ABSTRACT: With the use of bipolar membranes (BPMs) in an expanding range of applications, there is an urgent need to understand and improve the catalytic performance of BPMs for water dissociation, as well as to increase their physical and chemical stability. In this regard, electrospinning BPMs with 2D and 3D junction structures have been suggested as a promising route to produce high-performance BPMs. In this work, we investigate the effect of entangling anion and cation exchange nanofibers at the junction of bipolar membranes on the water dissociation rate. In particular, we compare the performance of different tailor-made BPMs with a laminated 2D junction and a 3D electrospun entangled junction, while using the same type of anion and cation exchange polymers in a single/dual continuous electrospinning manufacturing method. The bipolar membrane with a 3D entangled junction shows an enhanced water dissociation rate as compared to the bipolar membrane with laminated 2D junction, as measured by the decreased bipolar membrane potential. Moreover, we investigate the use of a third polymer, that is, poly(4-vinylpyrrolidine) (P4VP), as a catalyst for water dissociation. This polymer confirmed that a 3D entangled junction BPM (with incorporated P4VP) gives a higher water dissociation rate than does a 2D laminated junction BPM with P4VP as the water dissociation catalyst. This work demonstrates that the entanglement of the anion exchange polymer with P4VP as the water dissociation catalyst in a 3D junction is promising to develop bipolar membranes with enhanced performance as compared to the conventionally laminated membranes.

KEYWORDS: bipolar membrane electrodialysis, water dissociation, electrospinning, bipolar 3D junction, electrospun bipolar membrane

1. INTRODUCTION

The development of bipolar membranes (BPMs) has allowed the emergence of several electrodialysis-based processes in which water dissociation is catalyzed inside the BPM (if a sufficient overpotential is applied), resulting in the production of hydroxide and protons from a neutral solution. BPMs have been used for the development of several industrial and environmental applications, including the production and purification of acid and base, and novel applications such as CO₂ capture, flow batteries, and fuel cells. For an effective integration of BPM into current and potential new applications, a number of requirements should be met, a high dissociation rate of water, excellent perme selectivity, and good chemical and physical stability.

A typical bipolar membrane consists of its most basic form of two oppositely charged layers, an anion exchange layer (AEL) and a cation exchange layer (CEL), which can be adhered together via different techniques (e.g., casting or
lamination). The interfacial area between the anion and cation exchange layers is also referred to as the bipolar membrane junction. This junction is normally a 2D region where the electrocatalytic water dissociation occurs, and to explain its function an analogy with semiconductor p–n junctions is often reported. On the basis of the fabrication method, conventional bipolar membranes (i.e., with 2D junctions) can be multilayered employing single sheets of anion and cation exchange membranes that are glued or pressed together at high pressure and temperature. Additionally, controlled subsequent casting of the anion and cation exchange layers is used to fabricate BPMs. In a different fabrication approach, a blister-free single film bipolar membrane can be made by functionalizing the opposite sides of a single ion exchange membrane (either anion or cation), by chemically adding anion-exchange and cation-exchange sites. However, this approach is hindered by lacking a distinguished interfacial region or junction for the resulting bipolar membrane, as well as the difficulty of efficiently introducing the catalyst for water dissociation.

A different approach to the fabrication of bipolar membranes is based on electrospinning. Electrospinning has become an attractive technology to make functional materials like membranes with features such as high specific surface area and good tunability. During the electrospinning process, nanofibers are fabricated under the effect of a high electric field, and different polymer nanofibers can be oriented at the BPM junction to increase the contact region between the cation and anion exchange layers. This resulting 3D open structure at the junction promotes the water transport inside the BPM, thus enhancing the water dissociation performance at higher current densities. Shen et al. have been the first to pioneer this technique to fabricate BPMs, in combination with a high performing water dissociation catalyst (aluminum hydroxide nanoparticles) using quaternized poly(phenylene oxide) and SPEEK as ion exchange layers to fabricate BPMs. A recent study combined the benefit of fabricating BPM with electrospinning and the use of graphite oxide as water dissociation catalyst to improve the performance of BPM. Electrospun bipolar membranes prepared and investigated in this work with a 3D junction of entangled fibers of the cation and anion polymers are classified as a single film BPM because there are no physically separated layers.

Electrospinning is a versatile technique that provides an advantageous approach to fabricate BPMs with controllable junction thicknesses, thus overcoming the drawbacks of lamination and casting methods. For instance, one of the major drawbacks in conventional layer-by-layer casting is the interaction of the casted top layer solvent with the layer below, resulting in a degraded quality of the final membrane: such a drawback is overcome with electrospinning, where both polymers can be electrospun at high rates and under controlled conditions for the solvent evaporation.

1.1. Water Dissociation Mechanism and Selection of Catalysts. Water dissociation has also been observed in bipolar membranes without any catalyst present at the junction. In that case, the enhancement of water dissociation kinetics is typically explained by Onsager’s theory of the second Wien effect, which describes the phenomenon as a result of a strong electrical field at the junction, causing an increase of the dissociation degree and ion mobility of electrolytes as compared to bulk conditions. However, this theory predicts very high values of electric field at the junction (in the range of 10^6–10^7 V/m), and it has been long debated that such a theory alone cannot fully explain all of the electrocatalytic phenomena occurring inside bipolar membranes. Another theory to describe the water dissociation mechanism has been suggested by Simons and consists of a reversible protonation–deprotonation reaction involving a catalyst site (“B”), according to the following two-step mechanism:

\[
B + H_2O \rightleftharpoons BH^+ + OH^- \quad (1)
\]

\[
BH^+ + H_2O \rightleftharpoons B + H_2O^+ \quad (2)
\]

1.2. Catalysts for Water Splitting. Several metal hydroxide-based (e.g., Fe(OH)₃, Al(OH)₃, and Cr(OH)₃) and polymer-based catalysts (e.g., P4VP, PVA, and PEG) have been explored in previous works that assist the water dissociation in the bipolar membrane. These catalysts are typically dissolved in a solvent, and either sprayed or cast onto the interface before dissociation of the membrane, or blended into the ion exchange polymer solution and cast as an interfacial layer between the cation and anion exchange layers. The catalyst plays a crucial role in lowering the required voltage across the bipolar membrane during water dissociation. In fact, recent studies suggest that the role of catalyst in water dissociation in BPMs is more important than electric-field enhancement. Besides the role of catalytic particles in the junction, the chemical composition of the anion exchange layers can also contribute to enhance water dissociation. In particular, anion exchange membranes (AEMs) with secondary and tertiary amines are more catalytic than AEMs with quaternary amines for water dissociation.

Poly(4-vinylpyrrolidone) (P4VP) was used in previous research to catalyze the water dissociation reaction in BPM. For the junction of the bipolar membrane, other polymeric materials were integrated as catalysts like polyelectrolyte multilayers, poly vinyl alcohol, and poly(acrylic acid). Kim et al. presented how a multilayered BPM with a layer of polyacrylonitrile enhances the water dissociation efficiency. The catalysis of the water dissociation of some polymer functional groups accelerates the water dissociation rate \( k_{\text{SWH}} \) up to 10^9 s⁻¹.

The aim of this study is to assess the performance of 2D- and 3D-junction bipolar membranes, using the same anion and cation polymers. The 2D-junction BPMs were fabricated via conventional lamination, while the 3D-junction BPMs were produced via a dual electrospinning process. Moreover, we investigated the influence of poly(4-vinylpyrrolidone) (P4VP) as a water dissociation catalyst, against reference BPMs with the same chemical composition and without any catalyst. In this way, we aim to provide a systematic investigation of the effect of the junction morphology and on the role of catalyst on the water dissociation rate in bipolar membranes.

2. MATERIALS AND METHODS

2.1. Electrospinning Setup and Materials. A dual electrospinning benchtop machine (Fluidnatek LE-50, Bionicia, Spain) was used throughout this research. The electrospinning machine was equipped with two independent spinning heads for simultaneous electrospinning of two different polymer solutions and a climate control system (for both temperature and relative humidity).
The two ion-exchange polymers utilized for the fabrication of the bipolar membrane were sulfonated poly(ether ether ketone) (SPEEK) with an IEC of 1.9 meq/g (for the cation exchange layer) and anion exchange ionomer Fumion FAA-3 with an IEC of 2 meq/g (for the anion exchange layer). Both polymers were obtained in a dry state from Fumatech BWT GmbH (Germany) as polymeric films. Poly(4-vinylpyridinolone) (P4VP) with a molecular weight of 60 000 g/mol was purchased from Sigma-Aldrich as a dry powder. P4VP was incorporated into the 3D junction as a catalyst by dissolving in dimethylacetamide (DMAc) as a solvent. Dimethylacetamide (DMAc) and dimethylformamide (DMF) (VWR Chemicals) were used as solvents for the preparation of the polymer solutions. All of the solvents were used as received.

### 2.2. Preparation of BPMs with 2D and 3D Junctions.

BPMs were fabricated following two main different methods, electrospinning and conventional lamination by hot-pressing (for benchmarking electrospun BPMs with conventional laminated bipolar membranes). Table 1 summarizes the list of the different BPMs fabricated in this work, including the type of catalyst.

#### 2.2.1. Fabrication of BPMs by Lamination and Hot-Pressing.

The fabrication of the BPM started with the electrospinning of the anion exchange layer using two single nozzles at both the horizontal X-axis and the vertical Y-axis. The 26 wt % FAA-3 solution (using DMAc as solvent) was electrospun for 3 h at a feed flow rate of 0.5 mL/h. After 3 h of anion exchange layer electrospinning, the process was paused, and the Y-axis polymer solution was exchanged for a 20 wt % SPEEK (using DMAc as solvent) solution to proceed with the dual electrospinning of FAA-3 and SPEEK polymer solutions, to allow the random entanglement of FAA-3 and SPEEK fibers, and therefore to fabricate the bipolar junction. After 2 h of electrospinning the 3D junction, we similarly electrospun the cation exchange layer from 20 wt % FAA-3 into the 3D junction as a catalyst by dissolving in DMAc as a solvent. Dimethylacetamide (DMAc) (VWR Chemicals) was used as solvents for the preparation of the polymer solutions. All of the solvents were used as received.

#### 2.2.2. Fabrication of BPMs by Electrospinning and Hot-Pressing.

The electrospinning phase, hot-pressing was used to densify the electrospun porous BPM and to laminate the planar BPMs in a conventional way. The fibrous mats of the BPM were placed inside a hot-pressing machine (P300S, VOGT Labormaschinen GmbH, Germany) between two Teflon sheets, and hot-pressed at 150 °C at 200 bar for 1 h. The fabricated BPMs were then immersed in 2 M NaCl solution for 24 h for conditioning. Note that the temperature used during hot-pressing (150 °C) is close to the glass transition temperatures of the polymers (approximately 157, 215, and 143 °C for P4VP, FAA-3, and SPEEK, respectively37), but well below the degradation temperatures of the polymers.

## Table 1. Overview of the Bipolar Membranes Fabricated in This Work

| BPM code     | fabrication method                  | thickness (µm) | junction composition                        | catalyst                        |
|--------------|-------------------------------------|----------------|---------------------------------------------|---------------------------------|
| BPM-L1       | lamination and hot-pressing          | 80–90          | laminated SPEEK/FAA-3 layers                 | no catalyst                     |
| BPM-L2       | (2D junction)                       |                |                                             |                                 |
| BPM-E1       | electrospinning and hot-pressing     |                | electrospun SPEEK/FAA-3 fibers randomly     | no catalyst                     |
| BPM-E2       | (3D junction)                       | 80             | electrospun SPEEK/FAA-3 fibers randomly     | 7.7 wt % P4VP in the FAA-3 fibers | |
| BPM-E3       | electrospinning and hot-pressing     |                | electrospun SPEEK/FAA-3 fibers randomly     | 15 wt % P4VP in the FAA-3 fibers | |
|              | (tip to tip)                        |                | electrospun SPEEK/FAA-3 fibers randomly     |                                 |

### Table 2. Composition of Solutions and Electrospinning Operational Parameters Used in This Work to Fabricate the Electrospun BPMs

| polymer          | anion exchange layer | cation exchange layer |
|------------------|----------------------|-----------------------|
| FAA-3            | SPEEK                |                       |
| DMAc             | (SPEEK)              | (FAA-3)               |
| concentration    | 24 wt % FAA-3        | 20 wt % SPEEK         |
| (DMAc)           |                      | (DMAc)                |
| substrate        | polyethylene carbon black | polyethylene carbon black |
| work distance    | (tip to drum)        | (tip to drum)         |
| temperature      | 30 °C                | 30 °C                 |
| relative humidity| 20%                  | 20%                   |
| feed flow rate   | 0.5 mL/h (20 mL syringe) | 0.7 mL/h (20 mL syringe) |
| drum rotation rate| 200 rpm             | 200 rpm               |
| negative voltage | (V_{min})           | (V_{min})             |
| positive voltage | +6.0 kV             | +18.0 kV              |

### 2.3. Morphological Characterization of Electrospun Materials and Final Membranes.

Electrospun ion exchange layers and bipolar membranes were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a JEOL JSM-6480 LV scanning electron microscope equipped with an Oxford Instruments x-ray SDD energy-dispersive X-ray (EDX) spectrometer. The samples were coated with gold prior to the imaging procedure, and liquid nitrogen fracturing was utilized to prepare the samples for the cross-sectional images of the prepared BPMs. Additionally, the BPM samples were treated with 2 M NaCl solution and dried in a vacuum oven at 50 °C to help identify the different ion exchange materials during the EDS mapping.

### 2.4. Electrochemical Characterization.

The electrochemical characterization of the bipolar membranes was performed using a homemade five-compartment testing cell (see Figure 2). Each compartment was separated by either a cation or an anion exchange membrane (Fumatech FKB-PK-75/FAB-PK-130) as shown in Figure 2, with a membrane active area of 7 cm² (20 cm² total area) placed between two plastic plates with circular holes. For each membrane, a single sample was used for all of the tests, with all of the experiments conducted in triplicate. Furthermore, the setup consisted of two platinumized titanium electrodes (Magneto Special Anodes, The Netherlands) placed in electrode compartments. Two Haber–Luggin capillaries positioned at both sides of the BPM were connected to two
Ag/AgCl reference electrodes (QM711X, QIS, The Netherlands) to measure the voltage drop across the bipolar membrane. Both reference and working electrodes were connected to a potentiostat (IviumStat.XRi, Ivium Technologies, The Netherlands) for registration of the voltage drop across the investigated BPM while a current was applied. The electrode rinse solution consisted of 0.25 M FeCl₂ and 0.25 M FeCl₃. All solutions were circulated at a rate of 400 mL/min through the cell compartments.

The current efficiency was calculated with

\[
\text{current efficiency (\%)} = \frac{N \cdot F}{I \cdot t}
\]

where \(N\) is the equivalent of produced HCl and NaOH, \(F\) is the Faraday constant (96 485 C/s), \(I\) is the applied current, and \(t\) is the time of the experiment.

The open-circuit voltage of the BPM is measured by placing the BPM between two electrolyte solutions of acid (0.5 M HCl) and base (0.5 M NaOH). The open-circuit voltage of the bipolar membrane accounts for the potential of the BPM to neutralize the associated electrolytes. Protons and hydroxide ions migrate toward the BPM junction where water is formed by the reaction of \(H^+\) and \(OH^-\). Via use of the Nernst equation (eq 4), the theoretical open-circuit voltage of the BPM is 0.792 V for 0.5 M HCl and 0.5 M NaOH when we assume activities can be approximated by concentrations and assume that the ideal permselectivity of the anion and cation exchange layer of the BPM is equal to 100%.

\[
E_{\text{total}} = E_{\text{acid}} + E_{\text{base}} = \frac{RT}{zF} \ln \left( \frac{[H^+]_{\text{acid}}}{[H^+]_{\text{junction}}} \right) + \frac{RT}{zF} \ln \left( \frac{[OH^-]_{\text{junction}}}{[OH^-]_{\text{base}}} \right) = 0.792 \text{ V}
\]

where \(E\) is the voltage, \(R\) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \(T\) is the absolute temperature in K, \(z\) is the ion valence, and \(F\) is the Faraday constant (\(F = 96 485 \text{ C/mol}\)).

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Electrosprayed P4VP on the BPM 2D Interface.
Laminated BPMs were fabricated with hot-pressing of two planar SPEEK and FAA-3 membrane sheets with and without introduction of P4VP as a catalyst. The thin layer of P4VP was deposited at the BPM junction through electrospraying. Our work proved that this method is capable and effective in introducing a thin homogeneous layer of catalyst at the junction of the BPM. Furthermore, it also surpasses many of the issues that arise with conventional casting, such as interactions of the polymer solution with the lower layers and controlling the thickness of the desired thin polymeric catalyst layer.

Figure 3 shows the SEM images of the junction for both laminated BPMs, with and without the electrosprayed P4VP layer. The 2D junction has a thickness of approximately 200 nm. Laminated BPMs were shown to be stable and had a total dry thickness of 80–90 mm as measured. The basic bipolar membrane, being a laminate of anion and cation exchange membranes without any catalyst (BPM), was used as the reference bipolar membrane throughout this study.

#### 3.2. Preparation of Bipolar Membrane with Electrospinning/Hot-Pressing.

3.2.1. Influence of the Solution Concentration Parameter on Nanofiber Morphology.
To prepare electrospun membranes, several parameters were investigated to optimize the making of the fibers, and among those are the tip-to-drum distance, the solvent used, and the concentration of the polymer solutions. From our experiments, we found that both DMF and DMAc are suitable for the electrospinning of SPEEK and FAA-3. However, electrospinning solutions with DMAc showed more stability with less needle clogging and interference of the spinning jet, which deems this solvent more favorable for the longer (up to several hours) electrospinning operations. The concentration of the polymer in solution is another crucial parameter that affects the
nanofiber morphology. The concentration determines the degree of entanglement of the polymer chains, which is required to maintain the polymer jet and results in the formation of the fibers.39

3.2.1.1. Effect of SPEEK Solution Concentration on Fiber Morphology. The concentration of the polymer in solution is another crucial parameter that affects the nanofiber morphology, as it determines the degree of entanglement of the polymer chains that is required to maintain the polymer jet and results in the formation of well-defined fibers in the nanometer range.39 We investigated the effect of SPEEK concentration on the final fiber morphology by electrospinning different SPEEK solutions in DMAc, with a SPEEK concentration varying in the range of 14–22 wt % while keeping constant all of the other process parameters. FAA-3 is an AEM based on quaternary ammonium poly(arylene ether) and has been already reported to be successfully dissolved in dimethylformamide (DMF) and electrospun at various concentrations.40 However, the use of DMAc as solvent in this work has been preferred, so as to use only one solvent for both SPEEK and FAA-3 during the dual electrospinning for the fabrication of the whole BPMs (see next section).

The SEM images (see Figure 5) of the electrospun films show that a concentration of 20 wt % FAA-3 was insufficient for the production of a solid and mechanically integral mat. A minimal concentration of 24 wt % FAA-3 was needed to create an acceptable nanofiber network (Figure 5C). Further increase of the concentration of FAA-3 (Figure 5D,E) improved the nanofibers’ morphology, eliminating entirely the presence of beads and droplets in the nanofiber network. Measurement of the nanofiber diameter of the 22, 24, 26, and 28 wt % FAA-3 (DMAc) mats resulted in nanofibers with average diameters of 209 ± 16, 275 ± 60, 324 ± 55, and 387 ± 75 nm, respectively. Similar to the case of electrospun SPEEK fibers, the increase of nanofiber diameter and variation with increasing concentration can be observed from the larger standard deviation.

3.3. Electrospun Bipolar Membranes. The preparation of the bipolar membrane with the dual electrospinning process enabled fabrication of a 3D junction with randomly entangled anion and cation exchange fibers. This dual electrospinning process increases the interfacial contact area between the anion exchange polymer and the cation exchange polymer drastically. Anion exchange nanofibers were electrospun out of FAA-3 solution in DMAc, while cation exchange nanofibers were electrospun out of SPEEK solutions in DMAc. The dual electrospinning of SPEEK and FAA-3 solutions in DMAc for making the 3D junction was successfully performed, leading to stable electrospinning process conditions and without causing any interactions between the emerging spinning jets of both polymers.

Figure 6 shows the SEM surface images of the resulting random entanglement of fibers during the dual electrospinning process. These SEM images clearly show the random distribution of both types of fibers in the 3D junction, while beads or droplets are hardly observed. Figure 6 also shows fibers of different diameters. On the basis of the tests performed during the electrospinning of single polymers (section 3.2), SPEEK (20 wt % in DMAc) fibers have an
average diameter of approximately 324 ± 55 nm, while the FAA-3 (26 wt % in DMAc) fibers have an average diameter of approximately 104 ± 18 nm. Therefore, we can conclude that the larger diameter fibers in Figure 6 are the FAA-3 fibers, while the smaller fibers can be associated with the SPEEK fibers. It should be stated that addition of P4VP to FAA-3 will cause a slight change in the diameter of the nanofibers, but this change is not significant as the P4VP concentration in FAA-3 is low.

After the dual electrospinning process, the obtained film was then hot-pressed to convert the fibrous, porous structure of the whole electrospun BPM mat including a 3D junction into a dense bipolar membrane. Cross-sectional SEM images (Figure 7A) present the morphology of the deposited layers via the sequential electrospinning of the anion exchange layer, then the 3D junction composed of randomly entangled FAA-3 and SPEEK fibers, and finally the cation exchange layer.

By comparing Figure 7A and B, it can be seen that the densified bipolar membrane after the hot-pressing process displays an excellent fusion of the fibers into a single film, which appears to be free of any cracks or voids. Moreover, from these cross-sectional SEM images we can clearly identify three distinct regions (Figure 7B), thus confirming a homogeneous compression of the electrospun anion exchange layers during hot-pressing.
Energy-dispersive X-ray spectroscopy (EDS) elemental mapping provides further insight into the formed layers of the BPM. EDS was conducted after treating the hot-pressed-electrospun bipolar membrane with 2 mol L$^{-1}$ NaCl solution and subsequent vacuum drying. EDS confirms the absence of undesired diffusion of the CEL and AEL into the other layer of the BPM.

Figure 8A shows the cross-sectional original SEM image of the prepared electrospun hot-pressed BPM-E1. As shown in Figure 8B, the regions marked with yellow and blue colors are associated with chloride and sodium ions in the cation exchange layer, while in Figure 8C the regions marked with turquoise and dark red represent sulfide and bromide ions in the anion exchange layer. Moreover, EDS shows that the middle layer is clearly linked to both anion and cation exchange layers, thus indicating the existence of two oppositely charged ion exchange polymers in the junction, as result of the dual electrospinning process.

3.4. Voltage–Current Behavior and Water Dissociation Performance of Fabricated BPMs. To assess the water dissociation activity, the developed BPMs have been tested in a wide range of current density (up to 1000 A/m$^2$) using a homemade five-compartment cell at different NaCl concentrations, that is, 0.5 M NaCl and 2.0 M NaCl. The resulting polarization curves are plotted in Figure 9. First, it is worth noting that the two “reference” BPMs (i.e., BPM-L1 and BPM-E1, without catalyst) show the highest voltage and, therefore, the worst performance in terms of water dissociation. For these membranes, water dissociation can be enhanced exclusively as an effect of the high electric field at the junction, because both
FAA-3 and SPEEK fibers have functional groups (quaternary ammonium and sulfonate, respectively) with poor catalytic activity toward water dissociation. Such a low catalytic activity of both anion and cation exchange layers allows comparison of the water dissociation performance resulting mainly from changing the morphological structure of the junction from a 2D to a 3D junction (enlarging the junction area) and from the addition of catalytic materials.

Despite having no catalyst, BPM-E1 showed a lower transmembrane voltage as compared to the conventionally laminated membrane (BPM-L1). This can be mainly attributed to the different morphological structure, due to the increased contact surface area between AEL and CEL fibers by introduction of an electrospun 3D junction. In particular, the randomly entangled anion and cation nanofibers at the junction provide a continuous pathway for the water...
dissociation products (H⁺ and OH⁻), from the junction toward the outer solutions through each corresponding layer. However, protons and hydroxide ions might partially be recombined into water in the junction, thus reducing the water dissociation performance. This might occur as a result of the longer and tortuous routes for both ions around the entangled

Figure 8. Cross-sectional SEM-EDS images of final electrospun BPM. (A) SEM image of the electrospun BPM. (B) Elemental mapping for sodium (blue) and chloride (yellow) ions. (C) Elemental mapping for sulfide (red) and bromide ions (turquoise) (Br⁻: from brominated FAA-3).

Figure 9. Voltage—current curves of the fabricated BPMs in 0.5 M NaCl solution: (A) Laminated (2D junction) and electrospun-hot-pressed (3D junction) BPMs tested in a narrow current density range of 0–100 A/m²; and (B) laminated (2D junction) and electrospun-hot-pressed (3D junction) BPMs tested in a wide current density range of 0–1000 A/m². Error bars showing standard deviations are in most cases not visible due to the small standard deviation values.
fibers, thus increasing the probability of protons and hydroxide ions’ leakage into the oppositely charged adjacent fibers.

Addition of P4VP to the BPMs fabricated in this work was done using two approaches: (i) Electrospraying P4VP polymer solution to form a very thin layer on top of the casted cation exchange membrane layer before the process of lamination with the anion layer and (ii) incorporating P4VP during the electrospinning by blending it with the anion exchange solution FAA-3 prepared for the electrospinning of BPM-E2 and BPM-E3. The reason for this is that the polymer solution of P4VP in DMAc is only stable with FAA-3 and not stable with SPEEK due to the complexes formed between P4VP and SO$_4^{−}$ groups present in SPEEK. For BPM E2, the P4VP was incorporated only into the anion exchange fibers at the 3D junction at a weight concentration of 7.7%. Meanwhile, during the fabrication of BPM-E3, the P4VP was added to the anion exchange fibers at both the 3D junction and the AEL with a concentration of 15 wt %. It is worth noting that a higher concentration of P4VP might be counterproductive, as a higher content of uncharged polymer to the polymer blend would inevitably increase the electrical resistance of the final membrane. Therefore, there is trade-off between the increasing catalytic activity and electrical resistance. Although we have limited the P4VP concentration to 15 wt % in this work, future research should focus on identifying an optimal concentration of the polymer catalyst.

Figure 9 also shows that all of the bipolar membranes with incorporated P4VP exhibit lower voltage than do the reference BPMs, thus suggesting that the incorporation of P4VP enhances water dissociation in those membranes (in the case of both lamination and electrospinning). The use of P4VP as water dissociation catalyst also has advantages in terms of catalyst immobilization at the junction. Several studies have reported the risk of catalyst leakage (leaching) when utilizing heavy metal salts as catalysts for water dissociation, while P4VP has the capability of forming a coordination complex with several metal salts, such as ZnCl$_2$ and AuCl$_3$.

Besides the homogeneous dispersion at the junction, the concentration of the catalyst also affects the water dissociation performance of the membrane. In general, an increase in the concentration of the polymeric catalyst will lead to a more effective water splitting BPM due to the increase in catalytic active sites. However, some studies have also reported that the catalytic capacity of conventional (laminated) BPMs does not necessarily increase with the increasing catalyst concentration in the junction due to steric effects caused by excessive quantities of catalyst. The effect of catalyst concentration can be seen by comparing BPM-E2 and BPM-E3 in Figure 9, where the further increase of P4VP content by including it in both the 3D junction and the AEL has improved the water dissociation performance of BPM-E3 as compared to BPM-E2. Blending of P4VP into the fibers of the anion exchange layer overcomes the limitations of introducing the catalyst into the 2D junction, because depositing catalysts into the 2D junction would eventually compromise the attachment of the BPM layers.

In addition, the prepared BPMs were tested for water dissociation at moderate current densities (up to 1000 A/m$^2$) using 0.5 M NaCl solutions. The voltage–current (V–I) curves were found to be almost linear after the limiting current densities were reached, which were primarily found in the lower current density range (<100 A/m$^2$). With the implementation of the pyridine-based catalyst P4VP in BPM-L2 (2D junction), BPM-E2 (3D junction), and BPM-E3 (3D junction and AEL), the water splitting efficiency of BPM has increased significantly as was found by evaluating the V–I curves at higher current densities. The slope of the V–I curve is most likely attributed to the catalytic water dissociation mechanism of the polymeric catalyst P4VP that contains the pyridine group with a water dissociation reaction rate constant of $k_{lim} = 1.44$.

Figure 10 shows the polarization curves for all of the BPMs using 2 M NaCl as a feed solution. The resulting values of BPM potential are comparatively lower in 2 M NaCl than in 0.5 M NaCl solution. V–I curves in the narrow current density range (0–100 A/m$^2$) depict the different regions evolved when the bipolar membrane potential is lower than the estimated theoretical water dissociation voltage ($V_{th} = 0.83$ V). We can deduce the limiting current density for the electrosprun BPMs to be in the range of 5–10 A/m$^2$ in the case of 0.5 M NaCl and in the range 10–20 A/m$^2$ in 2 M NaCl, while the limiting current density is less distinguishable for the laminated bipolar membranes (BPM-L1 and BPM-L2). Overall, the reduction of BPM potential in 2 M NaCl is attributed to the higher contribution of salt co-ion leakage of Na$^+$ and Cl$^−$ toward conductivity.

Current efficiency was measured at a constant current density of 100 A/m$^2$ for the fabricated BPMs to evaluate the
BPMs showed higher current efficiencies in comparison with the laminated ones. In particular, the laminated BPMs show low current efficiency values (in the range of 25%–32%), which indicate a poor efficiency of the water dissociation and transport of product from the junction to the outer solutions. Regarding the electrospun BPMs, Figure 11 shows that the increase in the P4VP content leads to a remarkable increase in the current efficiency and, therefore, of the membrane performance toward water dissociation. In particular, the introduction of P4VP in the junction gives a 26% increase in the current efficiency as compared to the reference BPM without catalyst. Finally, BPM-E3 recorded the highest current efficiency, with an average of 90%.

3.5. Open-Circuit Voltage in Acid and Base Solutions.

In the previous sections, we have tested all of the BPMs only using (pH-neutral) electrolyte solutions, to assess their performance toward acid-base production. However, it is also worth examining the behavior of BPMs in concentrated acid and base solutions, as such conditions are of interest in some novel applications (e.g., energy storage47), and some membranes might exhibit different behavior under high acid/base concentrations. In this regard, we have tested the OCV of all BPMs in 0.5 M HCl/0.5 M NaOH solutions, to assess the membrane selectivity and the effect of co-ion leakage under open-circuit conditions. Results of the measured OCV and corresponding apparent permselectivity (i.e., calculated as a ratio of measured and theoretical OCV) for each BPM are shown in Figure 12. In particular, Figure 12 shows that all of the BPMs have lower OCV than the theoretical value (i.e., 0.792 V at 25 °C), due to the nonideal behavior of both anion and cation exchange layers. Although SPEEK and FAA-3 are proven to be highly selective for both Cl− and Na+ ions, respectively, leakage of hydroxide ions and (especially) protons is dominant under relatively high acid/base concentration. In general, BPMs with electrosprayed P4VP showed higher open-circuit voltages as compared to the laminated membrane without catalyst (BPM-L1). This could be due to the effect of the thin layer of electrosprayed P4VP catalyst, which reduces the effect of unwanted proton leakage, as was similarly observed in some previous studies.12 Previous works of similar to 3D-junction electrospun BPMs, using (hexamethyldi-terphenyl poly(benzimidazole) (HMT-PMBI)) as AEL and SPEEK as CEL, reported an open-circuit voltage of 0.62 V (with Al(OH)3 catalyst) and 0.45 V (without catalyst), when measured in 1 M acid and base.19

Figure 12 also clearly shows that BPM-E2 has lower OCV than does BPM-E1, likely as a result of a much larger interface between the anion and cation exchange fibers for BPM-E2. Furthermore, upon the addition of P4VP into the AEL, BPM-E3 gives the highest OCV among all of the fabricated membranes. The drop in OCV for BPM-E2 is most likely caused by the co-ion transport of protons through the anion exchange layer (FAA-3). This high loss of protons through anion exchange membrane fibers could be potentially tackled, for instance, by increasing the cross-linking of AEL.48

4. CONCLUSIONS

In this study, the effect of a 2D and 3D junction on the water dissociation rate of the bipolar membrane has been systematically studied by using the same anion and cation polymeric materials. This has been accomplished by employing a dual electrospinning manufacturing process to prepare bipolar membranes and using chemically stable SPEEK and FAA-3 materials as alternatives for cation and anion exchange layers. It was found that the 3D junction has an accelerating effect on the water dissociation as compared to the 2D junction, excluding the effect of added catalyst. To demonstrate the flexibility of the electrospinning technique, the use of a polymeric water dissociation catalyst poly(4-vinylpyrrolidone) was investigated by incorporating it into both the 2D junction and the 3D junction. The catalytic effect of poly(4-vinylpyrrolidone) on the water splitting rate was observed to be higher for the fabricated electrospun BPM with the 3D junction in comparison to bipolar membranes with a 2D junction with the polymeric catalyst as galvanostatic tests in 0.5 M NaCl and 2 M NaCl solutions under water splitting conditions revealed. Such an observation can be explained by the three-dimensional entanglement of the anion and cation polymer fibers resulting in a desired higher specific surface area of the junction. Finally, open-circuit voltages were measured for all fabricated BPMs using 0.5 M HCl and 0.5 M NaOH solutions. Higher open-circuit values were found for BPMs containing an electrospayed poly(4-vinylpyrrolidone) layer at the 2D junction and for the BPM with this polymer blended with its anion exchange layer. This work provides a platform for the manufacturing approach of bipolar membranes for water splitting with a 3D catalytic junction with the chosen dual electrospinning path, which is considered superior and
more robust than a casting process leading to a 2D catalytic junction, opening the possibility of incorporating various polymeric materials as catalyst for the water dissociation process.

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Notes
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