Porous Composite Bifunctional Membranes for Lithium-Ion Battery Separator and Photocatalytic Degradation Applications: Toward Multifunctionality for Circular Economy

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Circular economy paradigms will benefit materials with multifunctional properties allowing to be implemented in more than one application, after processed, or in one application after already being used in another. In this context, membranes based on TiO$_2$/poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) with different filler contents were prepared for battery and photocatalytic degradation of pollutants by a temperature-induced phase separation process (TIPS). It has been shown that the morphological, thermal and mechanical properties, porosity, contact angle, the ionic conductivity and lithium transference number are dependent on the TiO$_2$ content. The membranes with 10 wt% TiO$_2$ content show an ionic conductivity of 0.59 mS cm$^{-1}$, lithium transference number of 0.72, discharge capacity of 128 mAh g$^{-1}$ and low capacity fade (17%) at 2C. Further, this membrane presents a high photocatalytic response, being able to be used for ciprofloxacin remediation from water after 300 min of exposure to UV. Further, a second life was confirmed for this membrane by being implemented as a lithium ion battery separator after its use for water remediation applications. This work explores a new concept for the efficient use of the same membranes in very different applications, demonstrating the multifunctionality of the material in the scope of the circular economy paradigm.

1. Introduction

Energy and environment are at the top of the global problems that need to be addressed in the next decades.[1] In these fields, the focus is being shifted toward the development of technologies and devices for clean energy—conversion, storage, and conservation without fossil fuel dependence and environmental prevention, monitoring, and remediation avoiding the use of hazardous materials.[2]

Recent advances in materials for environmental and energy application tend to be in line with the circular economy (CE) principles.[3] The main actions of CE are usually known as the 3R’s: reduction, reuse, and recycling.[3c] The use of multifunctional materials, such as titanium dioxide (TiO$_2$), enables different applications, including batteries,[4] environmental remediation,[5] and antimicrobial,[6] among others,[7] allowing, therefore, multiple applications for specifically fabricated materials and even reuse in the same or different applications, providing materials with a second life.

The area of multifunctional materials is increasing, with continuous research and application on an industrial scale and with
strong impact on a significant number of application areas, such as sensors and actuators, energy storage systems, tissue engineering, and photocatalytic applications, among others.

Concerning energy storage systems, rechargeable batteries, and, in particular, lithium-ion batteries (LIBs) are playing an essential role based on their high energy density (both gravimetric and volumetric) and are present in various modern electronic equipment, such as mobile phones or laptops, among many other devices. LIBs are composed of three main components: cathode, anode, and a separator placed between these two electrodes, which is typically soaked in a liquid electrolyte, responsible for providing the ionic conductivity, whereas the separator prevents direct contact between the anode and the cathode, regulates cell kinetics, and promotes safety during charge and discharge processes. Its properties mainly depend on the thickness, permeability, overall porosity, pore size, pore interconnectedness, wettability, electrolyte absorption and retention, chemical, thermal, and mechanical stability, and the chemical interaction with the salts.

Most of the polymer materials used to fabricate the separators have some limitations, such as thermal and mechanical stability. To improve the separator properties, nanocomposites can be produced by adding different fillers to the polymer membranes. These fillers can be inert ceramic oxides, such as BaTiO$_3$, SiO$_2$, or TiO$_2$, lithium salts, or ionic liquids and may improve mechanical strength and wettability, thermal stability, or ionic conductivity.

TiO$_2$ is a widely used filler for separator membranes and has been combined with different polymeric matrices, including poly(vinylidene fluoride-co-hexafluoropropylene), (PVDF-HFP), polyethylene (PE), and polyvinylpyrrolidone (PVP). Porous membranes based on TiO$_2$ nanoparticles, in turn, have been often implemented in photocatalysis for the degradation of contaminants/organic pollutants from water. This process has some advantages, such as being eco-friendly, low cost, and simple.

TiO$_2$ is the most used photocatalyst due to its high photocatalytic activity, chemical stability, low toxicity, remarkable optical and oxidizing properties, durability, and low cost. Among the variety of works using TiO$_2$ as photocatalyst, TiO$_2$/poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) membranes have been demonstrated, suitable for the degradation of the antibiotic ciprofloxacin (CIP), one of the most prescribed antibiotics with increased persistence in effluents. The development of a highly functional porous matrix loaded with TiO$_2$ nanomaterials improves membrane performance, as it allows water percolation throughout the pores decorated with well-attached and functional nanoparticles.

The main objective of this work is to demonstrate, in the scope of the CE paradigm, the possibility of reusing TiO$_2$/PVDF-TrFE membranes as battery separator after being used in a photocatalytic application for CIP degradation. It is also important to mention that the CIP is a resilient pollutant that resists biological and chemical wastewater treatments (emerging concern pollutants). The obtained results validate the dual use of TiO$_2$/PVDF-TrFE membranes as well as the possibility of a second life, paving the way for a promising area for multiapplication and reuse of materials, ultimately assuring a more sustainable economy and environment.

Once again, environmental concerns imply focusing not only on application efficiency but also on materials sustainability and environmental impact. The robustness of the developed membranes allows efficient performances in both applications, the presented concept paving the way to process cost and environmental impact reduction by decreasing used material waste.

2. Results and Discussion

2.1. Physical-Chemical Properties of the TiO$_2$/PVDF-TrFE Membranes

The membrane morphology and the nanoparticle dispersion are essential parameters determining the membrane functional characteristics. In this way, surface and cross-sectional scanning electron microscopy (SEM) images of TiO$_2$/PVDF-TrFE membranes with different TiO$_2$ contents are shown in Figure 1.

Regardless of the TiO$_2$ content, all TiO$_2$/PVDF-TrFE membranes show a porous morphology with well-distributed pores all along the membrane (Figure 1a–d). The porous morphology is obtained due to the liquid/liquid spinodal decomposition, followed by the polymer crystallization, which is dependent on the solvent evaporation and polymer crystallization temperature. In addition, it is observed that the number and the size of the pores increase with increasing TiO$_2$ content.

The surface image of the TiO$_2$/PVDF-TrFE membrane with 20 wt% TiO$_2$ (Figure 1d) shows that the pores deviate from the circular shape due to the TiO$_2$ nucleation properties in the PVDF-TrFE that influence the solvent evaporation kinetics resulting in more ellipsoidal shape.

Figure 1e,f shows the cross-sectional images of the TiO$_2$/PVDF-TrFE membranes with 0 and 20 wt% TiO$_2$ content in two different magnifications, confirming the homogeneous distribution of the pores all along the membrane thickness, and that the pores are interconnected, which will allow electrolyte/water circulation within the membrane.

In addition, it is observed that the inclusion of TiO$_2$ affects the pore distribution of the TiO$_2$/PVDF-TrFE membranes and, their average pore size, ranging from 20 to 16 μm for 0 and 20 wt% TiO$_2$ content membranes, respectively.

Figure 1f shows that the TiO$_2$ nanoparticles are not incorporated within the polymer structure but decorate the inner walls of the polymer pores. This fact is related to the polymer crystallization process and has been observed for other fillers, such as zeolites and montmorillonite, among others.
Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra allow to identify and quantify the characteristic bands of the PVDF-TrFE polymer (Figure 2a). The characteristic vibrations bands of the all-trans chain conformation of the polymer (1402, 1180, 886, and 851 cm$^{-1}$) are identified, showing that the polymer crystallizes in this conformation regardless of the TiO$_2$ presence and contents. Furthermore, the nanoparticles show that the characteristic bands at 1624 and 3404 cm$^{-1}$ for Ti–O, Ti–OH, and OH groups bands (insert in Figure S1, Supporting Information), respectively, do not affect the polymer vibration bands.

The thermal properties of the pristine and TiO$_2$/PVDF-TrFE membranes were evaluated by means of differential scanning calorimetry (DSC) and thermogravimetric (TGA) techniques (Figure 2b,c). DSC curves for the different TiO$_2$/PVDF-TrFE membranes present two characteristic peaks at around 100 and 150 °C. The DSC scans for the pristine polymer and the TiO$_2$/PVDF-TrFE membranes are similar excepting for the membrane with 20 wt% TiO$_2$ content, which shows both peaks displaced to lower temperatures. Thus, larger filler contents slightly destabilize the different polymer phases and, therefore, the transition temperatures. The peak around 100 °C corresponds to the ferroelectric–paraelectric phase (FE–PE) transition phase, and the second peak around 150 °C corresponds to the melting of the crystalline phase of the PVDF-TrFE polymer. The melting temperature and degree of crystallinity for all TiO$_2$/PVDF-TrFE membranes are shown in Table 1, and the addition of TiO$_2$ nanoparticles does not affect the characteristic transition temperatures ($T_m$ and $T_c$) of the polymer.

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Table 1 shows the degree of crystallinity for TiO$_2$/PVDF-TrFE membranes, evaluated from the DSC thermograms, as a function of TiO$_2$ content, showing that it slightly decreases with increasing TiO$_2$ content in the polymer matrix, due to defective crystallization (nucleation and growth) of the PVDF-TrFE structure around the TiO$_2$ nanoparticles. In addition, TiO$_2$ inhibits the formation of polymer crystals when the content of TiO$_2$ nanoparticles increases, acting as a defect during polymer crystallization. The degree of crystallinity of the pristine PVDF-TrFE membrane is similar to that reported previously in the literature.

Figure 2c shows the TGA thermograms of the TiO$_2$/PVDF-TrFE membranes. Regardless of the TiO$_2$ content, the samples show a similar single degradation stage between 400 and 500 °C that corresponds to the chain stripping and bond scission between the carbon and the hydrogen (C–H), leading to hydrogen fluoride (HF). It is also observed that the TiO$_2$ content affects the polymer degradation step due to the increase in the interphase volume between the nanoparticles and the polymer. Furthermore, the presence of TiO$_2$ nanoparticles affects the
residual mass after 800 °C, which can be related to the interaction between the nanoparticles and the polymer matrix. In particular, for high filler loading contents (20 wt%), this mass is similar to the TiO$_2$/PVDF-TrFE membrane with 10 wt% of TiO$_2$ content due to larger interphase effects between the nanoparticles and the polymer for the latter, leading to a larger polymer residual mass.

To assess the mechanical integrity of the membrane separators applied to LIBs, Figure 2d shows the stress–strain curves of the PVDF-TrFE membranes with different TiO$_2$ contents. The membranes present the typical mechanical behavior of a thermoplastic polymer, characterized by elastic and plastic regions separated by the yielding region, and the addition of TiO$_2$ affects the mechanical properties.

The dimensional stability of the separators was evaluated through thermal treatment, the separator membranes showing high thermal stability as demonstrated by the photographic images of the TiO$_2$/PVDF-TrFE membranes with 0 and 10 wt% filler content (Figure S2, Supporting Information) before and after thermal treatment at 100 °C for 1 h.

This mechanical behavior is characterized by cold draws with necking down of the cross section in a limited area of the specimen that decreases with the addition of TiO$_2$ nanoparticles. The Young modulus of the membranes was determined at 2% of the maximum elongation in the elastic region by the tangent method, and the values are shown in Table 1. From Figure 2d and Table 1, it is observed that the Young modulus decreases with increasing TiO$_2$, indicating that the filler acts as defects in the polymer membrane, mainly due to aggregates from polymer–filler interface acting as defects for mechanical load distribution. In any case, the membranes show suitable mechanical properties to be used as separators in batteries systems, because the forces involved in the assembly of the batteries are around 1 MPa, lower than those shown in Figure 2d. Furthermore, the mechanical integrity is suitable for photocatalytic degradation applications.

The porosity of the membranes was evaluated by mercury intrusion porosimetry (MIP), and the obtained values are shown in Table 2. The degree of porosity of the polymer increases with the introducing of the TiO$_2$ filler in the matrix, excepting when 20 wt% of TiO$_2$ content was added. The presence of the filler affects the solvent evaporation kinetics and the degree of porosity of the pristine membrane that is ≈72%. For high

![Figure 2](image_url)
TiO₂ content of 20 wt%, the degree of porosity decreases due to the TiO₂ placement in the sidewalls of the polymer pores. The contact angle allows to determine the polarity of the membranes and, consequently, the wettability with the electrolyte solution. A high contact angle is obtained for the membranes up to 10 wt% of TiO₂ content (Figure S3a, Supporting Information), indicating that the hydrophobic nature of PVDF-TrFE[38] remains unaltered up to that filler content. The sample with 20 wt% TiO₂ content presents a lower contact angle, which is attributed to the TiO₂ nanoparticles that may interact with water through van der Waals forces. Furthermore, the incorporation of 20 wt% of TiO₂ into the polymer matrix leads to a different porous morphology, with irregular pores and more irregular surface that allows water penetration, reducing water contact angle.[39]

### 2.2. Uptake Process and Electrochemical Properties

The uptake values of the electrolyte solution in the TiO₂/PVDF-TrFE membranes are shown in Figure 3a. It is shown that after submerging the membrane 15 s in the electrolyte solution, the maximum uptake value is achieved and remains constant over time. The membrane with the highest uptake value is the PVDF-TrFE membrane without TiO₂ (1100046), due to the homogeneous porosity with interconnected pores where the electrolyte first fills the pores and then swells in the amorphous phase, being thus absorbed by the polymeric matrix. Moreover, the uptake value strongly decreases with the increase in the TiO₂ content, because the filler is placed on the sidewalls of the pores, reducing the electrolyte uptake. The lower electrolyte uptake is due both to the lower swelling of the amorphous phase of the polymer matrix due to the mechanical constrains imposed by the polymer–matrix interactions and to the lower degree of porosity and contact angle values.

Impedance spectroscopy was used to determine the ionic conductivity value of the membranes with the electrolyte solution, and Figure 3b shows the Nyquist plots for all TiO₂/PVDF-TrFE membranes, at room temperature. Typically, the Nyquist plot is characterized by a semicircle that corresponds to the charge transfer process. As measurements were carried out between Li electrodes, a second semicircle appears, corresponding to the Li electrode/electrolyte interface. With the addition of TiO₂, this semicircle decreases, indicating an improvement of the charge transfer process, as TiO₂ nanoparticles provide more channels for Li⁺ transport compared with the PVDF-TrFE membrane without TiO₂, resulting in the improved transport properties. The ionic conductivity (σ) is calculated from Equation (4), allowing to obtain the bulk resistance of the membranes through the fitting of such semicircle with the proposed equivalent circuit. The equivalent circuit is composed by an initial ohmic resistance (R₁) at higher frequencies due to the connections, a main semicircle which corresponds to the charge transfer process, and a second semicircle, typical when measuring between nonblocking electrodes, attributed to the Li electrode/electrolyte interface. It is observed that membranes with TiO₂ improve the ionic conductivity value in comparison with the pristine membrane, as the TiO₂ nanoparticles improve the transfer process, through the enhancement in the number of free ions and the reduction of the degree of crystallinity of the polymer matrix.[27] The low ionic conductivity value of the PVDF-TrFE membrane without TiO₂ is due to the higher degree of crystallinity, because the ion transport occurs in the amorphous region.[40] The obtained values are shown in Table 2. The membrane with 5 wt% of TiO₂ exhibits a higher conductivity, which is related to the high value of the degree of porosity, determining the uptake process.

Other important parameters of the separator membranes are the tortuosity (τ) and MacMullin number (Nm), which have been calculated from Equation (5) and (6), respectively (Table 2). It is observed that the addition of TiO₂ to the membranes decreases τ and Nm with respect to the pristine membrane.

### Table 2. Porosity, ionic conductivity, tortuosity, MacMullin number, and lithium transference number of the TiO₂/P(VDF-TrFE) membranes.

| %wt TiO₂ | Porosity [%] | nᵢ [mS cm⁻¹] | τ | Nm | t₁⁺ |
|----------|--------------|---------------|---|-----|-----|
| 0        | 72           | 0.026         | 16.54 | 308.0 | 0.25 |
| 5        | 87           | 1.02          | 2.90  | 9.7  | 0.48 |
| 10       | 76           | 0.59          | 3.58  | 16.8 | 0.72 |
| 20       | 68           | 0.305         | 4.69  | 32.4 | 0.81 |

Figure 3. a) Electrolyte uptake value as a function of time and b) Nyquist plot for the TiO₂/PVDF-TrFE membranes (insert: equivalent circuit).
This fact is due to the decrease in the pore size in the membranes compared with the pristine membrane and also due to the TiO$_2$ fillers on the side pore walls that affect the pore connectivity, resulting in lower values of tortuosity and MacMullin number. Those issues lead to an improvement of the mobility of Li$^+$ ions due to their interaction with the polar phase of the polymer.\cite{41}

The lithium-ion transference number, $t_{Li^+}$, determined from Equation (7) by a combination of alternating current (AC) impedance and direct current (DC) polarization measurements, Figure S3b and Table S1, Supporting Information, is an important parameter related to the Li-ion concentration carriers with respect to the total charge carriers in the electrolyte\cite{42} and shows a value between 0 and 1.\cite{43} For liquid electrolytes, a typical Li$^+$ ion transference number ranges between 0.3 and 0.4.\cite{44} Also, for PE separator, the typical value is 0.35.\cite{45} Table 2 shows that the lithium-ion transport number increases when increasing TiO$_2$ content due to the higher conductivity resulting from the interaction between pore-space surface with fillers and the liquid electrolyte that facilitates ion-pair dissociation.\cite{42}

### 2.3. Battery Performance

The electrochemical performance of the TiO$_2$/PVDF-TrFE membranes was evaluated in half-cells composed of C-LiFePO$_4$ (C-LFP) as cathode and Li metal as anode. Figure 4a shows the typical charge–discharge profiles of half-cells for the different samples for the fifth cycle at a scan rate of C/5. The profiles are shown for half-cells with a glass fiber separator and for half-cells with the different TiO$_2$/PVDF-TrFE separator membranes in the potential window between 2.5 and 4.2 V. It observed the typical plateau at around 3.4 V that corresponds to the presence of a two-phase coexistence reaction for LiFePO$_4$ cathode (Fe$^{2+}$/Fe$^{3+}$ redox reaction between FePO$_4$ and LiFePO$_4$).\cite{46} A similar electrochemical behavior for the membranes with 0, 5, and 10 wt% TiO$_2$ content is observed, with a high capacity around 140 mAh g$^{-1}$, which corresponds to 82% of the theoretical capacity (C = 170 mAh g$^{-1}$), whereas the TiO$_2$/PVDF-TrFE membrane with 20 wt% of TiO$_2$ shows a much lower capacity value when compared with the other membranes (71 mAh g$^{-1}$, 42% of the theoretical capacity). This behavior results from the combination of several factors, such as high electrolyte uptake, ionic conductivity, and lithium transference number values. It can be confirmed that the capacity value of the battery using the glass fiber is ≈100 mAh g$^{-1}$, below the values obtained for the pristine PVDF-TrFE separator and for the composite ones with 5 and 10 wt% TiO$_2$ content. Furthermore, it is also observed that the polarization of the battery using the glass fiber as separator presents a value much higher (792 mV) than for the TiO$_2$/PVDF-TrFE membranes (289 mV for PVDF-TrFE separator, decreasing down to 140 and 102 mV, with 5 and 10 wt% of TiO$_2$ in the composition).

Figure 4b presents the fifth charge/discharge profile at C/10 and C/10 recovery for the membrane prepared without TiO$_2$ and with 10 wt% of TiO$_2$, where it is possible to compare not only the two membranes but also verify the reversibility of the process. This reversibility evaluation is essential to know if the half-cells return to the initial performance after cycling at different scan rates. The pristine PVDF-TrFE membrane shows a discharge value of 148 mAh g$^{-1}$ for C/10 and 125 mAh g$^{-1}$ for C/10 recovery, showing a capacity loss of 15.5%. Thus, it is observed that the polarization increases, indicating a higher resistance in the battery, as a result of structural harms, which lead to irreversibility of the initial capacity.

The membrane with 10 wt% TiO$_2$ content, on the other hand, is characterized by a discharge value of 142 mAh g$^{-1}$ for C/10 and 140 mAh g$^{-1}$ for C/10 recovery, decreasing just 1.4% of its initial capacity after the galvanostatic charge–discharge (GCD) test, and the polarization remains practically constant, indicating that the presence of TiO$_2$ in the composition of the separator helps the separator/electrode compatibility and stability. This behavior indicates that the half-cell with TiO$_2$/PVDF-TrFE membranes can recover the discharge capacity values of the C/10 rate after cycling at different rates due to the combination of a high ionic conductivity and a high lithium transference number.

Figure 4c shows the discharge capacity value as a function of the number of cycles for the TiO$_2$/PVDF-TrFE membranes at different scan rates (C/10, C/5, C/2, C, 2C, and C/10 recovery, ten cycles for each rate). Regardless of the TiO$_2$ content, the discharge capacity value decreases, as the scan rate increases due to the ohmic polarization effect.\cite{47} For each scan rate, it is observed that the discharge capacity value remains constant over cycling, and that the TiO$_2$/PVDF-TrFE membranes with 10 wt% TiO$_2$ show the highest discharge capacity value for all scan rates due to the high ionic conductivity value (Table 2) and high lithium transference number (Table 2). For C and 2C rates, all TiO$_2$/PVDF-TrFE membranes show good electrochemical stability, and the membrane with 10 wt% TiO$_2$ content offers overall better battery performance. All TiO$_2$/PVDF-TrFE membranes, except the pristine membrane, are present at the C/10 recovery rate stable and similar values when compared with the C/10 rate, which indicates that regardless of the rate and cycling, the batteries containing TiO$_2$ can recover the initial values.

Considering that the TiO$_2$/PVDF-TrFE membrane with 10 wt% TiO$_2$ content shows the best cycling behavior, Figure 4c shows the cycle life at 2C rate for 100 cycles. At 2C rate, the discharge capacity value decreases from 117 to 97 mAh g$^{-1}$, whereas the capacity fade is 17% over 100 cycles, demonstrating excellent cycle stability. This low capacity fade at 2C rate is due to high lithium transference number, resulting in the better interactions of the solvent and ions with the surface of the separator pores.\cite{42}

Figure S4a, Supporting Information, shows the discharge capacity retention as a function of the scan rate for all batteries, in which the batteries containing the membranes with 5 and 10 wt% TiO$_2$ show higher discharge capacity retention compared with the other membranes. This fact is attributed to the combination of high ionic conductivity value and lithium transference number (Table 2) through the enhanced separator–electrolyte interface interactions.

To analyze in detail the effect of TiO$_2$ content on battery performance, Figure S4b, Supporting Information, shows the differential capacity analysis (dQ/dV) over cycles 5 (C/10) and 55 (C/10 recovery) for the pristine membrane and the TiO$_2$/PVDF-TrFE membrane with 10 wt% TiO$_2$ content, where each peak represents the structural transformations that are taking place within the cathode. For the pristine PVDF-TrFE membrane, the polarization increases (value between peaks) from 108 to
120 mV during cycling. In relation to the membrane with 10 wt% TiO$_2$ content, the polarization remains stable at $\approx 62$ mV, indicating that the presence of TiO$_2$ improves the compatibilization between separator and electrode.

Electrochemical impedance spectroscopy (EIS) measurements of the half-cells were carried out in the frequency range from $7 \times 10^6$ to 1 Hz. Figure 4e,f shows the impedance spectra for the half-cells with different TiO$_2$/PVDF-TrFE membranes developed in this work before and after GCD measurements. In these two Nyquist plots, it observed a semicircle in the high-medium frequency region followed by a second semicircle at the low-frequency region. The semicircle represents the overall resistance, resulting from the ohmic (contact film resistance), contact, and charge-transfer reaction resistance, whereas the second semicircle is associated with the Li$^+$ diffusion process. The overall resistance for each membrane is 157, 66.7, 58.6,
and 81.7 Ω (0, 5, 10, and 20 wt% TiO$_2$ content) before GCD measurements and 400, 83.5, 78.0, and 83.2 Ω (0, 5, 10, and 20 wt% TiO$_2$ content, respectively) after GCD measurements. Comparing these results, it observed an increase in the resistance after cycling attributed to the formation of the solid electrolyte interphase (SEI) layer and simultaneous reduction of the lithium-ion diffusion with increasing number of cycles.\[49\]

This increase is much higher in the membrane without TiO$_2$.

2.4. Photocatalytic Degradation under UV Radiation

To confirm the photocatalytic properties and multifunctional properties of the TiO$_2$/PVDF-TrFE membranes, in addition to its application as separator in LIBs, these membranes were used to degrade CIP under UV radiation, as shown in Figure 5.

Figure 5 shows the evolution of the absorbance spectra over 300 min, at different time intervals, for the TiO$_2$/PVDF-TrFE with 0 (Figure 5a) and 10 wt% TiO$_2$ content (Figure 5b). For the pristine PVDF-TrFE membrane, Figure 5a shows that the peak at 278 nm related to CIP remains constant over time, which indicates that the polymeric matrix neither has a photocatalytic effect nor adsorbs CIP in solution. Regarding the 10 wt% TiO$_2$/PVDF-TrFE membrane, it observed a decrease in absorbance over time, which demonstrates the photocatalytic activity of the membrane (Figure 5b).

CIP degradation in aqueous solution follows a pseudo-first-order reaction, as shown in Figure 5c, and can be modeled by the Langmuir–Hinshelwood model presented in the following equation.\[50\]

\[
\ln \left( \frac{C}{C_0} \right) = -kt
\]

where \(C\) and \(C_0\) are the concentration at a given time interval (t) and the initial concentration (mg L$^{-1}$), respectively, and \(k\) is the apparent first-order rate constant (min$^{-1}$).

The 10 wt% TiO$_2$/PVDF-TrFE membrane was capable of degrading approximately a 77% of CIP in solution, with an apparent rate constant of 0.0047 min$^{-1}$, and an \(R^2\) value of 0.99, which is in line with the reported in the literature,\[20b\] and confirms the notable photocatalytic degradation of CIP under 300 min of UV radiation exposure.

Figure 5d shows the morphology after the photocatalytic process in which the membrane maintains its porous morphology.
2.5. Second Life Assessment: Battery Performance after Photocatalysis

After photocatalytic tests, the membranes were reused, and its electrochemical properties were re-evaluated, considering the CE perspective, and the results are presented in Figure 6. Figure 6a,b shows the electrochemical impedance for batteries before and after cycling. The Nyquist plots show a semicircle followed by a straight line.

The overall resistance for the membrane with the 10 wt% TiO$_2$ content before and after photocatalysis (PC) was 58.6 and 317 $\Omega$, and 78.0 and 3615 $\Omega$ before and after GCD measurements, respectively. The resistance increase is attributed to the formation of a SEI, not only by the GCD measurement but also by the photocatalytic study since CO$_2$ degradation product can remain in membrane reacting with the lithium ion, and simultaneous reduction of the lithium-ion diffusion with increasing number of cycles.$^{[49]}$

Figure 6c shows the typical charge/discharge curves of the fifth cycle at C/10 and C/10 recovery rates for this membrane before and after the PC tests. In addition, it also shows a discharge capacity value before PC of 142 and 140 mAh g$^{-1}$ for C/10 and C/10 recovery, which correspond to a capacity fade of 1.4%. After PC, the discharge capacity values are 131 and 126 mAh g$^{-1}$ for the same rates indicated earlier, respectively, corresponding to a capacity loss of 3.8%, retaining still a high capacity value.

Figure 6d shows the battery performance of the membrane with 10 wt% TiO$_2$ content before and after PC tests at the different scan rates. Regardless of the scan rate, it is observed that the PC test does not affect the capacity value at each rate, but for the membranes used in PC experiments, it observed a decrease in the discharge capacity value, which may be related to the decrease in the mechanical stability after the PC tests.

Therefore, in this work, it demonstrated the multifunctionality of TiO$_2$/PVDF-TrFE membranes for two different applications: LIBs and photocatalytic degradation. Furthermore, it is shown that a second life is possible for the membranes after photocatalytic use.

This work proves that after efficiently applying the membrane in water remediation, it can be applied as LIB separator. As environmental concerns are growing worldwide, it is paramount to prove that a given material is multifunctional and possess as many applications as possible—enlarging its life span and reducing process costs.

Figure 6. Electrochemical Impedance spectra for batteries with PVDF-TrFE with 10 wt% TiO$_2$ content before and after PC tests a) before GCD and b) after GCD measurements. c) Fifth charge and discharge cycle room temperature profiles at rates C/10 and C/10 recovery before and after photocatalytic tests and d) rate performance as a function of the cycle number.
3. Conclusion

Environmental and energy issues are inevitably linked and represent two of the main global concerns to be urgently addressed. The use of multifunctional and reusable materials that allow multiple applications and/or a second life can mitigate those issues and contribute to the establishment of the CE paradigm.

Taking advantage of the multifunctionality of TiO$_2$, different applications were envisaged for the produced porous membranes based on PVDF-TrFE polymer with different TiO$_2$ nanoparticle contents. These membranes were physicochemically characterized, and their application as LIB separators and photocatalytic systems is evaluated.

All membranes show well-defined porosity characterized by a uniform distribution of interconnected micropores, independently of the presence of the filler. The TiO$_2$ nanoparticles were located on the internal walls of the polymer pores, and the addition of TiO$_2$ affects the pore size and porosity, as well as the thermal and mechanical properties. Furthermore, the presence of the TiO$_2$ fillers allows to improve ionic transport.

Battery performance tests carried out on Li/C-LFP cathode half-cells revealed a discharge capacity of about 128 mAh g$^{-1}$ at 2C for TiO$_2$/PVDF-TrFE membranes with 10 wt% TiO$_2$ content. This membrane shows a low capacity fade (17%) for over 100 cycles, resulting from the combination of the ionic conductivity value (0.59 mS cm$^{-1}$) and lithium transference number (0.72). This suggests good compatibility of this TiO$_2$/PVDF-TrFE membrane with the C-LFP cathode. Furthermore, this membrane was applied for the degradation of 77% of CIP in aqueous solution and, after being used, also showed suitability for being reused in a second life as battery separator membrane.

Thus, it is demonstrated that the produced TiO$_2$/PVDF-TrFE membranes can be used, with suitable efficiencies, for energy and environmental issues based on their multifunctional properties. Furthermore, it is also shown that after specific applications, such as environmental remediation, the membranes can have a second life, being reused in other high-end applications (energy storage). This approach considers paramount issues, such as energy and environment, allaying a multifunctional material to be used in different applications and also assuring a second life in the scope of the CE paradigm. The use of the same processed materials for different applications and, in particular, the reutilization of materials to secondary application are a concept that can provide a solution to the important environmental issue we are facing nowadays, associated with the increase of polymers in ecosystem.

4. Experimental Section

Materials: For membrane fabrication, PVDF-TrFE, titanium dioxide (TiO$_2$) nanoparticles (P25-Aeroxide), and N,N′-dimethylformamide (99%) (DMF) solvent were purchased from Arkema, Evonik Industries AG, and Merck, respectively. In relation to materials for battery test, poly(vinylidene fluoride) (PVDF) (Kynar PVDF HSG900), N-methyl-2-pyrrolidone (NMP) solvent, and 1 M LiPF$_6$ in a mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in vol. ratio) were acquired from Arkema, Merck, and Fluka, respectively. Also, lithium iron phosphate, C-LFP, and carbon black were supplied by Phostech Lithium and Timcal Graphite & Carbon.

Membrane Preparation: Polymer composite membranes were prepared by a solvent casting process. Different amounts of TiO$_2$ (5, 10, and 20 wt%) were dispersed in 6 mL of DMF and subjected to an ultrasonic bath for 3 h. Subsequently, 1 g of PVDF-TrFE polymer was added in DMF with a 15/85 wt% polymer/solvent ratio, prepared under magnetic stirring at 40 °C during 1 h. After complete polymer dissolution, the solution was spread on a glass substrate followed by solvent evaporation at room temperature for eight days until the samples dried. A pristine membrane without fillers was also prepared. This preparation procedure allows obtaining homogenous porous polymer membranes. Figure 7 shows the schematic representation of the method used to prepare the TiO$_2$/PVDF-TrFE membranes.

Membranes Characterization: The morphology of the membranes was evaluated by SEM, Zeiss EVO 40, with an accelerating voltage of 20 kV. The samples were previously coated with a gold layer by magnetron sputtering, Polaron, model SC502. The average pore size was obtained after measuring more than 200 pores using the Image J software.

FTIR spectroscopy in the ATR mode was performed at room temperature in a Jasco FT/IR-6100 from 4000 to 600 cm$^{-1}$ collected with 64 scans at a resolution of 4 cm$^{-1}$.

DSC measurements were carried out in a Perkin-Elmer DSC 6000 in the temperature range between 25 and 200 °C at 10 °C min$^{-1}$ under nitrogen atmosphere.

The degree of crystallinity ($\Delta X_c$) was evaluated from the DSC thermograms using the following equation.

$$\Delta X_c = \frac{\Delta H_f}{\Delta H_{100}}$$

in which $\Delta H_f$ corresponds to the melting enthalpy of the sample, and $\Delta H_{100}$ is the enthalpy of a fully crystallized sample ($\Delta H_{100} = 103.4$ J g$^{-1}$[23]).

The TGA analysis was carried out in a Perkin-Elmer Pyris-1 TGA apparatus between 25 and 800 °C at 10 °C min$^{-1}$ under a nitrogen atmosphere.

Mechanical stress–strain measurements of the membranes were carried out at room temperature in the tensile mode in a TST350.
Linkam Instruments setup at a strain rate of 15 μm s⁻¹ with a load cell of 20 N.

Porosimetry was determined by MIP in a Quantachrome Instruments Poremaster-60 GT setup operating in the pressure range from vacuum (10⁻⁴ MPa) to 414 MPa. Samples were degassed in situ at 110 °C during 12 h prior to measurement. A contact angle of 140° and a surface tension of 480 dyn cm⁻¹ for mercury and a pressure equilibration time of 11 s were used.

The contact angle of the different membranes was measured using a Dataphysics Contact Angle System OCA20 depositing an ultrapure water drop (3 μL) for the test.

Electrochemical Measurements: Electrolyte uptake of the membranes was obtained by submerging the samples in an electrolyte solution (1 M LiPF₆ in EC: DMC) for different times (15, 30, 60, 120, and 240 s). After those times, the samples were weighed, and the uptake value (ε) was evaluated using the following equation.

\[
ε = \left( \frac{M - M_0}{M_0} \right) \times 100
\]

where \( M \) and \( M_0 \) correspond to the initial weight of membrane and the mass of the membrane after submerged in the electrolyte solution, respectively.

EIS measurements were carried out using a Solartron 1260A Impedance Analyzer with frequencies ranging between 7 × 10² and 1 Hz and a 50 mV excitation amplitude. Symmetric (Li | separator membrane | Li) and half- (C-LFP | separator membrane | Li) cells were prepared inside a CR-2032 coin cell, closed within an Ar-filled glove box. Then, EIS measurements were acquired at room temperature, before and after cycling of the cells.

The ionic conductivity (\( σ_i \)) of the membranes was calculated using the following equation.

\[
σ_i = \frac{t}{A \times R_b}
\]

where \( R_b \) is the bulk resistance, \( t \) is the thickness, and \( A \) is the area of the separator.

Tortuosity and MacMullin number of the membranes were determined using the following equations.

\[
τ = \sqrt{\frac{ε \sigma_o}{\sigma_i}}
\]

\[
N_M = \frac{ε \sigma_0}{\sigma_i}
\]

where \( ε \) is the porosity of the membrane, \( \sigma_o \) is the ionic conductivity of the electrolyte solution (9.8 mS cm⁻¹ at 25 °C), and \( \sigma_i \) is the ionic conductivity of the membrane and the electrolyte solution at room temperature.

The Li-ion transference number (\( t_{Li}^- \)) was measured in a potentiostat/galvanostat (Biologic VMP3) at room temperature by a combination measurement of AC impedance and DC polarization using a symmetric cell containing the separator membrane soaked in the commercial electrolyte (13 mm diameter) and two Li electrodes (diameter 10 mm), assembled in an Ar-glove box. The cell was subjected to a DC voltage (10 mV) until a steady current was obtained (6 h). The initial (\( I_0 \)) and steady (\( I_s \)) currents were measured. The impedance spectra were recorded before and after DC polarization, to obtain the initial (\( R^0 \)) and final (\( R^\circ \)) resistances of the Li metal electrode/electrolyte. Based on these values for the parameters mentioned earlier, the Li-ion transference number (\( t_{Li}^- \)) was then calculated by Equation (7), after the method proposed by Bruce, Evans, and co-workers.²

\[
t_{Li}^- = \frac{R^0(\Delta V - R^\circ \Delta I)}{R^\circ(\Delta V - R^0 \Delta I)}
\]

Cathode Electrode, Half-Cell Preparation, and Battery Testing: Cathode electrodes were manufactured by mixing active material (C-LFP), conductive material (Super P-C45), and polymer binder (PVDF), in a weight ratio of 80:10:10 (wt%), respectively, with 2.25 mL of NMP for 1 g of solid material. The slurry was spread onto the aluminum foil current collector by a doctor blade coating method and dried in an air atmosphere at 80 °C in a conventional oven (ED 23 Binder). After the drying process, the electrodes were placed in a vacuum overnight at 90 °C and transferred to an argon-filled glove box.

C-LFP/Li CR 2032-coin cells were assembled in an argon-filled glove box (where O₂ and H₂O levels were kept <0.1 ppm). The half-cells were prepared using the PVDF-TrFE with different wt% of TiO₂ membranes as separators (13 mm diameter), soaked in a commercial electrolyte solution (1 M LiPF₆ in EC: DMC 1:1). Lithium metal discs (10 mm diameter) were used as anode and C-LFP-based electrode (theoretical capacity 170 mAh g⁻¹ as cathode (10 mm diameter). GCD experiments were performed at room temperature in the voltage range of 2.5–4.2 V at current rates from C/10 to 2C and back to C/10 recovery using a multichannel Maccor potentiostat.

Photocatalytic Degradation of CIP: Photocatalytic tests were performed using TiO₂/PVDF-TrFE membranes with an area of 18 cm² and evaluating the photocatalytic degradation of CIP under UV radiation. A beaker with the sample and the solution of CIP was stirred in the dark for 30 min to achieve the adsorption–desorption equilibrium. After that, UV light was turned on in the photoreactor for photocatalytic degradation. This photoreactor has eight lamps (Philips 8 W), with a peak of maximum intensity at 365 nm. Samples were taken from the solution at 0, 2, 5, 10, 15, 20, 30, 40, 60, 90, 120, 240, and 300 min, and CIP degradation was assessed. The samples were analyzed in quartz cells, with an optical path of 1 cm, in a Shimadzu UV-2501PC UV/Vis spectrophotometer.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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