3c and d) an interconnected porous structure is obtained in PVDF-TrFE membrane, the pore sizes being consistent with ZnO particles size. The pores are well distributed along the membrane and their quantity increases with increasing initial ZnO content in the composite. It is to notice that an interconnected porous structure is essential for uptake of the electrolyte solution for battery applications.

Fourier transform infrared spectroscopy (FTIR) allows to determine whether ZnO removal affects the vibration spectra of PVDF-TrFE polymer (figure 4a). The FTIR spectra of PVDF-TrFE is characterized by the vibration bands at 844, 880, 1402 and 1432 cm^{-1} identified in figure 4a) and corresponding to the of CF_2 symmetric stretching or CF_2 rocking, CH_2 wagging and CH_2 bending, respectively [55]. These vibration peaks do not suffer any variation in the different PVDF-TrFE membranes, indicating that the removal of ZnO does not change the crystal phase of PVDF-TrFE (figure 4a).

The characterization of the mechanical behavior of the membranes is relevant in order to apply them as lithium-ion battery separators, since their integrity is necessary to obtain excellent cycling performance [56].

The stress-strain characteristic curves of the PVDF-TrFE membranes obtained after ZnO removal are shown in figure 4b).

It is observed that the porosity present in the different membranes determines the overall mechanical properties of the membranes, leading to a decrease of the Young modulus with increasing porosity, i.e. ZnO concentration in the composite (figure 4b).

With respect to the final stress and strain, they are the lowest for the PVDF-TrFE membrane prepared after 50 wt.% of ZnO removal, which may be related to poor pore interconnectivity, when compared to the remainder membranes.

Considering that the mechanical properties of the separator are essential to obtain excellent cyclability [56] and taking into account the results of figure 4b), the mechanical properties of the PVDF-TrFE membranes decrease with the presence of the pores (e.g. decrease of the final stress-strain). In any case, all membranes show mechanical integrity for being used as separator membranes for lithium ion battery applications.

The DSC thermograms of the different membranes are shown in figure 4c) and are all characterized by two endothermic peaks: one at 105 °C, that corresponds to the ferroelectric–paraelectric phase transition (Curie transition), and other at 150 °C, corresponding to the melting of PVDF-TrFE [57].

The area of the melting peak allows to calculate the degree of crystallinity [54], which is the same (~28%) for all membranes, independently of the initial ZnO concentration.

The low value of the degree of crystallinity is appropriate for battery separator applications, since ion transport occurs in the amorphous region of the membrane, as well as the electrolyte uptake [58].

Figure 4 - FTIR-ATR spectra (a), Stress-strain curves (b), DSC curves (c), and Degree of porosity (d) for all PVDF-TrFE membranes.

Figure 4d) shows the degree of porosity calculated using equation 2 as a function of ZnO removal. It is observed that the degree of porosity of the PVDF-TrFE membranes is proportional to the ZnO removal within the experimental error and that a maximum degree of porosity of $\sim 60\%$ is obtained for the sample obtained after 70% ZnO removal.

3.3. Thermal shrinkage, electrolyte uptake and ionic conductivity

Thermal shrinkage analysis is extremely important as it affects battery safety and mitigates thermal damage in lithium-ion batteries [59]. Figure 5 shows the photographs of membranes prepared after 70wt.% ZnO removal with no thermal treatment and after thermal treatments at 50 °C and 100 °C for xxx minutes.

Figure 5 - Photographs of PVDF-TrFE separators before and after different thermal treatments at 50 and 100 °C for XXX minutes.

As it is demonstrated in figure 5, the developed PVDF-TrFE membranes exhibit excellent thermal stability: after thermal treatment at 100 °C, the size of the membrane is the same as for the as prepared membranes at 25 °C. For the rest of the PVDF-TrFE membranes, the same behavior is obtained.

For fluorinated membranes, the uptake of the electrolyte solution depends on the relative proportion of pores within the membranes [58] and, therefore uptake has been just evaluated for PVDF-TrFE membranes with degree of porosity above of ~ 7%. The uptake of the PVDF-TrFE membranes is reported in figure 6a) as a function of the dipping time. Uptake is determined by swelling of the amorphous regions of the polymer to accommodate the electrolyte [60].

Figure 6 - Uptake value (a) and Nyquist plots (b) at room temperature for different PVDF-TrFE membranes.

For all PVDF-TrFE membranes, saturation is obtained approximately after 5 minutes of immersion and the maximum uptake value for the membranes increase with increasing porosity (insert in figure 6a).

The uptake behavior is a result of the porosity and the gelation of PVDF-TrFE with the electrolyte, which results from the electrostatic interaction between the solvents and the surface polar $-C-F$ groups of the polymer [61].

The ionic conductivity of the membranes was determined by impedance spectroscopy at 25 °C, the corresponding Nyquist plots are presented in figure 6b). The Nyquist plots of all membranes show an inclined straight-line (typical of the blocking electrode capacitive behavior) whose intercept with the real axes, Z' , provides the ionic resistance of the PVDF-TrFE membrane [62] which can be used to calculate the ionic conductivity through the equation 4. The obtained value of the ionic conductivity is presented in Table 1.

Table 1 shows that the different PVDF-TrFE membranes show a high ionic conductivity with a value proportional to the degree of porosity and, therefore, to the electrolyte uptake. Thus, the highest ionic conductivity value of 1.6 mS/cm is found for the PVDF-TrFE membrane after 70wt.% of ZnO removal, but all membranes show ionic conductivity values above $> 10^{-4}$ S/cm, being therefore adequate for lithium-ion battery separator membranes [63].

Another relevant parameters for separator membranes such as tortuosity and Macmullin number were calculated for the PVDF-TrFE membranes using equations 5 and 6 and the corresponding values are presented in Table 1.

Table 1 - Room temperature ionic conductivity (σ_i), tortuosity (τ), and MacMullin number (N_M) for the different PVDF-TrFE membranes

Sample	$\sigma_i / \pm 0.3 \text{ mS.cm}^{-1}$	$\tau \pm 2$	$N_M \pm 5$
30 wt.%	0.1	5	94
50 wt.%	0.6	3	21
70 wt.%	1.6	2	7

The tortuosity (τ) describes the ionic transport path due to the porous structure with respect to a straight line d and the MacMullin number (N_M) describes the influence of the porous microstructure of the separators on the electrochemical performance of the lithium ion battery [64], the value of both parameter (ideal values of 1) will decrease with the increase in degree of porosity and increase in electrolyte uptake. The obtained values are similar to those found for commercial separators [64], indicating these porous PVDF-TrFE membranes could be a promising alternative candidate as battery separator.

3.4. Battery performance

The electrochemical performance of the PVDF-TrFE membrane electrolytes was investigated in Li/C-LiFePO₄ half-cells. LiFePO₄ represents one of most promising cathode active materials for the next generation lithium-ion batteries in transportation applications [65, 66]. Figure 7a) shows the charge-discharge voltage profiles of the Li/C-LiFePO₄ half-cells in the potential window of 2.5 and 4.2 V at different C-rates (C/10 to 2C) using PVDF-TrFE membranes prepared after 70 wt.% ZnO removal as the separator. For other PVDF-TrFE membranes (presented in Table 1), the cycling behavior as a function of C-rate is similar to that reported in the figure 7a). For the corresponding charge-discharge profile for 5th cycle at each C-rate is presented in figure 7a), where in all case the typical flat voltage profiles are observed at around 3.3–3.5 V. This voltage profile corresponds to the presence of a two-phase coexistence reaction for LiFePO₄ cathode (Fe²⁺/Fe³⁺ redox reaction between FePO₄ and LiFePO₄) [67] and is independent

of the cycle number and C-rate. On the other hand, an oblique line is observed for high C-rate (2C), that demonstrates the capacitive behavior [68].

In addition, figure 7a) shows that the difference between charge and discharge potentials is higher when the C-rate increases, ~ 0.6 V due to the polarization caused by lower transference number of Li^+ ions also on the interfacial reaction resistance on the lithium electrode [69].

For the PVDF-TrFE membrane prepared after 70 wt.% ZnO removal the discharge capacity values are 137 mAh.g^{-1} , 134 mAh.g^{-1} , 127 mAh.g^{-1} , 116 mAh.g^{-1} and 108 mAh.g^{-1} at the C-rates of C/10, C/5, C/2, C and 2 C, respectively, which corresponds to 80%, 79%, 75%, 68% and 64% of the theoretical capacity of C-LiFePO₄ (170 mAh.g^{-1}), indicating an excellent electrochemical behavior. This excellent electrochemical behavior is due to the high ionic conductivity of the PVDF-TrFE separator membrane.

Figure 7b represents the fifth charge–discharge curve at 2C-rate for the different PVDF-TrFE membranes, where the discharge capacities are 108 mAh.g^{-1} , 87 mAh.g^{-1} , and 79 mAh.g^{-1} for the PVDF-TrFE membranes after 70wt.%, 30wt.% and 50wt.% ZnO removal, respectively, showing that the behavior depends on the ionic conductivity (table 1) and mechanical stability of the membranes (figure 4b).

For the PVDF-TrFE membranes prepared after 30 wt.% and 50 wt.% ZnO removal, the ionic conductivity value of both samples are similar within experimental error, the best battery performance being for the PVDF-TrFE membrane after 30 wt.% ZnO removal due to the better mechanical properties of this membrane when compared to the PVDF-TrFE membrane prepared after 50 wt.% ZnO removal, which can lead to failure strain [56] and consequently lower cycling performance.

In relation to the PVDF-TrFE membrane prepared after 70 wt.% ZnO removal, the higher charge-discharge behavior compared to the other membranes is due to the higher ionic conductivity value. Despite the lower mechanical properties of this membranes in comparison with the other two, the higher ionic conductivity value leads to obtain excellent cycling performance and demonstrated that the mechanical properties are good enough for separator applications.

Figure 7 - 5th charge and discharge cycle room temperature profiles at rates from C/10 to 2C (a) for the membrane prepared after 70wt.% ZnO removal. Charge and discharge profiles at 2C for 5th cycle for different PVDF-TrFE membranes (b). Rate performance as a function of the cycle number (c) and capacity retention at different C-rates (d) for different PVDF-TrFE membranes.

Figure 7c shows the discharge capacity as a function of cycle number for different PVDF-TrFE membranes. Regardless of the C-rate, the discharge capacity is very stable as a function of the cycle number and the PVDF-TrFE membrane with the lowest cycle performance is the PVDF-TrFE membrane prepared after 50 wt.% ZnO removal. The observed differences in cycling performance for the PVDF-TrFE membranes are basically due to two main factors: the ionic conductivity value and the mechanical properties. The difference between the PVDF-TrFE membranes prepared after 30 wt.%

and 50 wt.% ZnO removal are mainly due to the mechanical properties since the ionic conductivity values are similar, as well as the degree of crystallinity. For the PVDF-TrFE membrane prepared after 70 wt.% ZnO removal, the highest cycle performance is due to the high ionic conductivity value, showing also that the mechanical properties are good enough for battery applications.

Figure 7d shows the charge capacity retention for the different C-rates calculated through the normalization of the delivered capacity for each scan rate with respect to the nominal value for C/10 rate for the different membranes. Independently of the PVDF-TrFE membrane, it is observed that the capacity retention decreases with increasing C-rate, due to the diffusion phenomena taking place within the electrode active material phase [70]. This decrease in capacity retention is higher for membranes with low ionic conductivity (30 wt.% and 50 wt.% of ZnO removal). The best capacity retention at 2C observed for the PVDF-TrFE membrane with 70 wt.% ZnO removal, leading to excellent cycling behavior. Given the good rate capability of all PVDF-TrFE membranes with different degrees of porosity (figure 7), Figure 8 shows the cycle stability at C/5 (figure 8a) and 2C-rate (figure 8b) for 50 cycles.

For C/5-rate (figure 8a), good stability is observed with high discharge capacity values over 50 cycles for all PVDF-TrFE membranes. The differences observed in the discharge capacity value between the PVDF-TrFE membranes are due to the interplay of both factors: the ionic conductivity value and the mechanical properties of the PVDF-TrFE membranes.

Figure 8 - Cycling performance of the PVDF-TrFE membranes when cycled at C/5 (a) and 2C (b).

In relation to 2C-rate (figure 8b), the battery performance for all PVDF-TrFE membranes is practically constant as a function of the number of cycles, with a capacity fade lower than 1%, the best cycling performance being observed for PVDF-TrFE membrane prepared after 70wt.% ZnO removal, due to the larger ionic conductivity. The coulombic efficiency shown in figure 8b is ~ 100% for all PVDF-TrFE membranes regardless of the number of cycles, showing the reversibility of the process.

Considering the excellent charge-discharge results presented in figures 7 and 8, table 2 compares the electrochemical properties of PVDF and copolymer separator membranes with pore sizes below 4 μm and degree of porosity above 50% and soaked with the electrolyte solution. The selected membranes from the literature also use same electrode. Table 2 shows that the electrochemical results of our present work even at high C-rates are similar or even superior in comparison to other recent reported results for PVDF based separator membranes.

Table 2 - Electrochemical parameters for different PVDF and copolymers separator membranes.

Polymer	Pore size / μm	Porosity / %	$\sigma_i/\text{mS cm}$	Capacity/ mAh.g^{-1}	Ref
PVDF	~0.72-1.1	78.9	1.72	110.3@5C (after 10 cycles)	[71]
PVDF	< 1	20	0.23	56@2C (after 50 cycles)	[72]
PVDF-HFP	<1	70	3.2	-----	[73]
PVDF-HFP	0.8	78	1.03	145@C/2 (after 50 cycles)	[74]
PVDF-CTFE	2	60	1.5	92@2C (after 50 cycles)	[75]
PVDF-CTFE	0.043-0.1	74	0.8	~89@8C (after 5 cycles)	[76]
PVDF-TrFE	2.5-4	72	1.1	87@2C (after 50 cycles)	[43]
PVDF-TrFE	< 1	70	1.6	107@2C (after 50 cycles)	This work

Thus, considering the electrochemical results from figure 7 and 8 and table 2, PVDF-TrFE membranes prepared after removal of 70wt.% of ZnO are excellent for lithium-ion battery applications.

As a proof of concept, a full cell battery was fabricated. The anode electrode was produced by the procedure presented in [50] with the following slurry composition: graphite powder, Super P carbon and PVDF binder with a ratio of 80:10:10. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 10 Hz to 10 KHz. Figure 9 shows the impedance spectra for the full cell battery with the PVDF-TrFE separators developed in this work.

Figure 9 – Impedance spectra for the full batteries prepared with the PVDF-TrFE separator membranes.

The Nyquist plots presented in figure 9 are characterized by a semicircle (overall resistance, which is the sum of the ohmic resistance, that represents the contact film resistance, and resistance contributions from the charge-transfer reaction) in the high and medium frequency regions and a straight line that is associated to the Li^+ diffusion process in the low frequency regions [50]. For the batteries prepared with the different PVDF-TrFE membranes, the overall resistance is below 200 Ω , which demonstrates the good compatibility with both electrodes.

The separator membrane presented in this work represents a novel separator for this application with controlled porosity after a simple and reproducible production method.

Conclusions

Mesoporous membranes of poly(vinylidene fluoride-co-trifluoroethylene) with controlled porosity were prepared through ZnO particle removal from the polymer matrix. The membranes were prepared with different ZnO initial contents between 10wt.% and 70 wt.%. The ZnO removal from the PVDF-TrFE membranes is fast and efficient and the ZnO removal originated the porosity of the PVDF-TrFE matrix. The morphology, mechanical properties, uptake value and ionic conductivity value of the membranes depend on the final porosity of the membrane but the thermal properties (melting behavior), degree of crystallinity and polymer phase are independent on the membranes preparation procedure.

The PVDF-TrFE membrane after removal 70wt.% of ZnO show the best ionic conductivity value of 1.6 mS.cm^{-1} , a tortuosity and Macmullin values of 2.3 and 7.3, respectively, and suitable mechanical properties. Further, those membranes lead to excellent electrochemical performance of Li/C-LiFePO₄ half-cells up to C-rates of 1C, the discharge capacity being between 137 mAh.g^{-1} at C/10 and 108 mAh.g^{-1} at 2C. Further, a high capacity retention of 79 % at 2C it is observed. The suitable performance of the developed separators is also demonstrated in full battery cells.

Thus, it is concluded that the separators developed in this work and prepared after a simple and reproducible method, **allowing control of overall porosity and pore size, are** suitable for high performance lithium-ion battery applications.

Acknowledgments

The authors thank the FCT (Fundação para a Ciência e Tecnologia) for financial support under the framework of Strategic Funding grants UID/FIS/04650/2013, UID/EEA/04436/2013 and UID/QUI/0686/2016; and projects no. POCI-01-0145-

FEDER-028157 and POCI-01-0145-FEDER-028237. The authors also thank the FCT for financial support under grant SFRH/BPD/112547/2015 (C.M.C.). J.N.P. wish to thank the financial support of the project Centro-01-0145-FEDER-000017 - EMaDeS - Energy, Materials and Sustainable Development, co-financed by the Portugal 2020 Program (PT 2020), within the Regional Operational Program of the Center (CENTRO 2020) and the European Union through the European Regional Development Fund (ERDF). Financial support from the Spanish Ministry of Economy and Competitiveness (MINECO) through project MAT2016-76039-C4-3-R (AEI/FEDER, UE) (including FEDER financial support) and from the Basque Government Industry Department under the ELKARTEK and HAZITEK Program is also acknowledged

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