Supercapacitors are the subject of augmented scientific attention in recent years as storage energy systems due to their exceptional cycling stability and power densities. These devices have the capability of delivering higher amounts of energy in shorter time intervals than batteries. Recent improvements of these devices has allowed this technology to be utilized in large-scale systems such as hybrid vehicles and renewable energy plants. Capacitors store energy in the...
form of electrical charge across two conducting plates with opposed polarity that are separated by a dielectric material (ie, separator). These separators are important to achieve proper charge separation, which is critical to ensure high power densities. Most of the research efforts on the field have focused on the development of carbon electrode materials, and consequently, the optimization of separator technologies has become a favorable opportunity to further increase the efficiency of supercapacitors. Most commonly, materials with high dielectric constants are employed to achieve high power and energy densities. A wide variety of dielectric materials have been proposed as separators, the most promising being either polymers or ceramics. On one side, polymers have good chemical and mechanical stability. The disadvantage of utilizing polymers as separators is that they suffer from relatively low dielectric constants, and poor thermal stability. On the other hand, ceramic separators have high dielectric constants, high ionic conductivity, and exceptional thermal stability. Unfortunately, they lack the mechanical strength to withstand handling in cell assembly. In order to obtain the myriad of positive properties from both ceramics and polymers, we propose to prepare porous polymer/ceramic composites (ie PCC’s) as separators for supercapacitors. In this work, the separators are prepared via phase inversion by solvent precipitation, a facile and scalable technique that is known to produce porous polymer membranes. Phase inversion by solvent precipitation involves the immersion of a polymer casting solution in a bath filled with a precipitation fluid. When the cast film is immersed in the bath, the solvent of the cast solution disseminates, and the precipitant enters in contact with the polymer. The result of this procedure is a sponge-structured film. Most of the literature suggests that nonporous and monolithic separators provide advantages over porous separators. Nevertheless, other studies suggest that porous films for energy storage devices have advantageous elements such as better ion conductivity, higher electrolyte retention, and lower ionic resistance. In this work, we expect to shed light in terms of the conflicting reports between porous and nonporous separators. We focused our efforts in producing highly porous separators, which provide high electron transfer rates. The challenge related to the auto discharge phenomena was expected to be addressed by the ceramic addition within our PCC separators. For the fabrication of the separators, PVDF and PPG were used as the polymer component due to their known mechanical strength, chemical resistance, and their solubility in organic solvents. Moreover, for the ceramic material, different titanates with increasing cationic radius were employed, namely calcium titanate (CaTiO3), strontium titanate (SrTiO3), and barium titanate (BaTiO3). The porosity of the fabricated films was systematically optimized using lithium chloride (LiCl). Additionally, the effects of membrane and ceramic thermal heating was analyzed as ceramic grain sizes are affected by thermal infusion. The fabricated separators were characterized by means of physical and electrochemical techniques. The final performance is compared to commercially available Celgard separators, namely 2500 and Ez 2090.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Polyvinylidifluoride (PVDF, average Mw 534,000), Polypropylene grafted (PPG, average Mw ~9,100 and Mn ~3,900, maleic anhydride 8-10 wt %) CaTiO3 (Mw 135.94 g/mol, nano powder < 100 nm, >99% trace metal), SrTiO3 (Mw 183.49 g/mol, nano powder <100 nm, >99% trace metal), BaTiO3 (Mw 233.19 g/mol, nano powder <100 nm, cubic crystalline phase, >99% trace metal), lithium chloride (LiCl, ACS reagent 99.0%), formic acid (reagent grade, >95%), acetone (HPLC grade, >99.9%), N,N-Dimethylformamide (DMF, anhydrous, >99.8%), and Tetrabutylammonium perchlorate (TBA, electrochemical analysis reagent, >99.0%) were all purchased from Sigma-Aldrich. Also, Acetonitrile (reagent grade > 99.5%) was bought from VWR. All chemicals and solvents were used as received without further purification. The ceramics were submitted to an annealing process for 24 hours as described in the sample preparation. Nanopure water (18.2 MΩ·cm2, MilliQ Direct 16, EMD Millipore, Co., Burlington, MA, USA) was used at all times. Ez 2090 and 2500 commercial separators were bought from Celgard (Charlotte, NC, USA).

2.2 | Sample preparation

First, PVDF (7.5% w/w) was mixed in an acetone:DMF solution of a ratio of 1:3 (v/v) and it was stirred for two hours at 45°C. Thereafter, LiCl, PPG and the ceramic powder were added to the mixture at 0.94%, 3.0%, and 0.5% (w/w), respectively, under constant stirring for 2 hours as well. The PPG utilized in the previously mentioned procedure was prepared by mixing a 12.8% (w/w) solution of PPG in toluene and kept in a closed vial under constant stirring for 24 hours at 110°C. Then, using a doctor blade film caster, 3.0 mL of the solution film casted over a glass plate in open air to let the solvent evaporate. Using a razor knife, the PPG was scraped from the glass surface. To prepare the separator, the PCC (matrix used for the films, contains PVDF, LiCl, PPG) mixture was film casted over a glass plate and then submerged in a bath of nanopure water at room temperature. Three different ceramics were added separately to the mixture as well: SrTiO3, CaTiO3, BaTiO3 at 0.5% (w/w). To test the effect of grain size by thermal infusion on the overall execution of the PCCs, the ceramics were also submitted to an annealing process at 1000°C for 24 hours. The prepared films were then air-dried, followed by an oven heating step at 160°C for 4 hours in vacuum. Table 1 lists all the fabricated separators with their corresponding...
TABLE 1  Sample fabrication list with corresponding label and lettering for future reference

| Precursor material | Ceramic | Ceramic modification | Thermal heating | Label | Lettering |
|--------------------|---------|----------------------|-----------------|-------|-----------|
| PVDF               | /       | /                    | As prepared     | PVDF  | A         |
|                    |         |                      | Heated          |       |           |
| PVDF/PPG           | /       | /                    | As prepared     | PVDF/PPG | B     |
|                    |         |                      | Heated          |       |           |
| PVDF/PPG/LiCl      | /       | /                    | As prepared     | PCC   | C         |
|                    |         |                      | Heated          |       |           |
| PVDF/PPG/LiCl/CaTiO3| As prepared | /             | As prepared     | PCC/CT | D     |
|                    |         |                      | Heated          |       |           |
|                    | Annealed|                     | As prepared     | PCC/CTA | E    |
|                    |         |                      | Heated          |       |           |
| PVDF/PPG/LiCl/SrTiO3| As prepared | /             | As prepared     | PCC/ST | F     |
|                    |         |                      | Heated          |       |           |
|                    | Annealed|                     | As prepared     | PCC/STA | G    |
|                    |         |                      | Heated          |       |           |
| PVDF/PPG/LiCl/BaTiO3| As prepared | /             | As prepared     | PCC/BT | H     |
|                    |         |                      | Heated          |       |           |
|                    | Annealed|                     | As prepared     | PCC/BTA | I    |
|                    |         |                      | Heated          |       |           |
| Celgard            | /       | /                    | 2500            | 2500  | J         |
|                    |         |                      | Ez 2090         |       |           |

FIGURE 1  Schematic summarizing the polymer/ceramic composites separator preparation

label and letter for future reference in work. Figure 1 shows a schematic that summarizes the PCC preparation process.

2.3  Electrochemical analysis setup

The setup to analyze the electrochemical properties of the separators consisted of two fluorine doped tin oxide (FTO) conductive glasses cut to measure 10 × 2.5 cm (L × W). The sample area for the experiments was a square measuring 6.25 cm². PCC films with dimensions of 3.8 × 3.8 cm were cut to ensure that all of the cell was covered by the separator. Before securing the separator between both conductive crystals, a solution of 0.1 mol/L of tetrabutylammonium (TBA) dissolved in acetonitrile was added on both sides of the separator. We then carefully placed the separator between both crystals, while making sure there were no trapped air bubbles in the system and the 2.5 × 2.5 cm square was filled completely with the electrolyte. Figure 4A is a representation sketch of the electrochemical setup utilized for the experiments. Finally, the setup was clamped together and an SP-150 potentiostat/galvanostat in low current mode with EIS capabilities from Biologic USA was utilized as the power source. The working electrode was connected on one glass, and the auxiliary and reference electrodes on the other. The method for obtaining the ohmic resistance, as it has been previously reported, was taken as the impedance value at the high frequency limit (Figure 4B). Similarly, cyclic voltammograms (CV) were run to obtain the specific capacitance of the system with the different separators (Figure S4). The
CVs were run from 0.1 to 0.8 V at a scan rate of 100 mV/s. The specific capacitance was determined by a previously reported method, with equation (1) the interfacial capacitance ($C_{\text{in}}$) was calculated and then used in equation (2) to determine the specific capacitance ($C_{\text{Sp}}$).^25

\[
C_{\text{in}} = \frac{i}{(dV/dt)} \quad (1)
\]

\[
C_{\text{Sp}} = \frac{C_{\text{in}}}{m} \quad (2)
\]

where ($i$) is current, ($dV/dt$) is scan rate, and $m$ is the mass of the separator.

### 2.4 Mechanical analysis setup

The mechanical properties of the separators were determined using a CT3 Texture Analyzer from Brookfield. PCC samples were cut to initial dimensions of 7.6 × 0.8 cm, and then clamped to a Dual Grip Fixture (TA-DGA) for tensile testing. The target value was set to 20.0 mm and the trigger value was tested, and the $A$ is the area of the separator being tested, and the $\varepsilon_0$ is the dielectric constant of the vacuum.\(^26\)

### 3 RESULTS AND DISCUSSION

#### 3.1 Physical characterization of ceramics

In an effort to characterize the individual components of the final PCC’s separators, the titanate-based ceramics were physically characterized first. Figure 2A shows the XRD patterns for such compounds before and after the annealing process. The Scherer equation was used to determine the crystallite sizes at the miller indexes [101]. Where $D_{hkl}$ is the crystallite size in the direction perpendicular to the lattice planes, $hkl$ are the Miller indices of the planes being analyzed, $K$ is a numerical factor frequently referred to as the crystallite-shape factor, $\lambda$ is the wavelength of the X-rays, $B_{hkl}$ is the full-width at half-maximum (FWHM) of the X-ray diffraction peak in radians and $\theta$ is the Bragg angle.\(^27\) The $K$ used was 0.9, and the values for the $D_{hkl}$ are in Table 2. It can be observed that the crystallite size for CaTiO$_3$ and SrTiO$_3$ increased with the annealing process from 18.62 to 49.18 nm and 27.63 to 45.09 nm respectively. These changes can be attributed to the high temperatures (1000°C) applied to the ceramics, which increased crystallite size of the particles. Also, it can be observed that for the CaTiO$_3$ and SrTiO$_3$, the crystallites have agglomerated after the annealing step, as noted by an increment in the intensity of the diffraction peaks. Moreover, strain in the crystallites causes broadening of the peaks; the annealing causes the crystallites of the ceramics to rearrange and be more organized which can be observed by the more defined and less broad peaks in the annealed ceramics. Additionally, the XRD pattern of the BaTiO$_3$ shows that annealing at 1000°C does not affect the crystallite size, this can also be observed in the value of $D_{hkl}$ that there was not a significant change. SEM micrographs show further evidence of particle infusion in Figure 2B.

#### 3.2 Physical characterization of PCC separators

##### 3.2.1 SEM images of PCC separators

After the PCC separators were fabricated, SEM images were recorded to assess the integrity and topography of the final
films. The images in Figure 3 were taken from the back and cross-section. In general, these results reveal that, in all cases (ie, PVDF, PVDF/PPG, PCC, PCC/CTA, and Heated PCC/CTA), the backside of the membrane shows a highly porous film with spaghetti-like polymer connections. When LiCl is added to the film mixture, the effect is an open porous structure, with pores in the range of ca. 10 μm. These pores are then collapsed when the ceramic is added to the polymer mixture, resulting in a sponge-like structure as observed on the cross-sectional images. A thermal treatment at temperatures highly above the PVDF transition temperature was performed in order to allow thermodynamic arrangement of the components in the separator. It is observed that the pore structure is similar to the sample without thermal treatment, although this sample shows better defined edged and overall flat surface. Lastly, the method of fabrication of these separators yielded similar thicknesses (17.93 ± 5.2 μm) to the commercial separators (21.39 ± 2.8 μm), indicating that the phase inversion technique is a feasible, low cost alternative for the fabrication of separators. All the PCC separator SEM images are found in S1.

3.2.2 | Electrochemical Ionic conductivity of PCC separators and Specific capacitance

After physical visualization of the PCC separators, it was critical to assess the electrochemical ionic conductivity of the prepared membranes. The solution resistances were obtained by performing electrochemical impedance spectroscopy (EIS) since it provides direct information of the charge transfer across the separators. The data collection method can be observed in Figure 4B. The Nyquist curves recorded for the separators can be found in Figure S3, and a summary of the results is presented in Table 3. The average ohmic resistance (44.4 and 43.7 Ω for the as prepared and heated separators, respectively) of the developed PCC separators show comparable values to those obtained for the commercially available separator Celgard 2090 (47.1 Ω), which is a microporous separator (Figure S2). Even more, the thermal treatment had no significant effect on the ionic resistance, the average percentage difference after thermal heating was 7.65%, and the values are sufficiently high to prevent short circuits in the system. Equally important, the fabricated separators showed lower ionic resistance when compared to the Celgard 2500 (88.2 Ω) that has no porosity (Figure S2). Thus, we suggest that the low ionic resistances are a result of the high porosity of the fabricated separators as calculated in Table S2. This explains why the fabricated separators allow a greater charge transfer across the separator when compared to commercial separators. These results reveal that porous separators allow superior charge transfer in the material when compared to nonporous dielectric components. As for the specific capacitance, it can be observed that heated separators trend to lower their capacitance. This can be due to an increase in density in the material. Since the pores are closing through the heating process, this causes the separators to have higher mass in the same volume, therefore the specific capacitance drops. Also, an increase in capacitance can be observed when employing the ceramics. Furthermore, the annealed ceramics showed an increase in capacitance. The highest specific capacitance was obtained with PCC/CT separator.
An important factor of study of supercapacitor separators is their mechanical strength. It is desirable to obtain a film with high tensile strength rather than a brittle material that would be difficult to handle. To analyze the mechanical properties of the prepared PCC separators, the Young's modulus (YM), ultimate tensile strength (UTS), and fracture strain (FS) were obtained, see Figure 5. To approximate the

**FIGURE 3** SEM images of fabricated polymer/ceramic composites separators

### 3.2.3 Mechanical testing of PCC separators

An important factor of study of supercapacitor separators is their mechanical strength. It is desirable to obtain a film with high tensile strength rather than a brittle material that would be difficult to handle. To analyze the mechanical properties of the prepared PCC separators, the Young's modulus (YM), ultimate tensile strength (UTS), and fracture strain (FS) were obtained, see Figure 5. To approximate the
separator area, we utilized the cross-sectional SEM images of every PCC to calculate their average pore area and thus, obtaining our real separator area approximation (Table S2). The procedure was performed using ImageJ. We observed a 71.1% average increase in the YM of the PCC separators after thermal modification (Figure 5B). This indicates that the thermal modification promoted a homogeneous organization of the components in the separators and for that reason all the PCC separators, even with their ceramic composition, demonstrated a comparable elastic modulus to the commercial separators (1582.7 MPa in average vs 1925.9 MPa respectively). Nonetheless, the commercial separators sustained a 55.6% and 84.4% larger deformation with respect to the as prepared and heated PCC separators respectively (Figure 5D). These results are perhaps justified by the microporous structure of the commercial Ez 2090 separator and of the 2500 separator, which means that for the same area, the commercial separators enclosed a larger volume than the fabricated PCC separators which had a large pore area with large mesopores. Table S2 demonstrates that the pore area of the fabricated separators in this work approximate to 55.2% of the total cross-sectional area. That consequently indicates that the commercial separators contained more material to deform vs the prepared PCC separators. Similarly, commercial separators resisted a higher tensile stress (65.8% in average) compared to the

FIGURE 4  A. Electrochemical analysis setup representation; B, EIS Nyquist plot for obtaining initial resistance

TABLE 3  Average electrochemical resistance (Ω) and specific capacitance comparison of PCCs before and after thermal treatment

| Sample | $R_{\text{electrolyte}}$ (Ω) | Specific capacitance (F/g) |
|--------|-----------------|-----------------|
|        | As-prepared     | Heated          | As-prepared     | Heated          |
| a. PVDF| 45.6            | 43.5            | 67.03           | 76.395          |
| b. PVDF/PPG| 51.7        | 45.6            | 117.81          | 65.17           |
| c. PCC | 43.3            | 43.3            | 118.76          | 67.68           |
| d. PCC/CT| 40.8          | 49.1            | 242.61          | 119.26          |
| e. PCC/CTA| 44.8          | 40.7            | 380.56          | 157.64          |
| f. PCC/ST| 47.3           | 42.4            | 173.33          | 127.65          |
| g. PCC/STA| 45.4           | 41.5            | 140.32          | 157.20          |
| h. PCC/BT| 45.6           | 44              | 132.34          | 247.37          |
| i. PCC/BTA| 42.5           | 44.2            | 305.93          | 84.66           |
| j. Celgard 2500| 88.2    |                 |                 |                 |
| k. Celgard Ez 2090| 47.1    |                 |                 |                 |
PCC separators (Figure 5C). This result can be attributed to the brittleness of the ceramics in the separators because the UTS of the heated precursor materials of the PCC separators (PVDF, PPG/PVDF) was higher (23.9% greater) than the commercial separators’ tensile strength.

3.2.4 | Dielectric properties of PCC separators

After considering physical and mechanical characteristics of the PCC separators, experiments to determine the dielectric properties of the materials in a metal-composite-metal array at 0.01 V were conducted. These experiments were performed in an effort to estimate the PCC separators performance in a final application. Their dielectric constant and dissipation factor at different frequencies can be observed in Figure 6. The fabricated separators with the added ceramics had higher dielectric constants (Figure 6B,C,D) than the polymer matrix, as seen in Figure 6A. This result demonstrates that the ceramic component in the composites improves the dielectric properties of the material. On the other hand, an increase in the dissipation factor (Figure 6B,C,D) was observed for the PCC’s that were thermally treated. This behavior can be attributed to the significant loss of crystallinity and β-phase content of the PVDF matrix after treatment at 160°C for 4 hours. Previous reports have demonstrated that the optimum heating treatment to obtain the highest dielectric constant of PVDF is at 140°C for 6 hours because it renders the highest degree of crystallinity and β-phase (electroactive phase) content in the polymer.26,28 Exceeding or reducing that temperature and time of treatment reduces the amount of the electroactive phase of the PVDF, which explains the increment of the dissipation factor of the heated composites. Secondly, a summary of the dielectric constants of the PCC separators at $6.0 \times 10^5$ Hz is presented in Figure 7. The previously mentioned frequency was selected because the separators’ dielectric constant was stable at that region. Results demonstrate that the thermal modification of the separators decreased the PCC’s dielectric constant as well. For example, the PCC/CT’s dielectric constant decreased from 4.43 to 2.22 after thermal modification (Figure 7), and the tendency was observed across all of the PCC’s. These results are attributed to the same behavior that was mentioned previously. Nonetheless, thermal annealing of the ceramics improves the dielectric constant of the separators. More specifically, the dielectric constants of PCC/CT, PCC/ST, and PCC/BT was 4.43, 4.3, and 3.51, respectively, whereas the dielectric constants of PCC/CTA, PCC/STA, and PCC/BTA was 5.17, 5.39, and 4.33 respectively. Equally important, all of the PCC’s dielectric constant were higher than the commercial separator Ez 2090’s dielectric constant (Figure S5). The average dielectric constant for the as prepared separators was 4.52, which is 2.1 times higher than the Ez 2090’s dielectric constant (2.2). These final results indicate that, in a final application, the prepared separators in this work would allow greater charge separation and consequently, higher power densities when compared to commonly used commercial separators.
**4 | CONCLUSIONS**

On this research project, polymer/ceramic composites were developed as separators for supercapacitors applications. We strived to produce separators with the dielectric characteristics of ceramics and the mechanical attributes of the polymers, while preserving the electrochemical properties required for the charge transfer process needed in supercapacitors. Evaluation criteria, such as electrochemical impedance spectroscopy, mechanical assessments, X-ray diffraction, scanning electron microscopy, and dielectric studies were performed to analyze the quality of the developed separators. XRD results demonstrated an enlargement of the particle size of the ceramics after the annealing process. SEM studies provided direct information of the porosity of the composites and reveal that

**FIGURE 6**  A. Dielectric constant measurements for the polymer/ceramic composites (PCC) (PVDF/PPG/LiCl) separator. From B-D, are the plots of the separators as prepared on the right and the heated separators on the left, while black plots are for ceramics without treatment and red plots are for sintered ceramics. B, PCC/CT and PCC/CTA; C, PCC/ST and PCC/STA; D, PCC/BT and PCC/BTA

**FIGURE 7**  Dielectric constant stabilization frequencies of the as prepared (dark gray) and heated (orange) separators
Lithium Chloride, as an ingredient in the separators, increased the porosity of the material. EIS examination demonstrated that the fabricated separators had a lower electrochemical resistance than the nonporous commercial separator, and thus, indicating that porous separators have greater charge transfer rates.

Finally, dielectric constant analyses demonstrated that the addition of the ceramic in the separator improved their dielectric constant and consequently, the fabricated separators had higher dielectric constants than the commercial separators. After analyzing all the experimental data, the separators prepared in this research project proven to be highly comparable to the commercial separators commonly used from Celgard in their electrical, and mechanical properties. Equally important, the method of fabrication performed in this work presents an innovative and scalable alternative for the preparation of separators for supercapacitors. Further studies using these titanates, and natural additives (eg CNF), will be executed to further comprehend the influence of these materials in separator properties.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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