

Enhanced performance of fluorinated separator membranes for lithium ion batteries through surface micropatterning

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Keywords: PVDF-TrFE; patterned surface; membrane; lithium-ion battery; separator; polymer

Abstract:

The increasing demand on electronic and portable devices requires battery system with improved energy storage capacity. Thus, studies in all battery components are being carried out to increase their performance. One of those battery components in the separator membrane. The present work reports on porous poly(vinylidene fluoride-co-

trifluoroethylene) (PVDF-TrFE) separators with different patterned surfaces constituted by arrays of hexagons, lines, zig-zags and pillars microstructures and their influence on battery performance. Further, computer simulations allow to understand the influence of the patterned surface on battery response. It is observed that separator surface micropatterning increases battery performance. Thus, zig-zag surface micropatterning leads to a higher electrolyte current density (472.6 A.m^{-2}), improved uptake value (262%), and larger ionic conductivity (3.00 mS.cm^{-1}) than the non-patterned separator. The increase of electrolyte/separator contact area ($4.5 \times 10^{-7} \text{ m}$), leading to new pathways for lithium-ion diffusion, results in a discharge capacity efficiency $\sim 804\%$ (at 2C-rate) the one obtained for non-patterned separators. Thus, it is shown that micropatterning of separator membranes allow to significantly improve battery performance.

Keywords: PVDF-TrFE; patterned surface; membrane; lithium-ion battery; separator; polymer

1. Introduction

Nowadays, the area of energy is one of most studied ones due to its relevance both for supporting the technological advances and to address environmental issues. Further, the increasing energy consumption (in 2050 it is expected that the energy consumption double, compared with the present days) and the demand for electrical devices rises the necessity of improved energy storage systems. The efficiency of renewable energy sources has been increasing over the years, and, thus, the necessity of improved energy storage system is essential. In order to store the energy generated from renewable sources, different approaches have been developed, being lithium-ion batteries (LIBs) one of the most promising systems [1, 2].

Since their appearance in 1990's, LIBs were intensively investigated due to their low cost, no memory effects, high energy density, long cycle time and high-power density. With the increasing demand on electronic devices (including electrical vehicles), LIBs are forced to improve their performance, in order to be effectively applied in new/different fields. LIBs are mainly constituted by an anode, a cathode, an electrolyte solution and a separator and many efforts are being channeled to improve the performance, safety and recyclability of those components [3, 4].

The separator, although represents a passive component in the battery charge/discharge cycles, it was proven to play a key role in the performance, safety, durability and reliability of battery system. The separator is responsible for controlling the mobility and number of lithium-ions between the electrodes. Furthermore, the main purpose is to separate the anode and the cathode, avoiding short circuit of the system. The main characteristics of the separator include chemically stability, electrical insulation, ionic conductivity, thermal and mechanical stability, porous structure and wettability by the electrolyte, among others, in order to assure proper performance of the battery system [5]. The nature of the separator also influences battery performance, being the polymer matrix with electrolyte solution the most commonly used separator system. Separators can be classified in polymer blend electrolytes (PBE), single polymer electrolytes (SPE) and composite polymer electrolytes (CPE). One of the most used polymers for the development of these systems is poly(vinylidene fluoride) (PVDF) and its copolymers such as poly(vinylidene fluoride-*co*-trifluoroethylene) (PVDF-TrFE) [6].

SPE based on PVDF and copolymers show specific advantages for battery application when compared to other polymers, such as polyolefins, due to their chemical resistance, mechanical properties, high anodic stability, high dipolar moment, dielectric constant and

semi-crystallinity. The excellent properties of these polymers allow lithium salts ionization, good contact between electrodes and electrolyte and full control of porosity and structure [2, 6].

Together with the separator surface chemistry, the separator morphology also influences the ion diffusion and tortuosity. As a consequence, the electrochemical behavior and performance of the battery are deeply influenced by the lithium ion transport through the separator [7]. For example, separators with 3D structures with carbon and metallic particles within the polymer leads to an improvement of the ionic conductivity in an order of magnitude, from 10^{-7} to 10^{-6} S.cm⁻¹ [8].

In fact, the electrochemical performance of porous separators is highly influenced by the electrolyte distribution within their structure, porosity, tortuosity and wettability [9]. Simulations have been proven that high ion insertion capacity within the cathode can be achieved by increasing surface contact area with the separator, allowing to reach higher discharge rates [10].

Different separator structures with varying pore size distribution have been studied. The most commonly used separator structures are porous membranes [11] and electrospinning fiber membranes [2]. Different approaches to develop and use both structures have been implemented but up to now there is no established correlation between the structure and battery performance. On the other hand, general correlations have been demonstrated. Thus, it has been shown that the electrolyte ion transport characteristics are influenced not only by the chemical properties but also by the structure of the separator [12]. Separators membranes with linear pathways and low-tortuosity lead to stress-free pathways for ion transport, improving the separator performance [13]. Also, the interaction between lithium ions and the separator is influenced by the morphological features of the separator [14].

In this context, the present work evaluates the influence on battery performance of porous PVDF-TrFE separators with microstructured arrays of hexagons, lines, zig-zags and pillars on the membrane surface. Furthermore, a simulation study at different discharge C-rate was carried out to further understand the influence of the specific micropatterning on battery performance. Finally, the results are correlated with the morphology, structural, thermal, physical and electrochemical properties of the developed separators.

2. Experimental

2.1. Materials

Epoxy-based negative photoresist SU-8 100 and SU-8 developer were purchased from Microchem. Polydimethylsiloxane (PDMS) Sylgard® 184 was acquired from Dow Corning. Poly(vinylidene fluoride-*co*-trifluoroethylene) (PVDF-TrFE) 70/30 (70 mol% vinylidene fluoride monomer; 30 mol% trifluoroethylene) powder and N,N-dimethylformamide (DMF) were obtained from Solvay and Merck, respectively. Isopropyl alcohol (IPA) was purchased from Sigma Aldrich. Poly(vinylidene fluoride) (PVDF) was obtained from Solef 5130 Solvay, carbon black Super P-C45 from Timcal Graphite and Carbon, LiFePO₄ from Phostech Lithium and N-methyl-2-pyrrolidone (NMP) from Fluka at 99.9% purity. Lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate electrolyte (LiPF₆-EC-DMC) 1 M was purchased from Solvionic. All chemicals and solvents were used as received.

2.2. SU-8 and PDMS molds fabrication

SU-8 and PDMS molds were obtained by photolithography and replica molding techniques, respectively. SU-8 allows the fabrication of structures with good definition in the micrometer scale but present high stiffness and reacts with DMF. In turn, PDMS molds obtained through the SU-8 molds are chemically resistant and flexible, facilitating the detachment of the PVDF-TrFE membranes after processing. Both SU-8 and PDMS molds can be used dozens of times before being damage, reducing production costs [15]. SU-8 microstructures in an area of 2 cm² with arrays of hexagons, lines, zig-zags and pillars with width and spacing between arrays of 75 μm were fabricated, adapting protocol described in detail in [15]. A summary of the processing conditions is described in Table 1. Clean standard microscope glass slides (26 × 76 mm) were used as substrates. Further, during the pre- and postbake steps, the samples were submitted to a controlled heating rate of 2.5 °C.min⁻¹. Moreover, during the UV exposure, photolithographic masks previously designed and acquired from Microlitho were used. At the end of processing, the SU-8 structures were properly cleaned with IPA and gently dried with compressed air.

Before the fabrication of the PDMS molds, the glass slides with SU-8 microstructures along with clean glass slides free of structures were surrounded by aluminum adhesive tape to obtain molds with walls, capable of retaining PDMS solution [16]. Thus, 5 g of degassed PDMS mixture (1/10 wt% curing agent/base) were slowly poured in each mold, left to rest for approximately 10 min and cured using a hot-plate (Präzitherm PZ23-2) at a temperature of 100 °C during 30 min. Flat PDMS films were cut to obtained one piece with 3 mm wide walls that fit the back of the structured PDMS films. Thus, a very small amount of uncured PDMS solution was gently dispersed in the PDMS walls, glued around the structured PDMS films previously cut, peeled off from the SU-8 molds and cured for more 1 h at 100 °C. Alongside, structured-free PDMS molds were also fabricated to produce flat PVDF-TrFE membranes.

2.3. Fabrication of patterned PVDF-TrFE membranes

PVDF-TrFE/DMF solution with a copolymer volume fraction of 8 % was prepared dissolving the powder under magnetic stirring until a homogenous and clear solution was obtained. For that, a slight heating at 30 °C was used in the first 15 min of dissolution followed by approximately 1 h of mixing at room temperature. Then, the PVDF-TrFE solution was poured in each PDMS mold previously treated by oxygen plasma. This step is required to decrease the hydrophobic surface of the PDMS molds and guarantee the appropriate spread of the copolymer solution through the structures. For that, each PDMS mold was submitted to a plasma power of 100 W under an oxygen pressure bar of 0.8 mbar for 20 min (Electronic Diener Plasma-Surface-Technology, Zepto). The PDMS molds filled with PVDF-TrFE solution were left to dry at 25 °C during approximately 1 week in an air oven (JP Selecta 200208) to allow a slow and total evaporation of the solvent and consequently a porous morphology [17, 18]. After total crystallization, conventional non-patterned porous and patterned porous PVDF-TrFE membranes were removed from the respective molds and properly stored for further characterization and evaluation. The PDMS molds were gently cleaned with acetone and water and stored for further use.

2.4.Cathode and battery fabrication

The cathode used in all half-cell batteries was prepared by mixing the active material (LiFePO_4), the conductive material (Super P-C45) and the polymer binder (PVDF) in a solvent (NMP). The weight ratio of these solid components was 80:10:10 (wt%) and the solid/solvent ratio (wt%) was 1/2.25. Their thickness and porosity were 20 μm and 60 %, respectively.

The cathodes were dried at 90 $^{\circ}\text{C}$ in vacuum overnight and after transferred to a homemade argon-filled glove box, the batteries were assembled in Swagelok type cells. The Li/LiFePO₄ half-cells were prepared with a metallic lithium foil (8 mm diameter) as counter/reference electrode, a separator porous structure (10 mm diameter) soaked into the electrolyte (EC-DMC LiPF_6) and the prepared LiFePO_4 electrode film (8 mm diameter) as cathode. For the microstructured separators the patterned surface was placed in contact with the cathode electrode.

2.5.Characterization procedures

2.5.1 Physico-chemical characterization

The SU-8 and PDMS molds were evaluated using a stereomicroscope Leica M80, while the dimensions of the microstructures were confirmed using a surface profilometer Veeco Dektak 150. All processed PVDF-TrFE separators were also topographically and morphologically characterized by means of a scanning electron microscope (SEM) Quanta 650 FEG from FEI. The surface contact angle of the separators was measured using the Data-Physics Contact Angle System and the OCA20 software, using ultrapure water and the electrolyte (drop volume of 3 μL and rate of 0.5 $\mu\text{L.s}^{-1}$). Attenuated total reflection Fourier transformed infrared (FTIR-ATR) spectra of the separators were obtained in a Spectrum TwoTM from Perkin-Elmer, with 64 scans in the range between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} . Differential scanning calorimetry (DSC) was used to determine the degree of crystallinity of the samples. The measurements were performed using a DSC 6000 from Perkin-Elmer in pieces of approximately 6 mg cut and placed into a 40 μL aluminum pans. Thermogravimetric analysis (TGA) was carried out using a TGA 4000 from Perkin-Helmer in order to evaluate the thermal properties of the separators. Samples with 10 mg were cut and analyzed during heating scans between 30 and 800 $^{\circ}\text{C}$ at a heat flow of 10 $^{\circ}\text{C.min}^{-1}$.

2.5.2. Battery characterization

The uptake value of the separators at different times (0, 15, 30, 60 and 120 s), was obtained by the immersion of the separators into the EC-DMC electrolyte. The uptake percentage was obtained according to: $\text{uptake\%} = (m_i - m_0)/m_0 \times 100$, where m_0 is the mass of the dry separator and m_i is the mass of the separator after immersion. Ionic conductivity (σ_i) was calculated for all porous separators by complex impedance spectroscopy in the 500 mHz to 65 kHz frequency range, with an amplitude of 10 mV at room temperature, using Autolab PGSTAT-12 (Eco Chemie) equipment. To evaluate the cycling performance of the prepared half-cells a galvanostatic equipment Landt CT2001A was used. The measurements were performed at room temperature between 2.5 and 4.2 V at C/8, C/5, C/2, C and 2C scan rates ($C = 170 \text{ mA.g}^{-1}$ and the active mass loading is $\sim 2 \text{ mg.cm}^{-2}$). The cycling behavior was evaluated for each separator membrane in 6 half-cells. The electrical properties of the half-cells were evaluated, before and after cycling, by complex impedance spectroscopy using an Autolab PGSTAT12 instrument in the frequency range of 1 MHz - 10 mHz and an amplitude of 10 mV.

3. Theoretical study

3.1. Theoretical model

A typical lithium-ion half-cell structure [lithium foil | porous membrane of the different PVDF-TrFE separators soaked in 1M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate-dimethyl carbonate (EC-DMC) | porous positive electrode, (Li_xFePO_4)] was considered for the battery simulations at 25 °C, by applying the electrochemical model based on the Newman/Doyle/Fuller equations [19-21]. This electrochemical model describes all electrochemical processes that occur in the different battery components (electrodes and separator), based on a set of partial and ordinary differential equations, that were solved by finite elements numerical resolution method. The partial thermal model was coupled to the electrochemical behavior since some relevant parameters are dependent on battery temperature, such as the diffusion coefficient of Li-ions in the electrode, the ionic conductivity and the diffusion coefficient of the electrolyte and the reaction rate coefficient of the cathode [22, 23].

The evaluated porous separators (**Figure 1**) were the ones with hexagons, pillars, lines and zig-zag microstructures, together with the non-patterned separator.

Table 2 shows the main equations that govern the electrochemical phenomena that occur in the operation of a half-cell during to discharge and charge processes.

3.2. Specific parameters/initial values

For the different batteries (different separators) defined parameters were introduced according to the materials that were used as battery components (electrodes, separator and electrolyte) as well as the initial conditions of battery operation. The values of each parameter for the different components and initial values implemented are shown in **Table 3**.

According to the surface topography of the separators, the values of the corresponding geometrical parameters were defined as shown in **Table 4**.

4. Results and discussion

4.1. Simulation results

Computer simulations were performed to predict the contribution of the patterned surface of the separators to battery performance with respect to the conventional non-patterned separator. According to that, simulated discharges at different C-rates (1C, 10C, 20C, 30C, 40C, 50C and 60C, with $C = 170 \text{ mA.g}^{-1}$) were carried out for each case (**Figure 2**). Figure 2a represents the discharge capacity for each battery at 50C-rate. Similar response was obtained for all batteries, regardless the type of separator, at all C-rates (data not shown). The migration of the lithium-ions results in higher internal losses at higher currents, observing a decrease in the discharge capacity value and voltage plateau with increasing C-rate. The maximum theoretical discharge capacity for each battery was 34.8, 124.9, 126.6, 125.0 and 124.6 mAh.g⁻¹ for conventional, pillar, zig-zag, line and hexagon separators, respectively at 50C-rate.

Figure 2b shows the theoretical discharge capacity for each battery for all C-rates. It can be observed that the battery with conventional separator stops cycling at 50C. The theoretical discharge capacity decreases with increasing C-rate. For the batteries with conventional separators, this decrease is more marked after the 30C-rate. Thus, the patterning of the separator surface not just increases the theoretical capacity discharge of the battery but also allows the battery to achieve higher C-rates.

To understand the influence of separator patterning in battery performance, the ionic diffusion and ionic current density were evaluated in the electrolyte and the separators. For that, non-patterned, pillar and zig-zag separators were selected once present the highest (pillars and zig-zags) and the lowest (conventional non-patterned) theoretical discharge capacity. Figures 2c-e show the color mapping of the electrolyte current density for the selected samples measured across a plane of the sample. The non-patterned separator (Figure 2c) shows a uniform ionic current density in all membranes. On the other hand, when the surface is patterned using, for example, pillars or zig-zags, the ionic current density distribution is changed across the membrane, and higher ionic current density is verified in the electrolyte region, compared with the separator region. To quantify the ionic current density on the separators (Figure 2f), the measurement of the interface between the separator and the cathode in a line situated on the plane represented in Figure 2c-e, was performed. The highest value of ionic current density for each separator was around 6.4, 4.2 and 472.6 A.m⁻², for non-patterned, pillar and zig-zag separators, respectively. The high ionic current density is attributed to a better diffusion of the ions in the channels formed within the zig-zag separators due to increased ions flow in this sample by improved effective conductivity of the separator membranes filled with electrolyte.

Further, **Figure 3** also shows the representation of the ionic current density vectors for the same samples.

It can be observed that the ionic current density varies across the sample. The ion diffusion mainly occurs in the electrolyte and less in the separator due to the high electrolyte ionic conductivity, as already reported in [7]. This high ionic conductivity and high number of ion transference prevents the formation of lithium dendrites once concentration near the electrodes is lower [24].

With the obtained results it is concluded that the separator with different patterned surfaces allows to tune the battery capacity discharge when compared to the conventional non-patterned separator. The ion diffusion is essentially realized by the electrolyte solution and less from the separator.

In the following, the experimental study is presented supporting the results obtained in the simulations.

4.2. Morphology and physico-chemical results

Proper characterization of the separator morphology is essential not only to confirm the patterned surface, but also to determine the membrane porosity, which is required when applied as separator in lithium-ion batteries. For that evaluation, SEM imaging was used and the results are shown in **Figure 4**. For all samples (Figure 4a-f) a high porosity is confirmed with a mean pore size of 8 μm , suitable for electrolyte uptake. To evaluate the interconnectivity between pores, cross-section SEM images are presented in Figure 4b, as representative of all processed samples, showing interconnectivity of the porous structure as well as the homogeneous distribution of the pores all along the sample thickness. The SEM surface images also confirm the good definition of the patterns and absence of defects: non-patterned (Figure 4a), lines (Figure 4c), zig-zags (Figure 4d), pillars (Figure 4e) and hexagons (Figure 4f).

The chemical structural and thermal properties of the different PVDF-TrFE separators were evaluated using FTIR-ATR, TGA and DSC techniques (**Figure 5**). The chemical structural evaluation results are shown in Figure 5a and shows that all membranes crystallize in the trans TTT' polymer chain conformation, corresponding to the electroactive and polar β -phase, as identified through the 1400 cm^{-1} (CH_2 wagging and CC antisymmetric stretching), 1287 cm^{-1} (CF_2 and CC symmetric stretching and CCC bending) and 840 cm^{-1} (CF_2 symmetric stretching) bands [25]. Thus, that the processing conditions leading to the different patterns do not change the chemical structure of the copolymer membranes.

The TGA analysis (Figure 5b) shows that the thermal degradation behavior is the same for all samples. A characteristic single degradation step is observed between 430 and 500 $^{\circ}\text{C}$, related to chain-stripping by the carbon-hydrogen scissions and formation of hydrogen fluoride [26].

The DSC analysis allows to determine both melting temperature and degree of crystallinity of the samples (Figure 5c). The DSC scans show two characteristic endothermic peaks. The first peak at ~ 90 $^{\circ}\text{C}$ corresponds to the ferroelectric-paraelectric transition and the second peak at ~ 140 $^{\circ}\text{C}$ corresponds to the melting temperature of the paraelectric phase. The degree of crystallinity ($\Delta\chi$), calculated after $\Delta H / \Delta H_{100} * 100$, taking into account the enthalpy of a full crystalline sample (ΔH_{100}) = 91.45 $\text{J} \cdot \text{g}^{-1}$ [18],

remains approximately the same for all samples, 27.0 ± 0.5 %, demonstrating that it is not affected by the patterning of the membrane surface.

The surface hydrophobicity of the membranes is an important characteristic for battery separator application, as it determines the interaction with the electrolyte. Thus, the contact angle of each sample was determined and the results are shown in Figure 5d. The sample with conventional non-patterned surface shows the lowest contact angle, 107.8 ± 2.6 °, while the patterned membranes feature contact angles of 133.0 ± 0.1 °, 133.0 ± 0.8 °, 130.0 ± 2.9 ° and 123.6 ± 1.4 °, for the lines, zig-zags, pillars and hexagons, respectively, showing that patterning the surface of the PVDF-TrFE membranes increases the hydrophobicity of the samples. The contact angle measurements with the electrolyte were also evaluated and the results show that the samples are fully and rapidly wetted by the electrolyte (see section 4.3), demonstrating their suitability for battery separator membranes.

The tensile strength mechanical properties of PP Celgard 2400 separator are 14 and 142 MPa for transversal and machine directions, respectively [27]. The mechanical properties of the different structures are very similar and characterized by a tensile stress around 16.3 MPa (see figure S1 in the supplementary information for the zig-zag microstructure), revealing their suitability for LIBs separator applications.

4.3. Uptake behavior, ionic conductivity value and impedance

The uptake measurements were performed in all membranes (**Figure 6a**) to evaluate the ability of the electrolyte absorption within the separator. The different samples were exposed to the electrolyte over time and the results show that all samples reach the maximum uptake after 30 s. It was verified that the zig-zag microstructured separator shows the highest uptake value, ~262 %, comparing to ~230 %, ~214 %, ~207 % and ~220 % for the line, pillar, hexagon, line and conventional separators.

The ionic conductivity of the samples was obtained at room temperature, after full uptake process of the electrolyte, and the results are shown by the Nyquist plots of Figure 6b. A typical inclined straight line, indicative of the electrode/electrolyte double layer capacitance behavior, is observed for all separators. The bulk resistance of each separator can be determined by the interception of the high frequency value with the Z' axis of the Nyquist plot [28], Figure 6c showing the results of the bulk resistances for each separator. All separators show bulk resistances in the same order of magnitude the ionic conductivity

being 3.81, 2.77, 3.45, 3.00 and 3.96 mS.cm⁻¹ for conventional, line, hexagon, zig-zag and pillar membranes, respectively. The high ionic conductivity of the samples contributes for a good diffusion of the lithium-ion in the porous separator membranes filled with the electrolyte.

Electrochemical impedance spectroscopy (EIS) measurements of the half-cells prepared with the different separator membranes before cycling (Figure 6d) allow to understand cycling performance and interfacial properties. The Nyquist plots display a semicircle in the high/medium frequency region, related to the overall resistances (composed by ohmic, contact film and charge transfer reaction) and a linear increase in low frequency region is associated to the lithium ion diffusion in the active material within the cathode. The overall resistance for each separator was 1251, 668, 1042, 1656 and 1389 Ω for the hexagon, line, zig-zag, pillar and conventional membranes, respectively.

Impedance measurements of the half-cells with the different separator membranes, after cycling, were also obtained (**Figure 7a**). The impedance characteristic response of the half-cells before cycle, the semicircle and the linear rise regions, were also identified in the half-cells after cycling. The overall resistances obtained were 1645, 1480, 1952, 1943 and 6942 Ω for the hexagon, line, zig-zag, pillar and non-patterned separators, respectively. Comparing the results of the overall resistance before and after cycling, it is verified an increase of the resistance due to the formation of the solid electrolyte interface (SEI) layer and simultaneous reduction of the lithium ion diffusion with increasing number of cycles. This increase is more marked in the half-cells with conventional separator membranes, which increases from ~1389 to ~6942 Ω before and after cycling, respectively. The half-cells with patterned separators, compared with the conventional one, show a lower SEI formation (less impedance) after cycling demonstrating that the patterned membranes have a positive influence in battery impedance.

4.4. Charge/discharge behavior

The charge/discharge cycles were obtained in batteries constituted by the different types of micropatterned separators to evaluate their performance during cycles. The results show that all batteries present the same response behavior for the different C-rates (figure S2 in the supplementary information) being the fifth charge/discharge curves presented at 2C-rate (Figure 7b), for comparison.

The typical curve profile characteristic of C-LiFePO₄ is observed for all batteries below 2C, where the charge/discharge voltage is situated between 2.3 and 4.2 V (versus lithium windows). This electrochemical behavior is originated by the lithiation and delithiation during discharge and charge cycles, respectively, of the cathode active material [29]. The patterning of the separators influences the charge/discharge capacity and it is observed that patterning improves the capacity value of the batteries when compared with batteries with conventional non-patterned separators. This influence in the battery capacity demonstrates that surface patterning of the separator increases the discharge battery capacity from ~10.3 to ~85.5 mAh.g⁻¹ (at 2C-rate), for the conventional and the zig-zag membranes, respectively. The discharge capacity for the hexagon, line and pillar membranes were ~34.3, ~47.3 and ~65.7 mAh.g⁻¹, respectively. It was also verified that increasing C-rate leads to a decrease of the discharge capacity due to electrode polarization, related to the low electronic conductivity and low diffusion of the lithium ion within the separator. The battery with zig-zag separator shows the highest discharge capacity, associated to the high uptake value, ensuring high electrolyte content in this sample. The capacity fade of the batteries with the different separators was obtained, being 0.69, 0.59, 0.39, 0.42 and 0.91 for the hexagon, line, zig-zag, pillar and non-patterned separators, respectively. It is thus confirmed that the fact of the separator presenting surface patterning decrease the capacity fade value of the battery.

Rate capabilities of the half-cells during the discharge process at different C-rates (C/8 to 2C) were also obtained (Figure 7c). It is verified that the capacity discharge decreases with increasing C-rate. The results also show that the battery with zig-zag separator stand out from the others. For high C-rates between C/2 and 2C, all samples show high discharge capacity proving that patterning the separator surface positively influences the electrochemical performance of the battery. It is also shown that all samples show good recovery, situated at the last step of the rate capability study for the C/8. The recovery percentages for all porous membranes were 97.1, 96.7, 97.7, 96.3 and 97.7 % for hexagon, line, zig-zag, pillar and non-patterned separators-based batteries, respectively. The discharge capacities at 2C for each battery were 34.0, 47.8, 86.0, 65.9 and 10.7 mAh.g⁻¹ for hexagon, line, zig-zag, pillar and conventional membranes, respectively. The high discharge capacities of the batteries with pillar and zig-zag separators at 2C are in agreement with the simulation study once the membranes that feature high current density show higher discharge capacity. Also, the low electrochemical impedance of the zig-zag separator supports the better performance of this pattern.

The cycle performance and coulombic efficiency percentage at C- and 2C-rate were obtained for the patterned separators and the results are shown in Figure 7d. Sixty discharge cycles were obtained at C-rate and one hundred cycles were obtained at 2C-rate. The discharge capacities at 2C-rate were 9.1, 14.8, 29.1 and 102 for batteries with hexagon, line, zig-zag and pillar separators, respectively. The coulombic efficiency percentage is ~99 % for all patterned separators, showing good cycling stability. The results show that proper insertion and deinsertion of the lithium ion in the electrodes are realized maintaining the high discharge capacity. Contrary to what happens in the rate capacity at 2C, the battery with pillar separator shows higher discharge capacity value compared with the zig-zag one. This effect is observed due to a higher lithium ion accumulation during the cycles at the corners of the zig-zag (Figure 2e) compared with the pillar microstructured (Figure 2d) separator, which decreases the discharge capacity of the zig-zag separator. Further, the change in the direction of ion vector current density (Figure 3) at the corners of the patterns prove this behavior.

Comparing the discharge capacities of all patterned separators-based batteries, it is shown that the use of some patterns on the surface of the separator improve the discharge capacities compared to conventional separators. According to this, **Figure 8a** shows the discharge capacity efficiency percentage. The values were obtained comparing the batteries with patterned separators with the conventional ones. The results show that the batteries with zig-zag separator presents higher capacity discharge efficiency (~804%) compared with the other patterns as hexagons (~318%), lines (~447%) and pillars (~615%).

Contact area between the separator and the electrolyte were calculated for the micropatterned samples (Figure 8b). The contact areas between separator and electrolyte was performed for 310 μm (diameter) separators and values of 4.5×10^{-7} , 2.3×10^{-7} , 2.1×10^{-7} and 1.9×10^{-7} m were obtained, for zig-zags, pillars, lines and hexagons structures, respectively. The simulated diffusion studies show that the diffusion of ions is preferentially realized through the electrolyte and therefore, a high contact area between the separator and the electrolyte will promote more pathways to the ions to cross from separator to the electrolyte and the opposite. This behavior will lead to a better battery performance due to the good ion diffusion into the electrolyte, as demonstrated in the experimental results and simulations.

5. Conclusions

The present work demonstrated the improvement of battery performance through micropatterning of the separator membrane. Thus, the influence of separators with patterned surfaces, including arrays of hexagons, lines, zig-zags and pillars, in battery performance was evaluated and compared with the one of conventional non-patterned separators. Simulations studies were carried out to predict and understand battery behavior for such separators and the results were confirmed experimentally.

Simulations studies show that for low C-rates the samples have almost the same discharge capacity, being the main differences observe at high C-rates due to higher internal losses at higher currents. The maximum theoretical discharge capacity were 34.8, 124.9, 126.6, 125.0 and 124.6 mAh.g⁻¹ for conventional, pillar, zig-zag, line and hexagon separators, respectively at 50C-rate. The current density of the lithium ion is different for each membrane, being the highest for the zig-zag microstructured separator. The obtained electrolyte current densities were 6.4, 4.2 and 472.6 A.m⁻², for non-patterned, pillar and zig-zag separators, respectively.

The morphology of the different separators is characterized by an interconnected porous structure with average pore size of ~8 μm. Further, surface patterning does not influence the chemical, thermal and crystallinity characteristics of the separator membranes.

Uptake capacities is the large for the patterned separators, leading also to larger ionic conductivities when compared to conventional non-patterned separators. Compared with the conventional separator, patterned separators also show less SEI formation (less impedance) after half-cells cycling.

Surface patterning of the separators increases the discharge capacity from ~10.3 to ~85.5 mAh.g⁻¹ (at 2C-rate), for conventional and zig-zag separators, respectively, as increased contact area between the electrolyte and the separator leads to improved ion diffusion. The discharge capacity efficiency of batteries with zig-zag micropatterned separators is the largest among the patterned separators, being 804 % higher than the one for batteries with non-patterned separators. Thus, it is concluded that a simple procedure of surface micropatterning of separator membranes, allows to significantly enhance battery performance.

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Annex I: Nomenclature

<i>List of symbols</i>	
a	specific interfacial area, $\text{m}^2.\text{m}^{-3}$
C_L	concentration of Li ions in the electrolyte, $\text{mol}.\text{m}^{-3}$
C_E	concentration of Li ions in the electrode, $\text{mol}.\text{m}^{-3}$
D	diffusion coefficient of the salt in the electrolyte, $\text{m}^2.\text{s}^{-1}$
D_{Li}	diffusion coefficient of Li ions in the electrode, $\text{m}^2.\text{s}^{-1}$
F	Faraday's constant, $96487 \text{ C}.\text{mol}^{-1}$
f_{\pm}	activity of the salt in the electrolyte, $\text{mol}.\text{m}^{-3}$
i_E	current density in the electrode, $\text{A}.\text{m}^{-2}$
i_L	current density in the electrolyte phase, $\text{A}.\text{m}^{-2}$
I_{TOTAL}	total current density, $\text{A}.\text{m}^{-2}$
j_{Li^+}	pore wall flux of Li ions, $\text{mol}.\text{cm}^{-2}.\text{s}^{-1}$
L	width, m
d_{line}	distance between the lines, m
d_{col}	distance between the columns, m
d_z	distance between the zig-zag lines, m
dv_{hex}	vertical distance between the hexagons, m
dh_{hex}	horizontal distance between hexagons, m
h_{line}	depth of each line, m
h_{col}	height of each column, m
h_z	depth of each zig-zag line, m
h_{hex}	depth of each hexagon, m
L_z	length of each segment of the zig-zag line, m
L_{hex}	length of each side of the hexagon, m
M	mass transport flux, $\text{mol}.\text{m}^{-2}$
r_{col}	radius of each column, m
R	reaction term of the mass balance equation, $\text{mol}.\text{m}^{-3}.\text{s}^{-1}$
R	gas constant, $8,314 \text{ J}.\text{mol}^{-1}.\text{K}^{-1}$
R_f	film resistance, $\Omega \text{ m}^2$
R_i	radius of the electrode spherical particles, m
T	temperature, K

T_{∞}	External temperature, K
t	time, s
t_{+}^0	transport number of the positive ions
th_line	thickness of each line, m
th_z	thickness of each zig-zag line, m
u^0	open circuit voltage, V
N	number of digits for interdigitated and gear battery
A_i	area of a given component in the battery $i(i = a,s,c)$
p	Porosity of the separator
$brugg$	Brugg parameter in the electrodes
$E_{ad,i}$	activation energy for diffusion of electrodes $i(i = a,c)$, J.mol ⁻¹
$E_{ak,i}$	activation energy for reation of electrodes $i(i = a,c)$, J.mol ⁻¹
<i>Greek symbols</i>	
δ_z	angle between the zig-zag line segments, degrees
ε_i	porosity of region i ($i = a,s,c$)
$\varepsilon_{f,i}$	volume fraction of the fillers in the electrode i ($i = a,s,c$)
τ	tortuosity of the separator
η	over-potential, V
j_E	potential of the electrodes, V
j_L	potential of the electrolyte, V
κ_l	ionic conductivity of the electrolyte, S/m
$\kappa_{ef,i}$	effective ionic conductivity of the electrolyte i ($i = a,c$), S.m ⁻¹
κ_f	effective ionic conductivity of the separator polymer film, S.m ⁻¹
σ	electronic conductivity of the solid phase of the electrode i ($i = a,s,c$), S.m ⁻¹
$\sigma_{ef,i}$	effective electronic conductivity of the solid phase of the electrode i ($i = a,s,c$), S.m ⁻¹
ρ_i	density of battery components i ($i = a,s,c$), kg.m ⁻³

<i>Subscripts referring specific components of the battery and initial condition</i>	
a	anode
c	cathode
s	separator
0	initial condition