

Regular Article

Tailoring poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) membrane microstructure for lithium-ion battery separator applications

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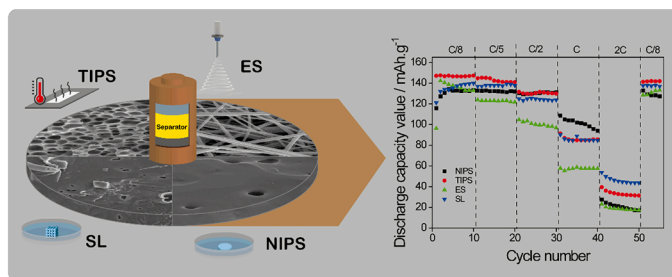
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HIGHLIGHTS

- P(VDF-TrFE-CFE) membranes have been developed for battery separator applications.
- The membranes were prepared by different processing techniques.
- The processing conditions allow tuning morphology and porosity.
- The best lithium transference number is 0.55, obtained for membrane prepared by salt leaching.
- A discharge capacity value of 74 mAh.g⁻¹ at 1C-rate has been obtained for the membranes prepared by salt leaching.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel battery separators based on poly(vinylidene fluoride-co-trifluoroethylene-chlorofluoroethylene)- P(VDF-TrFE-CFE)- were produced by different processing techniques (non-solvent and thermally induced phase separation, salt leaching and electrospinning), in order to evaluate their effect on separator morphology, degree of porosity and pore size, electrochemical parameters and battery cycling behavior. It has been demonstrated that the different processing techniques have a significant influence on the morphology and mechanical properties of membranes. The degree of porosity varies between 23 % and 66 %, for membranes obtained by salt leaching and thermally induced phase separation, respectively.

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The membranes present a high ionic conductivity value ranging between 1.8 mS.cm^{-1} for the electrospun membrane and 0.20 mS.cm^{-1} for the membrane processed by thermally induced phase separator. The lithium transference number value for all membranes is above 0.20, the highest value of 0.55 being obtained for samples prepared by salt leaching and thermally induced phase separation.

For all membranes, battery capacity values have been obtained at different C-rates with excellent reversibility. P(VDF-TrFE-CFE) samples present an excellent battery performance at 1C-rate after 100 cycles with 74 mAh.g^{-1} and excellent coulombic efficiency, for membrane processed by the salt leaching technique. This work demonstrates that P(VDF-TrFE-CFE) terpolymer can be used as a porous membrane in lithium-ion battery separator application, the membrane processing technique allowing to tailor its morphology and, consequently, battery performance.

1. Introduction

In today's highly technological society that largely depends on mobility and energy, the development of more environmentally friendly and efficient energy storage systems for portable electronic devices and electric vehicles becomes increasingly necessary [1,2]. Additionally, effective energy storage systems are key to reducing fossil fuels consumption as they can effectively store the power generated by renewable energy generation sources, which in turn helps mitigate climate change and global warming [3,4]. There are several energy storage systems that can be divided into electrochemical, mechanical, hydro, thermal, magnetic, or pneumatic, among others, where lithium-ion batteries (LIBs) belong to electrochemical devices [4]. Regarding LIBs, they are one of the most popular energy storage devices with a market growth rate of 8.5 % worldwide [5,6]. Despite this achievement and its applicability, further research is needed to improve the characteristic properties of its various components, i.e., the electrodes, the separator/electrolyte for conventional batteries and the solid electrolyte for solid-state batteries [7,8]. The global market for conventional LIBs was \$46.2 billion in 2022, and from 2023 to 2032, it is expected to increase by 15.2 % and that this increase is accompanied by performance and safety improvements [9]. The separator is a critical component for good operation of such devices, as it eliminates short circuits during charge-discharge processes, controls cell kinetics, and inhibits dynamics dendrite growth. Separators can be divided into different types, such as, single polymer, composites, polymer blends, electrospun, nonwoven and surface modified separators [10]. Independently of the separator type, it is composed of a porous membrane and an electrolyte solution where this solution is typically composed by lithium salts dissolved in an organic solvent and/or ionic liquids [11,12].

The morphology (porosity/pore size) of the separator, which influences its thermal, mechanical, and ionic conductivity, as well as its wettability and interaction with the electrolyte solution, are what determine the separator's primary characteristics and functional response [10].

In order to tailor the morphology of the separator, the membranes can be produced by different techniques, such as, electrospinning (ES), salt-leaching (SL), solvent casting with thermally (TIPS) and non-solvent induced phase separation (NIPS), among others. Different polymers have been implemented as separator membranes, including polypropylene (PP) [13], poly(acrylonitrile) (PAN) [14], poly(methyl methacrylate) (PMMA) [15], poly(ether-ether-ketone) (PEEK) [16], poly(ethylene oxide) (PEO) [17], polyetherimide (PEI) [18], poly(styrene-*b*-butadiene-*b*-styrene) (SBS) block copolymer [19], poly(vinylidene fluoride) (PVDF) and its copolymers [20,21], cellulose [22], silk fibroin [23], carrageenan [24], among others. In comparison to other polymer types, PVDF and its copolymers are heavily researched in the field of separator membranes due to their tailorable membrane forming properties, chemical inertness, compatibility with electrolyte solution, and stability at functional temperatures and high voltages. Additionally, they exhibit outstanding mechanical properties, a manageable degree of crystallinity, and high dielectric value that can enhance the ionization of lithium salts [25].

In order to obtain separators with high ionic conductivity value and improved thermal and mechanical properties, PVDF polymers' most recent separator research has focused on the study of composites and blends [21]. For PVDF base separators of this type, it is important to increase wettability, further adjust morphology to properly tune pore size, improve the suppression of dendrites, and improve lithium ions mobility in order to allow the widespread use and commercial success of this separator type.

Considering the dielectric constant value of PVDF, which is one of the most important properties of a separator membrane, the PVDF terpolymer poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene), P(VDF-TrFE-CFE), shows a high dielectric constant, ranging from 25 to 50 which is important for the ionization of lithium salts. Furthermore, this terpolymer presents chemical and radiation resistance, suitable thermal and mechanical properties, good electrolyte wettability and excellent processability, but it has never been used in energy storage applications [26].

In this scope, it is essential to properly tune membrane porosity and pore size, which are critical parameters in membrane properties for battery separators. This can be achieved by proper selection of the processing technique and their associated processing parameters. Given this, the development of porous membranes based on P(VDF-TrFE-CFE) processed by various methods, including TIPS, NIPS, electrospinning, and salt leaching, is the main objective of this work, aiming to demonstrate for the first time that this polymer may be suitable for battery separator membrane applications. The microstructural, thermal, mechanical and electrochemical properties of the developed membranes are presented and discussed, as well as their functional response once implemented as battery separators.

2. Experimental

2.1. Materials

Poly (vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) (Piezotech® RT-FS; $M_w = 500 \text{ kg.mol}^{-1}$; 62.5/29/8.5 mol.% of VDF, TrFE and CFE, respectively), the solvent *N,N*-dimethylformamide (DMF, 99 %) and Sodium chloride (NaCl) were supplied by Piezotech, Merck and Sigma-Aldrich, respectively. The solvent *N*-methylpyrrolidinone (NMP), the conventional electrolyte 1 mol.dm^{-3} LiPF_6 in ethylene carbonate-dimethyl carbonate (EC-DMC, 1:1 vol) and lithium-metallic were purchased from Sigma-Aldrich.

For cathode electrode development, poly(vinylidene fluoride) PVDF, Kynar PVDF HSV900, carbon black (Super P-C45) and C-LiFePO₄ (LFP) were acquired by Arkema, Timcal Graphite & Carbon and Phostech Lithium, respectively.

2.2. Membrane preparation

The membrane samples were prepared using four different preparation techniques: thermally induced phase separation (TIPS), non-solvent induced phase separation (NIPS), salt leaching (SL) and electrospinning (ES). First, four solutions were prepared by mixing P(VDF-

TrFE-CFE) in a DMF solution (20/80 wt%), under magnetic stirring. After the polymer was completely dissolved, two of them were submitted to a doctor blade technique in a glass substrate. After that, one was evaporated in an oven (JP selecta) at 25 °C (TIPS) and the other one was submerged in a non-solvent – distilled water (NIPS). The third solution was submitted to an electrospinning technique, starting by introducing the obtained solution into the electrospinning setup, using a plastic syringe connected to a flow regulator from Syringepump, USA. After that, a high voltage (model PS/FC30P04) was applied between the syringe and an aluminum foil substrate (where the electrospun fibers are collected, forming a mat), in order to create a jet. Deposition conditions were 20 kV bias, 0.4 mL.h⁻¹ flow rate, 0.5 mm needle diameter and 12 cm needle-collector distance.

With respect to the fourth solution, after the polymer was completely dissolved, NaCl was added to the solution, in a 1:1 polymer:NaCl weight ratio. Later, when the salt particles were properly dispersed, the solution was processed with the doctor blade technique in a glass substrate and placed in an oven, at 25 °C. After obtaining the dried film, it was washed in distilled water, under magnetic stirring for 72 h. The produced membranes are identified in the following according to their processing technique name, i.e., NIPS, TIPS, ES and SL. The thickness of the membranes is 75, 120, 169 and 193 μm for the membranes obtained by NIPS, SL, TIPS and ES techniques, respectively.

2.3. Characterization techniques

The morphology (surface and cross-section images) of P(VDF-TrFE-CFE) membranes was examined by scanning electron microscope (SEM, Carl Zeiss EVO 40 EDX Oxford Instruments) with a 20 kV accelerating voltage. The membranes were previously coated with a gold layer (Polaron, type SC502).

The porosimetry of the samples was determined by mercury porosimetry in an Auto Pore IV 9500 porosimeter (Micromeritics Instrument Corporation, Norcross, USA), where the penetrometer was evacuated to a pressure less than 7 Pa, followed by filling with mercury to 365 MPa. Samples were outgassed at 110 °C overnight prior to measurement. A contact angle of 140°, a surface tension of 480 dyn.cm⁻¹ for mercury and a pressure equilibration time of 10 s were used.

Contact angle measurements were performed using 3 μL droplets of ultrapure water and electrolyte solution (1 M LiPF₆ in EC:DMC) with a Data Physics OCA20 device at room temperature. For each membrane, three measurements were taken at different locations on the membrane to calculate the average contact angle.

A Jasco FT/IR-6100 was used to perform Fourier Transform Infrared Spectroscopy in Attenuated Total Reflection mode (FTIR/ATR) from 4000 to 600 cm⁻¹ with 64 scans at a resolution of 4 cm⁻¹.

A Mettler-Toledo DSC 822e was used to obtain differential scanning calorimetry (DSC) curves from 30 to 200 °C at a heating rate of 10 °C.min⁻¹ under a nitrogen flow of 20 mL.min⁻¹ in aluminum crucibles.

Using a NETZSCH STA 449F3 thermobalance, thermogravimetric (TGA) thermograms were obtained. Membranes were placed in alumina crucibles with approximately 10 mg of sample and heated between 30 and 800 °C at a rate of 5 °C.min⁻¹.

Stress-strain measurements were carried out in a TST350 Linkam instrument at a strain rate of 15 μm.s⁻¹ in order to assess the mechanical properties of the material at room temperature.

2.4. Electrolyte uptake and electrochemical characterization

The electrolyte uptake (ϵ) was estimated using Eq. (1) as a function of time while the membranes were submerged in a 1 mol.dm⁻³ LiPF₆ in EC:DMC solution:

$$\epsilon = \left(\frac{M - M_0}{M_0} \right) \times 100\% \quad (1)$$

where M_0 is the membrane weight and M is the membrane weight after immersion in the electrolyte solution.

Using an Autolab PGSTAT-12 (Eco Chemie) and a constant volume support (gold electrodes | separator membrane | gold electrodes), the ionic conductivity (σ_i) value for the porous membranes was calculated. The support was then placed within a Büchi TO 50 oven. With a 50 mV stimulation amplitude and a frequency range from 65 kHz to 500 mHz, impedance measurements were carried out at room temperature. The ionic conductivity value was calculated using Eq. (2):

$$\sigma_i = \frac{t}{A \cdot R_b} \quad (2)$$

where t is the thickness of the membrane, A is the area of the membrane and R_b is the bulk resistance obtained by intercept of the imaginary impedance (minimum value of Z'') with the slanted line in the real impedance (Z').

Eqs. (3) and (4), were used to obtain the Tortuosity (τ) and MacMullin number (N_M), respectively:

$$\tau = \sqrt{\frac{\sigma_0 \epsilon}{\sigma_i}} \quad (3)$$

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

where, σ_0 is the ionic conductivity of the 1 mol.dm⁻³ LiPF₆ in EC:DMC solution (11.6 mS.cm⁻¹ at 25 °C), ϵ is the porosity of the membrane and σ_i is the ionic conductivity of the membrane after the uptake process.

The electrochemical stability of the separator membranes was assessed through cyclic voltammetry in a glove box using a two electrodes configuration with a lithium disk as the counter electrode and a gold microelectrode as the working electrode. The measurements were performed with an Autolab PGSTAT-12 (Eco Chemie) at a scan rate of 0.01 V.s⁻¹.

A potentiostat/galvanostat (Autolab PGSTAT-12) was used to measure the Li-ion transference number (t_{Li}^+) using symmetric membrane cells (10 mm) sandwiched between two Li metal electrodes (8 mm) at room temperature [27].

The Li-ion transference number (t_{Li}^+) was calculated by Eq. (5) using the method proposed in [28,29]:

$$t_{Li^+} = \frac{I^s [\Delta V - I^0 R^0]}{I^0 [\Delta V - I^s R^s]} \quad (5)$$

where, I^0 and I^s are the initial and steady currents, respectively. R^0 and R^s are the initial and final resistances of the interfacial layers of the Li electrode/electrolyte.

2.5. Cathode and lithium cell preparation and cycling performance

The battery cathode was fabricated with the following component percentages: 80 wt% C-LiFePO₄, 10 wt% carbon black, and 10 wt% PVDF, combined in 2.25 mL of NMP as polymer solvent. The study in [30] provides more detailed information on the electrode preparation. The resultant slurry was then casted by doctor-blade onto and aluminum foil and allowed to dry at 80 °C for two hours. The active mass loading of the cathodes was approximately 3.8–4.2 mg.cm⁻².

In a homemade, argon-filled glove box, Swagelok type Li/C-LiFePO₄ half-cells were prepared with the following components: a porous membrane separator (10 mm in diameter) of the different types developed in the work immersed in electrolyte solution; a metallic lithium (8 mm in diameter) foil anode electrode; and of the previously developed C-LiFePO₄ based cathode electrode. Experiments with Whatman® commercial glass fibre separator were also performed for comparison. Charge-discharge tests were performed at room temperature using a Landt CT2001A instrument, in the voltage range of 2.5 V to 4.2 V, at

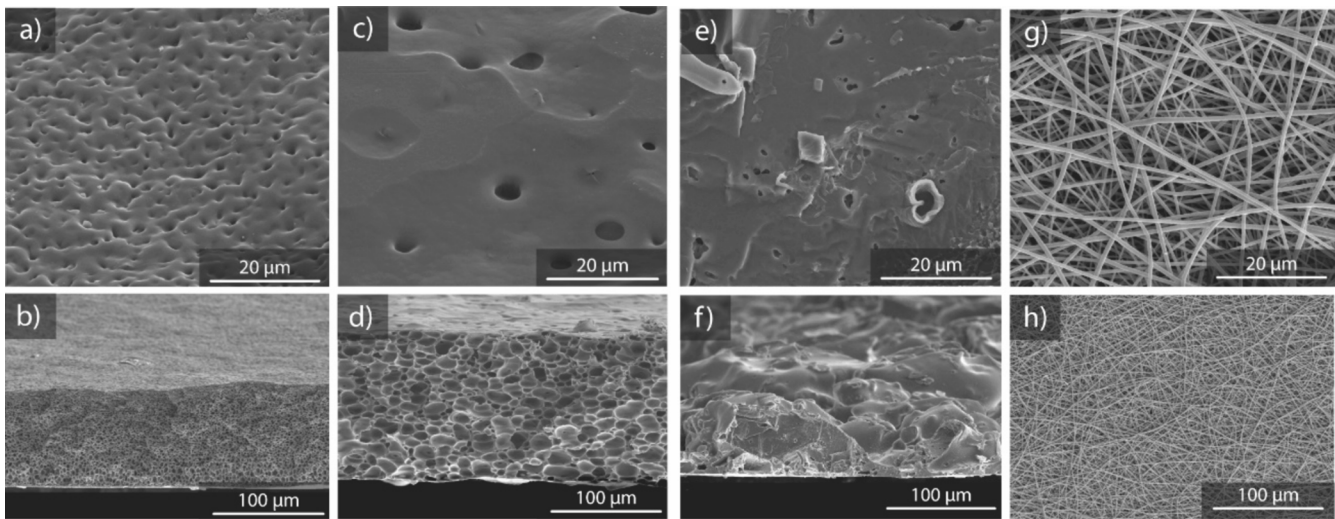


Fig. 1. SEM images of the membranes obtained by different processing techniques: a) NIPS surface b) NIPS cross section; c) TIPS surface d) TIPS cross section; e) SL surface f) SL cross section; g) ES surface and h) ES cross-section.

Table 1
Porosity, β -phase content, degree of crystallinity, Young modulus and yield stress and strain values of all P(VDF-TrFE-CFE) membranes processed by different technique.

Samples	Porosity/ $\pm 5\%$	β -phase/ $\pm 2\%$	$\chi_c/\pm 1\%$	$E'/\pm 40\text{ MPa}$	Yield stress/ $\pm 0.5\text{ MPa}$	Yield strain/ $\pm 2\%$
NIPS	24	83	11	131	1.5	22
TIPS	66	84	12	119	1.1	18
ES	56	84	9	17	0.2	14
SL	23	85	12	48	0.5	19

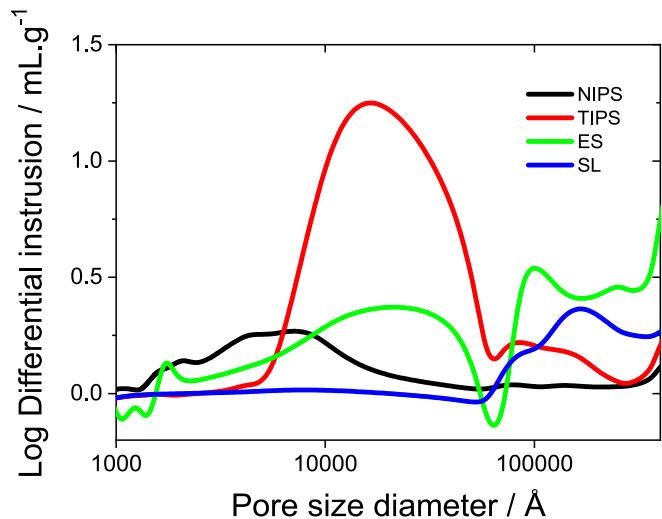


Fig. 2. Intruded cumulative volume as a function of pore size for the different membranes.

current rates of C/8 to 2C ($C = 170\text{ mA.g}^{-1}$).

Electrochemical impedance spectroscopy (EIS) (Autolab PGSTAT12) was used to examine the electrical characteristics of the Li/C-LiFePO₄ half-cells with the prepared separator membranes in the frequency range from 10 mHz to 1 MHz, with an amplitude of 10 mV AC voltage signal.

3. Results and discussion

3.1. Morphology and degree of porosity

The morphology of membranes is shown in the in surface and cross-

sectional SEM images presented in Fig. 1 for all processing techniques, all membranes showing a porous morphology.

For the sample prepared by NIPS (Fig. 1a–b) the porosity is evenly distributed throughout the samples. This morphology is due to the liquid–liquid de-mixing that caused the phase separation between the DMF solvent and distilled water (non-solvent) within the coagulation bath [31].

Regarding the samples obtained by TIPS, porous membranes with irregular pores with dimensions below 5 μm are obtained, shown in Fig. 1c. This behavior is also observed in the cross-section image (Fig. 1d) and is explained by the polymer/solvent phase diagram, the porous structure being determined by the initial polymer concentration in solution and the solvent evaporation temperature [26], leading, with the used processing conditions, to a liquid – liquid phase separation process that produces the porous morphology.

Fig. 1e–f show the SEM images of the membranes obtained by the salt-leaching method in surface and cross-section, respectively. A morphology with an irregular porous structure is also obtained due to the elimination of the salt during the preparation method.

For the electrospinning technique, two SEM images of the surface, with different magnifications, are shown in Fig. 1g–h, where a fiber structure without beads is observed. Furthermore, this microstructure is based on fibers with regular size and a diameter of $600 \pm 100\text{ nm}$.

The degree of porosity of the P(VDF-TrFE-CFE) membranes was determined using mercury intrusion porosimetry (MIP) and the obtained values are presented in Table 1. It is observed that the degree of porosity varies from 23 % for the membranes obtained by SL to 66 % for the ones obtained by TIPS, in correlation with the microstructure of the membranes. Fig. 2 shows the logarithm of the cumulative intruded volume as a function of pore size diameter for the different P(VDF-TrFE-CFE) membranes. A wide range of different pores sizes is observed for most of the membranes, in correlation with the SEM images (Fig. 1).

The membranes prepared by TIPS show a larger distribution of pore

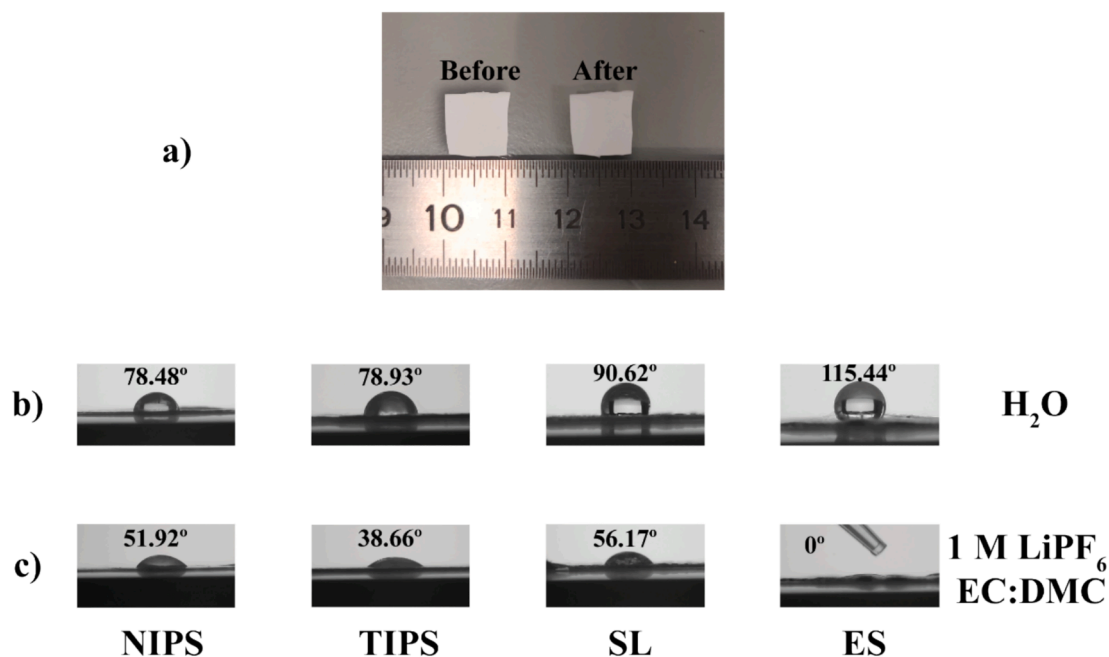


Fig. 3. a) Photographic images of TIPS membrane before and after thermal treatment at 100 °C for 1h. b) and c) contact angle of the different membranes with water and electrolyte solution, respectively.

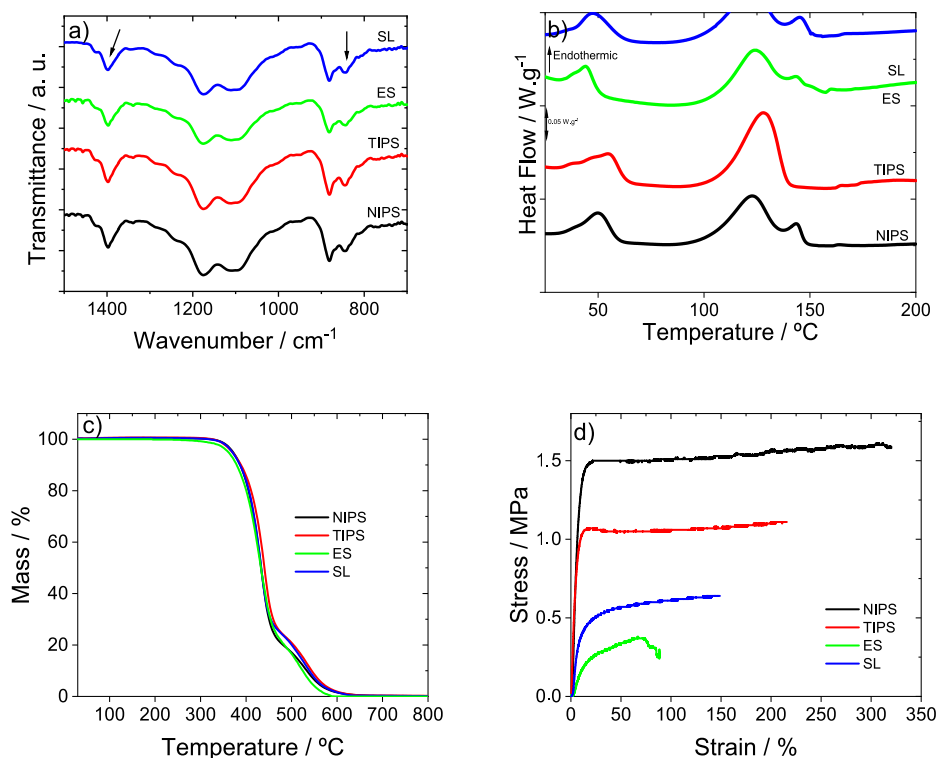


Fig. 4. a) FTIR spectra, b) DSC and c) TGA thermal characteristics and d) stress-strain mechanical curves for the P(VDF-TrFE-CFE) membranes.

sizes, following by the ones prepared by ES and NIPS. In relation to the membranes produced by SL, they present the smallest distribution of pore sizes.

Considering that membrane shrinkage is an important factor in battery systems, Fig. 3a) shows photographic images of the TIPS membrane before and after thermal treatment at 100 °C for 1 h. For other membranes, the behavior is similar. Fig. 3a) shows that the membranes

show high thermal stability, not showing any relevant shrinkage after the thermal treatment.

Fig. 3b) and c) show the contact angle for the different membranes in water and electrolyte solution, respectively. For water (Fig. 3b), it is observed that the contact angle is greater than 78°, demonstrating the hydrophobic character of this polymer [32]. The observed differences in contact angle between the membranes is fully related to the differences

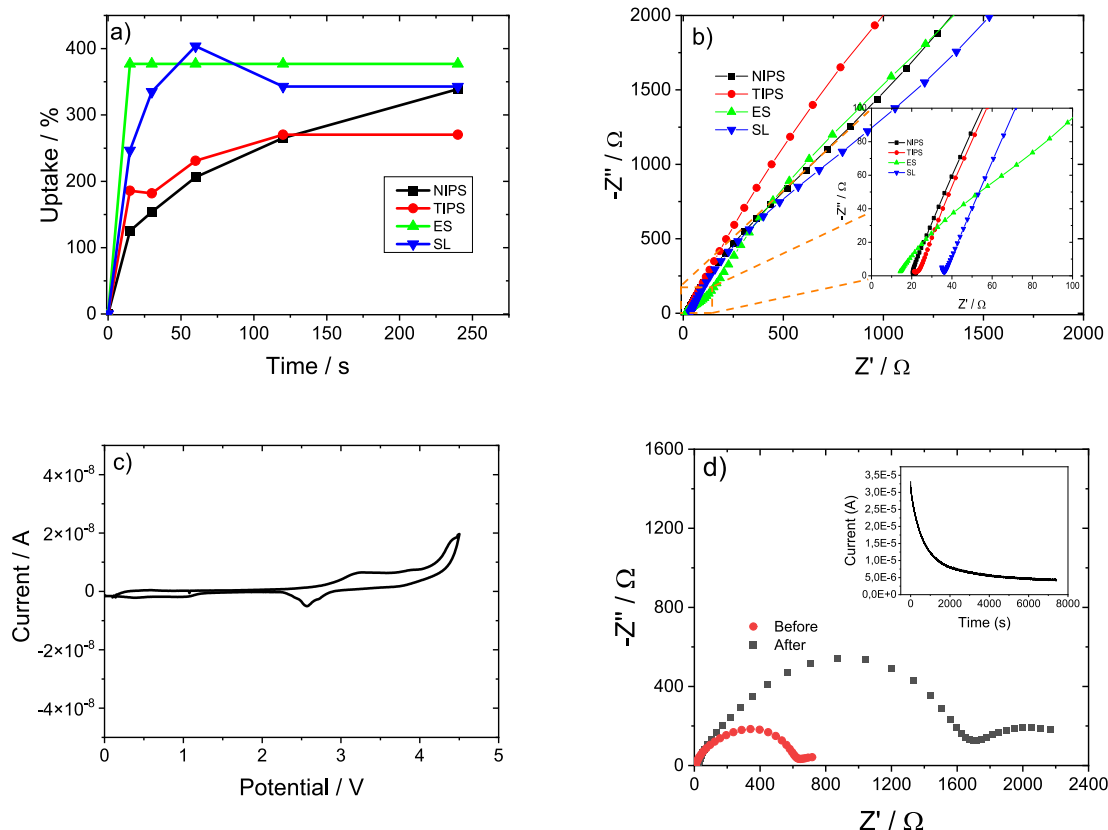


Fig. 5. a) Electrolyte uptake process, b) Nyquist plot at room temperature for the P(VDF-TrFE-CFE) membranes. c) CV curve and d) DC polarization measurements for the P(VDF-TrFE-CFE) membrane produced by salt leaching.

in morphology.

Fig. 3c) shows the contact angle of the membranes for electrolyte solution, the contact angle being less than 57° . For the ES membrane, the electrolyte droplet is immediately absorbed due to its morphology. Thus, good wettability of the P(VDF-TrFE-CFE) membranes by the electrolyte is demonstrated, due to the compatibility between polymer surface and the organic solvents in the electrolyte solution. This will allow efficient paths for migration of Li^+ ions across the membrane.

3.2. Infrared spectra, thermal and mechanical characteristics

The polymer phases present in the P(VDF-TrFE-CFE) membranes obtained through different processing techniques were evaluated by Fourier transform infrared spectroscopy (FTIR) and the respective spectra is shown in Fig. 4a.

Regardless of the processing technique, Fig. 4a shows the characteristic bands of the P(VDF-TrFE-CFE) polymer at 841 and 1400 cm^{-1} , related to the polar β -phase of the polymer, and CH_2 and CF_2 rocking and CF_2 antisymmetric stretching vibration bands, identified with an arrow in this figure [26].

The quantification of β -phase ($F(\beta)$) of the membranes was obtained through Eq. (6) [33]:

$$F(\beta) = \frac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right)A_\alpha + A_\beta} \quad (6)$$

where the absorbances A_α and A_β at 766 and 840 cm^{-1} correspond to the α or β phases, respectively, and K_α and K_β are the corresponding absorption coefficients, 6.1×10^4 and $7.7 \times 10^4\text{ cm}^2\cdot\text{mol}^{-1}$.

The β -phase ($F(\beta)$) content of different membranes is summarized in Table 1, showing values $\sim 84\%$ for all the samples, independently of the processing technique. Thus, the chemical composition of the terpolymer

and the low temperature processing determine the specific phase content in the samples [25].

The thermal behavior of the different P(VDF-TrFE-CFE) membranes was evaluated by the DSC (Fig. 4b) and TGA (Fig. 4c). Independently of the processing technique, the DSC heating thermograms of the membranes (Fig. 4b) show two endothermic peaks at $\sim 50^\circ\text{C}$ and 124°C , for all samples, related to the ferroelectric-paraelectric phase transition and the melting temperature, respectively [26].

Nonetheless, an additional peak above 124°C is observed for all membranes, excepting the ones prepared by TIPS, related to the melting of crystals of different sizes [34].

The degree of crystallinity value of the different membranes was calculated by Eq. (7):

$$\chi_c = \frac{\Delta H}{x\Delta H_\alpha + y\Delta H_\beta} \quad (7)$$

where ΔH is the melting enthalpy, x and y represent the α and β phase content of each sample, as calculated from the FTIR results, and ΔH_α and ΔH_β are the melting enthalpies of the α ($93.07\text{ J}\cdot\text{g}^{-1}$) and β phase ($103.4\text{ J}\cdot\text{g}^{-1}$) of PVDF [35], respectively.

The degree of crystallinity values of the P(VDF-TrFE-CFE) membranes is presented in Table 1, showing that it is practically constant

Table 2

Ionic conductivity (σ_i), tortuosity (τ), MacMullin number (N_M) and lithium transference number (t_{Li}) values of the different porous membranes.

Samples	$\sigma_i/\text{mS}\cdot\text{cm}^{-1}$	τ	N_M	t_{Li}
NIPS	0.4	2.6	29	0.2
TIPS	0.2	6.2	58	0.55
ES	1.8	1.9	6.4	0.37
SL	0.4	2.6	29	0.55

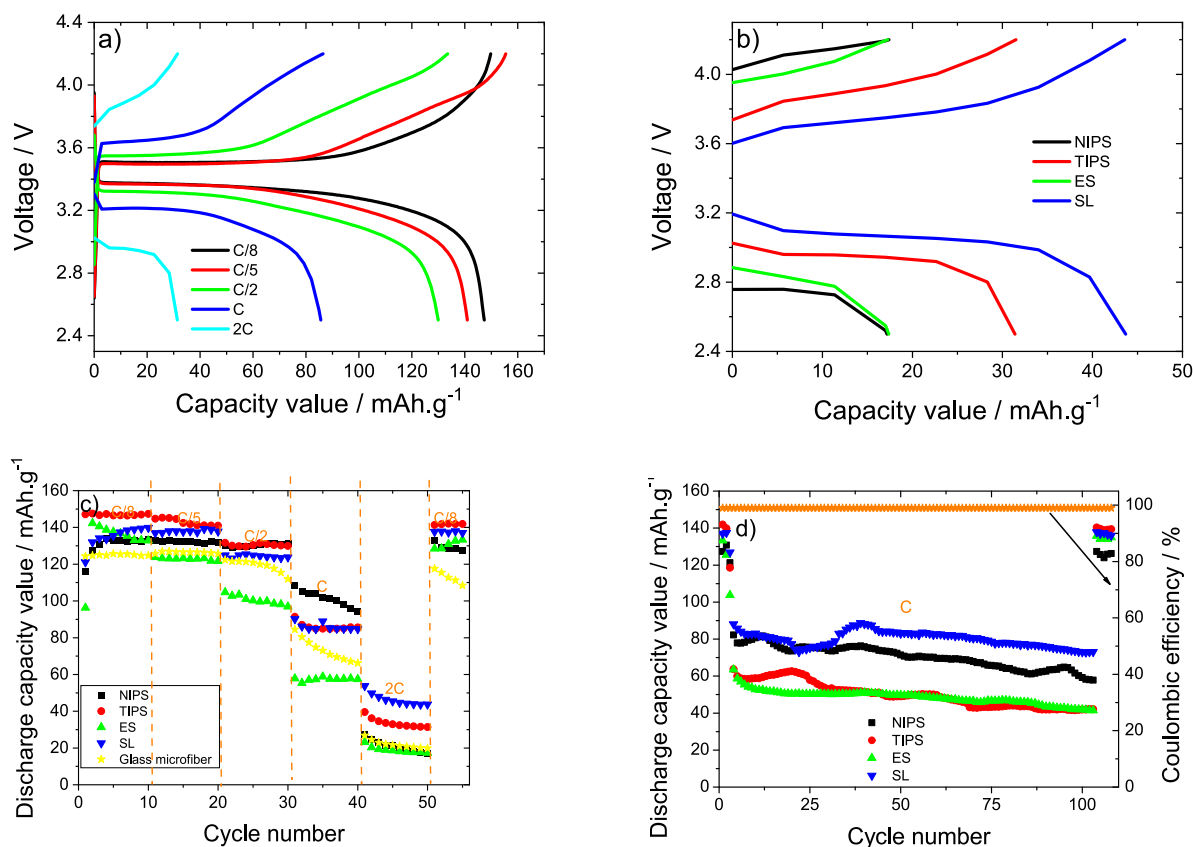


Fig. 6. a) 5th Charge/discharge profiles at different C-rates for P(VDF-TrFE-CFE) membranes produced by TIPS, b) 10th charge/discharge profile at 2C-rate for all P(VDF-TrFE-CFE) membranes, c) rate performance and d) cycle life behavior for the P(VDF-TrFE-CFE) membranes.

(9–12 %) for all membranes, independently of the processing conditions. The low crystallinity is due to the presence of the TrFE and CFE monomers which reduce the degree of crystallinity in relation to the PVDF polymer [36].

Fig. 4c shows the TGA curves of the different P(VDF-TrFE-CFE) membranes. Regardless of the processing technique, a single degradation step is observed at ~ 455 °C related to the scission of carbon – hydrogen (C–H) bonds in the polymer chains [26].

The mechanical properties were evaluated by tensile stress–strain measurements as shown in Fig. 4d, where porosity plays an important role in the mechanical response, since the degree of crystallinity is practically the same for all membranes, as verified by DSC analysis. Regardless of the processing technique, Fig. 4d shows the typical mechanical behavior of a thermoplastic polymer with elastic and plastic regions and yield point [36]. Table 1 shows the Young's modulus calculated from the secant method at 3 % of strain and yield stress and strain for all membranes. It is observed that the membrane processed by NIPS is the one with the highest Young's modulus, accompanied by a low degree of porosity. Nonetheless, the membrane produced by SL also shows a low degree of porosity but the lowest Young modulus, due to the irregular porous morphology. Furthermore, the electrospun membranes exhibit lower mechanical behavior due to the fiber structure. Despite the different mechanical properties observed, all membranes can be used as separators in lithium-ion battery applications [37].

3.3. Uptake and electrochemical characterization

Electrolyte uptake, ionic conductivity value and electrochemical stability of the separators are essential characteristics for battery applications. The absorption of electrolyte depends on the morphology and

also on the interactions between the electrolyte solution and the porous membrane, in which good wettability correlates with good transport behavior [38].

Fig. 5a shows the electrolyte uptake behavior for all P(VDF-TrFE-CFE) membranes, the processing technique and, therefore, microstructure of the membranes strongly affects this behavior. Independently of the processing technique, the uptake process is completely stabilized after 250 s. Furthermore, it is observed that this behavior does not depend on the degree of porosity, but rather on the size and structure of the pores (Fig. 5a) and Fig. 1).

The membrane with highest electrolyte uptake is the one produced by electrospinning, due to the fiber structure and the corresponding high surface area for interacting with the electrolyte. Furthermore, this behavior is similar for the membrane obtained by SL, due to the presence of large pores in this membrane and low porosity value.

For the other techniques (NIPS and TIPS), a similar effect is observed. All morphologies present empty pores with small size and different porosity value. Further, the electrolyte also enters within the amorphous phase and, therefore, affects the uptake process.

Separator-electrolyte interactions are critical for lithium transport behavior, affecting ionic conductivity and lithium transference number. Fig. 5b shows the Nyquist plot at room temperature for the P(VDF-TrFE-CFE) membranes. From Fig. 5b and Eq. (2), the ionic conductivity value is calculated through the bulk resistance and the corresponding values are shown in Table 2.

Independently of the processing technique, the Nyquist plot present a straight line related to the charge transfer process, indicating high ionic conduction [39].

Table 2 shows the ionic conductivity value for the P(VDF-TrFE-CFE) membranes and a correlation is observed between the electrolyte uptake

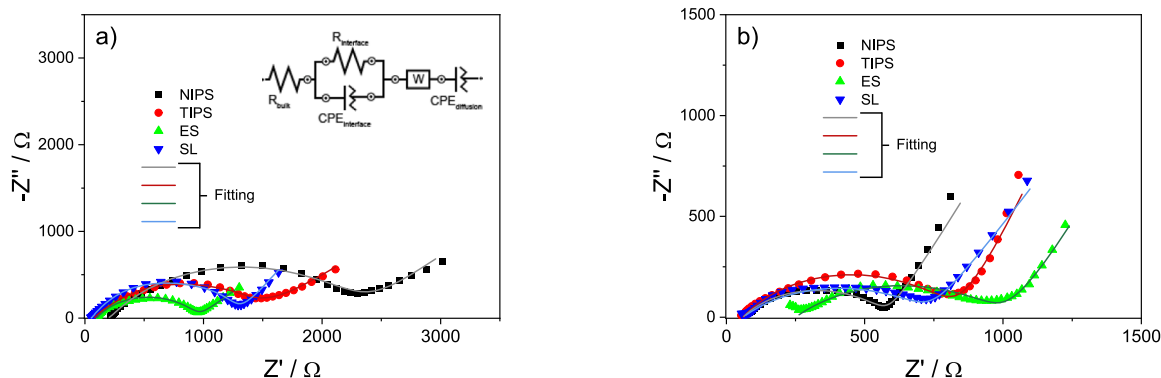


Fig. 7. Electrochemical impedance spectroscopy for the P(VDF-TrFE-CFE) membranes: a) before and b) after cycling process.

and the ionic conductivity, i.e., the membranes with the highest electrolyte uptake value show a higher ionic conductivity. The highest ionic conductivity ($1.8 \text{ mS} \cdot \text{cm}^{-1}$) is obtained for the electrospun membranes, resulting from its fibrous structure with high internal surface area, that promotes the best interaction between electrolyte solution and the polymer membrane. The lowest ionic conductivity value of $0.2 \text{ mS} \cdot \text{cm}^{-1}$ is observed for the membrane produced by TIPS, due to the low electrolyte uptake capacity.

Table 2 also presents the tortuosity (τ) and MacMullin number (N_m) parameters obtained from Eqs. (3) and (4), respectively. For both parameters, a correlation is observed with the ionic conductivity value, a low tortuosity value ($\tau = 1.9$) being obtained for the electrospun membrane. It is to notice that this value is close to the ideal tortuosity value ($\tau = 1$) and together with the high ionic conductivity, indicate an excellent ion transport path for this morphology [40].

Moreover, the MacMullin number (N_m) of the membranes range between 6.4 and 58.0, values obtained for the membranes produced by electrospinning and TIPS, respectively. The low N_m value is due to the higher ionic conductivity value. This value is lower than the values obtained for commercial separators [40], which is adequate to obtain excellent cycling behavior.

The electrochemical stability of the membranes was evaluated by room temperature CV measurements, as shown in Fig. 5c for the membrane prepared by SL in order to evaluate the oxidation (initial sweep in the positive direction) and reduction process (reverse sweep in a negative direction). This curve is representative for the rest of the membranes. Analyzing Fig. 4c, it is observed that the current value is below 10^{-8} A with good electrochemical stability between 0.0 and 4.5 V vs Li/Li⁺ without anodic peaks. The value of the small reduction peaks observed does not affect its stability.

DC polarization measurements were performed to evaluate the lithium-ion transference number, t_{Li}^+ , as shown in Fig. 5d. Fig. 5d shows these measurements for the P(VDF-TrFE-CFE) membrane produced by SL, which is representative for the other membranes. t_{Li}^+ was calculated using the Bruce and Evans method [28,29] and the values are presented in Table 2, which shows no correlation between electrolyte uptake and t_{Li}^+ values for the different membranes. Also, a high t_{Li}^+ is detected for the membranes prepared by SL and TIPS with lower ionic conductivity value, where their morphology and pore size play an important role in this behavior. Furthermore, the obtained values for the membranes produced by these techniques are higher compared to the ones of commercial polyethylene separator [41].

3.4. Battery performance

Half cells with LFP based electrodes were produced with the different P(VDF-TrFE-CFE) membranes to evaluate the room temperature charge-discharge behavior between 2.5 and 4.2 V, between C/8 and 2C-

rates. For each C-rate and P(VDF-TrFE-CFE) membrane, ten charge-discharge cycles were performed. Fig. 6a shows the cycling profile of the battery with P(VDF-TrFE-CFE) membranes produced by TIPS at C/8, C/5, C/2, 1C and 2C rates, the presented profile corresponding to the tenth cycle of each rate. For the rest of the membranes the profile is identical to those observed in Fig. 6a.

For all C-rates, Fig. 6a presents the anodic/cathodic peaks related to the LFP electrode that represent the lithium insertion in the discharge process and the lithium removal in the charging process, respectively. Furthermore, it is observed a flat charge-discharge plateau around 3.2–3.6 V, corresponding to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction [42]. Further, it is detected that the plateau potential and the capacity value decrease when the C-rate increases due to the polarization behavior inside the cathode electrode [43]. The discharge capacity value of the P(VDF-TrFE-CFE) membrane produced by TIPS is $147 \text{ mAh} \cdot \text{g}^{-1}$, $141 \text{ mAh} \cdot \text{g}^{-1}$, $129 \text{ mAh} \cdot \text{g}^{-1}$, $86 \text{ mAh} \cdot \text{g}^{-1}$ and $32 \text{ mAh} \cdot \text{g}^{-1}$ at the C rates of C/8, C/5, C/2, 1C and 2C (Fig. 6a), respectively, demonstrating good battery performance at different rates and excellent reversibility behavior due to the high lithium transference number of this membrane.

In order to assess the charge/discharge profile for the different membranes, Fig. 6b shows the tenth profile behavior at the 2C-rate. It is observed that the processing technique and the corresponding morphological variation of the membranes affects the cycle behavior and the discharge capacities at 2C-rate, which are $44 \text{ mAh} \cdot \text{g}^{-1}$, $32 \text{ mAh} \cdot \text{g}^{-1}$, $17 \text{ mAh} \cdot \text{g}^{-1}$ and $17 \text{ mAh} \cdot \text{g}^{-1}$ for SL, TIPS, ES and NIPS obtained membranes, respectively. These different discharge values are correlated with the lithium transference number of the membranes (Table 2), being higher for membranes with a higher lithium transference number.

Fig. 6c shows the rate performance of the different membranes as a function of the number of cycles. For each rate and membrane, the discharge capacity value remains constant for the different number of cycles.

Regardless of the membrane type and the C-rate up to the C/5-rate, it is observed that the discharge capacity is stable for all membranes. The ES membrane shows lower discharge capacity compared with the other samples independently of the applied C-rate, which can be associated to the high uptake value compared to the other samples. At C-rates above C/2, different cycling behaviors are observed for the membranes obtained by the different processing techniques. For 2C rate, the highest discharge capacity is observed for the membrane processed by SL due to the higher lithium transference number with respect to the other membranes. Fig. 6c) shows the battery performance at different C ratios of the different P (VDF-TrFE-CFE) membranes compared with commercial glass microfiber separators. It is observed that the discharge value of P(VDF-TrFE-CFE) membranes produced by SL and NIPS is higher compared to the glass microfiber separator.

This behavior is also demonstrated in Fig. 6d for the cycling stability evaluation at C-rate for 100 cycles, where the combination of different

Table 3

Equivalent circuit parameters of the assembled batteries.

		R1 (Ω)	R2 (Ω)	CPE (nF)
NIPS	before	123	2075	0,63186
	after	62	523	0,59407
TIPS	before	83	1342	0,6284
	after	57	760	0,62174
ES	before	100	850	0,36203
	after	252	747	0,4968
SL	before	58	1244	0,724
	after	62	677	0,50251

parameters of the separator, such as the degree of porosity, ionic conductivity value and lithium transference number are essential in cycling behavior. For the first cycles, it is detected that the discharge capacity decreases, as the C-rate increases until the C-rate is reached. After 100 cycles at C-rate, the discharge capacity values are 74 mAh.g^{-1} , 58 mAh.g^{-1} , 42 mAh.g^{-1} and 42 mAh.g^{-1} for SL, NIPS, TIPS and ES, respectively, with low capacity fade and excellent coulombic efficiency of $\sim 99\%$ for all samples, related to the excellent wettability of the electrolyte solution and its compatibility with the polymer membrane.

To evaluate the effect of the different membranes on battery performance, impedance spectroscopy measurements were performed before (Fig. 7a) and after (Fig. 7b) cycling, as represented by the corresponding Nyquist plots.

Fig. 7 shows that the Nyquist plots for all samples is characterized by Ohmic resistance at high frequency, represented by a semicircle, and an overall resistance that corresponds to the charge-transfer resistance at the solid-film interface and lithium resistance to ionic migration at the solid-electrolyte interface (SEI) in the medium frequency range [43]. At low frequency, an inclined line is observed that represents the Warburg impedance related to Li^+ diffusion [43]. The corresponding equivalent circuit and the fitting of the curves are presented in Fig. 7 [44,45]. In this circuit, two resistances are represented (R1 and R2) which correspond to the bulk resistance battery internal resistance, respectively. Additionally, there are two capacitors ($\text{CPE}_{\text{interface}}$ and $\text{CPE}_{\text{diffusion}}$) that correspond to the capacitance at high and low frequencies, and the Warburg element (W), representing the ion diffusion phenomena [46]. Further, the values of the different elements of the equivalent circuit obtained after fitting the experimental curves are shown in Table 3, before and after battery cycling.

Fig. 7a and Table 3 shows that the overall resistance before cycling is 2198Ω , 1425Ω , 1302Ω and 950Ω for NIPS, TIPS, SL and ES obtained membranes, respectively. After cycling (Fig. 7b and Table 3), it is

observed that the overall resistance values decrease due to the formation of the SEI layer during the cycling process. The overall resistance values are 585Ω , 739Ω , 999Ω and 817Ω for NIPS, SL, ES and TIPS obtained membranes, respectively.

Regardless the P(VDF-TrFE-CFE) membrane type, it is detected that, after cycling, the overall resistance is lower compared to the resistance before cycling (Table 3), due to the excellent compatibility between the separator and the electrode hinting a good interface between these components. A similar behavior is observed for the capacitance value (C), except for the ES sample. The capacitance value represents the capacity of the battery to store charge at the electrode/electrolyte interface. This means that higher capacitance values correspond to better surface properties. The high capacitance value of the SL corroborates the good performance results, while the loss of capacitance follows the trend of lower cycling stability after a prolonged number of cycles for all samples except the ES one.

Table 4 compares the main electrochemical parameters and discharge capacity value of the P(VDF-TrFE-CFE) membrane with related membranes based on PVDF and its copolymers reported in the literature.

This is the first time that this polymer type has been reported as a separator membrane for lithium-ion battery applications, and the battery performance is comparable to other PVDF polymer-based separators with special relevance considering the excellent cycling behavior at high C rate due to the low degree of crystallinity.

Therefore, the present work demonstrates that it is possible to obtain high-performance separators based on P(VDF-TrFE-CFE) polymers, the processing technique allowing to tailor their morphology and, consequently, electrochemical parameters and battery performance. In this sense, the membrane prepared by salt leaching is the most suitable for this application based on cycling behavior.

4. Conclusions

This work evaluated the effect of different processing techniques (non-solvent and thermally induced phase separator, salt leaching and electrospinning) on the battery performance of separator membranes based on poly(vinylidene fluoride-co-trifluoroethylene-chlorofluoroethylene), P(VDF-TrFE-CFE).

Using different processing techniques, distinct morphologies were obtained with variable degrees of porosity and pore sizes, which affect the mechanical behavior and porosity of the membranes, which ranges from 24% to 66% for the membranes obtained by NIPS and TIPS respectively.

There are no significant variations in the polymer phase content and thermal characteristics of the different membranes. The mechanical properties follow the tendency of the degree of porosity with different morphologies since the degree of crystallinity is practically the same for

Table 4

PVDF based separator membranes in LIB applications.

Polymer matrix	Electrolyte	Porosity/Uptake (%)	Ionic conductivity (mS. cm^{-1})	Discharge capacity (mAh. g^{-1})	Ref
PVDF	1 M LiPF_6 in EC:DMC	64.5/303.8	1.2	141@0.5C	[47]
PVDF	1 M LiPF_6 in EC:DMC	—/540	—	98@0.1C	[48]
PVDF	1 M LiPF_6 in EC:DEC	20/100	0.23	56@2C	[49]
PVDF	1 M LiPF_6 in EC/DMC/EMC	—/—	0.30	120@0.2C	[50]
PVDF-TrFE	1 M LiPF_6 in EC:DMC	70/120	1.6	107@2C	[51]
PVDF-TrFE	1 M LiPF_6 in EC:DMC	70/262	3	85.5@2C	[52]
PVDF-TrFE	1 M LiPF_6 in EC:DMC	72/84	2.6	155@0.1C	[53]
PVDF-HFP	1 M LiPF_6 in EC:DMC	72/77	1.3	122@0.1C	[54]
PVDF-HFP	1 M LiPF_6 in EC:DEC	228.5/—	—	80@2C	[55]
PVDF-HFP	1 M LiPF_6 in EC:DMC	78/86.2	1.03	145@0.5C	[56]
PVDF-CTFE	1 M LiTFSI in PC	60/275	1.5	92@2C	[57]
PVDF-CTFE + Sb_2O_3	1 M LiPF_6 in EC:DEC	72/356	2.88	167@1C	[58]
P(VDF-TrFE-CFE) produced by salt leaching	1 M LiPF_6 in EC:DMC	24/342	0.4	94@C	In this work

all membranes with adequate behavior of this application.

Regarding the electrochemical properties, the ionic conductivity and lithium transference number are significantly affected by the processing technique and a maximum ionic conductivity of 1.8 mS.cm^{-1} has been obtained for the electrospun membrane. For the lithium transference number, the values vary between 0.20 and 0.55 for the NIPS and SL membranes, this behavior being related to the membrane's morphology.

All separator membranes show excellent cycling behavior and reversibility. The membranes prepared by salt leaching show the best discharge capacity of 74 mAh.g^{-1} at 1C-rate after the 100 cycles.

Thus, it is concluded that the processing techniques allow to tailor the degree of porosity and pore size, which in turn has a significant influence on the electrochemical parameters and cycling behavior at different C-rates. In this scope, the membrane prepared by salt leaching represented an advanced compared to other PVDF polymers.

The new separator membranes based on P(VDF-TrFE-CFE) represent a step forward towards achieving higher performance lithium-ion batteries.

CRedit authorship contribution statement

Rafael S. Pinto: Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis. **João P. Serra:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **João C. Barbosa:** Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis. **Maria M. Silva:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Manuel Salado:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Arkaitz Fidalgo Marijuan:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Eder Amayuelas:** Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis. **Yaroslav Grosu:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Renato Gonçalves:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Senentxu Lanceros-Mendez:** Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Formal analysis. **Carlos M. Costa:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2024.11.013>.

Data availability

Data will be made available on request.

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