Low-cost wire-electrospun sulfonated poly(ether ether ketone)/poly(vinylidene fluoride) blend membranes for hydrogen-bromine flow batteries

Sanaz Abbasi\textsuperscript{a,b}, Antoni Forner-Cuenca\textsuperscript{a}, Wiebrand Kout\textsuperscript{b}, Kitty Nijmeijer\textsuperscript{a,c}, Zandrie Borneman\textsuperscript{a,c,*}

\textsuperscript{a} Membrane Materials and Processes, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, the Netherlands
\textsuperscript{b} Elestor B.V., P.O. Box 882, 6800 AW, Arnhem, the Netherlands
\textsuperscript{c} Dutch Institute for Fundamental Energy Research (DIFFER), P.O. Box 6336, 5600 HH, Eindhoven, the Netherlands

ARTICLE INFO

Keywords:
Hydrogen-bromine flow battery
Low-cost blend membrane
Wire-electrospinning
Sulfonated poly(ether ether ketone)
Poly(vinylidene fluoride)

ABSTRACT

Cost-effective dense membranes were developed by blending proton-conductive sulfonated poly(ether ether ketone) (SPEEK) with inert, mechanically stable poly(vinylidene fluoride) (PVDF) for hydrogen-bromine flow batteries (HBFBs). Wire-electrospinning followed by hot-pressing was employed to prepare dense membranes. Their properties and performance were compared to solution-cast membranes of similar composition and thickness. Electrospinning improved the ionic conductivity and bromine diffusion properties by providing interconnected ion-conductive SPEEK nanofiber pathways through a PVDF matrix. Relatively thin (~50–60 \(\mu\)m) electrospun membranes with a SPEEK/PVDF ratio (wt%/wt%) of 90/10 and 80/20 showed comparable \(\text{Br}_3\) diffusion rates as the relatively thick and commercially available perfluorosulfonic acid (PFSA) membrane (~100 \(\mu\)m) at a 35%–42% lower proton conductivity. The latter can be attributed to the poorer ion conductivity of SPEEK compared to PFSA and the presence of PVDF. The HBFB single cell featured the best polarization behavior and ohmic area resistance with the electrospun membrane containing 80/20 (wt%/wt%) SPEEK/PVDF. However, the low thickness and insufficient chemical/mechanical stability of the ES 80/20 causes a rapid decay in the HBFB cycling performance. This study promotes a life-time comparison study between the low-cost wire-electrospun SPEEK/PVDF blend membranes (~\(\varepsilon\)100 m\(^2\)) and the typically used PFSA membranes (~\(\varepsilon\)400 m\(^2\)) for a long-term HBFB performance.

1. Introduction

The worldwide demand for electricity production is anticipated to double by the next thirty years \cite{1}. At the same time, global electricity consumption is expected to be less dependent on fossil fuels due to their environmental and safety problems as well as resource limitations \cite{1,2}. This has inspired the generation of clean energy from renewable sources such as wind and solar power. However, due to the intermittent nature of these energy sources, a large-scale storage system is required to reduce instabilities and to guarantee the continuous supply of electricity \cite{2,3}.

Electrochemical energy storage is a promising technology for large-scale energy storage due to its reliable energy output at low cost \cite{2,4}. Among the electrochemical systems, redox flow batteries (RFBs) are cost-effective candidates combining a high response time with a more than 80% efficiency \cite{5,6}. Moreover, their ability to separately monitor energy and power for tunable operation periods (1–20 years) within high safety standards makes RFBs suitable for large-scale applications compared to systems that store the electrochemical cell and electrolytes in a single confinement such as Li-ion batteries \cite{5,7}.

Among the RFBs, growing attention has been directed towards hydrogen-bromine flow batteries (HBFBs). The main advantage of HBFBs is their low system capital cost per kWh. This is due to abundantly available hydrogen and bromine on a global scale, which

* Corresponding author. Membrane Materials and Processes, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, the Netherlands.
E-mail address: Z.Borneman@tue.nl (Z. Borneman).

https://doi.org/10.1016/j.memsci.2021.119258
Received 16 December 2020; Received in revised form 12 February 2021; Accepted 4 March 2021
Available online 11 March 2021
0376-7388/© 2021 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
and Br costs of HBFBs are their high power density and fast kinetics of the electrochemical reaction between H₂ and Br₂ [13]. This PEM must have a high electrical resistance to prevent a shunt that extends the lifetime of the catalyst and consequently, of the whole HBFB. Liquid and gas compartments is necessary. The presence of the PEM highly active materials for the HOR/HER but they suffer from poisoning and control the costs [12]. Platinum group metal (PGM) catalysts are amongst the tested membranes, the reinforced long-chain PFSA (LC PFSA) membrane possessed the best tradeoff between water uptake, and area specific resistance (ASR). Sulfonated poly(vinylidene fluoride) (SPVDF) showed comparable ASR to LC PFSA at relatively similar ion exchange capacity (IEC) and water uptake values. However, SPVDF and hydrocarbon-based membranes, e.g. sulfonated polyethylene (SPE) and sulfonated poly(styrene-co-divinylbenzene) (PS/DVB) lacked the well-defined and narrow ionic pathways of LC PFSA and/or chemical stability to achieve the preferred HBFB performance (IEC ~0.8 meq g⁻¹ and thickness <75 μm).

Wang et al. [11] showed that Br₂ rapidly dissolves in the HBr solution through the formation of tribromide (Br₃²⁻):

$$\text{Br}_2 + \text{Br}^- \rightarrow \text{Br}_3^{2-}$$  \hspace{1cm} (2)

Where K = 16 is the equilibrium constant at 25 °C [11].

Contrary to the rapid bromine species reactions, the rate of hydrogen oxidation and evolution reactions (HOR/HER) heavily depends upon the presence of the catalyst at the GDE surface to enhance the performance and control the costs [12]. Platinum group metal (PGM) catalysts are highly active materials for the HOR/HER but they suffer from poisoning in the presence of HBr and Br₂ [12,13]. To limit bromine species (mainly Br₂ and Br₃²⁻) crossover to the hydrogen electrode, a PEM between the liquid and gas compartments is necessary. The presence of the PEM extends the lifetime of the catalyst and consequently, of the whole HBFB [13]. This PEM must have a high electrical resistance to prevent a shunt current between the electrodes [14]. Furthermore, the membrane should promote the transport of protons and hinder the migration of Br₂ and Br₃²⁻ to the GDE [14,15].

Three key properties in the development of HBFB technology are a high peak power density (≥1 W cm⁻²), a long lifetime (≥20 years) and low costs per kWh electricity supplied (≤0.40 $ kWh⁻¹) [8]. Power density is mostly influenced by the membrane area resistance, while the major element affecting the lifetime is the membrane ion selectivity i.e. bromine species crossover [10,14]. Although the overall cost of reactants in the HBFB is considered low, developing a low-cost membrane-electrode-assembly (MEA) with long durability remains a challenge. Therefore, it is essential to optimize the balance between these crucial characteristics of the membrane being a high HBFB performance and durability at competitive costs [10,14,15].

To improve the ion selectivity and area resistance of the membrane in hydrogen-bromine technology, multiple studies have been carried out. So far, these studies have been dedicated to the employment of perfluorosulfonic acid (PFSA) polymer (known as Nafion®) as a dense proton conductive membrane [5,9,10,14,16-18]. The distinct micro-phase separation between the hydrophobic fluorinated backbone and the hydrophilic side chains of the PFSA membrane results in a controlled water uptake as well as a high ionic conductivity [19]. These are advantageous for the crossover of bromine species [14,22]. To reduce the water uptake without decreasing the proton transport, SPEEK can be blended with an inert polymer, e.g. polyethersulfone (PES) or PVDF [19,24]. Inspired by the previous research [15,20,22], PVDF is used as the low-cost, chemically and mechanically strong perfluorinated polymer (more than 200 times cheaper than Nafion®) to prevent bromine species cross-over. Both polymers are blended and nanofiber wire-electrospinning is employed to synthesise blend porous membrane mats. By implementing the wire-electrospinning, hundreds of nanofibers are produced simultaneously which allow, compared to nozzle spinning, the production of orders of magnitude higher areas per unit time that can be directly translated into lower costs per m² [26].

Subsequently, several electrospun layers were combined and hot-pressed to obtain dense, proton conductive blend membranes (Fig. 1). The effect of the SPEEEK/PVDF ratio and the number and type of electrospun layers in the final proton exchange membranes on the naturally makes them inexpensive active materials ($5.65 of HBr per kWh installed [8]). Additional factors contributing to the low storage costs of HBFBs are their high power density and fast kinetics of the electrochemical reaction between H₂ and Br₂ [9]. These features promote HBFBs as an advantageous electrochemical storage system to meet both cost and life-time targets [5].

HBFB systems consist of two separate tanks; one storing an aqueous HBr/Br₂ solution as the liquid electrolyte and the other one storing H₂ as the gaseous electrolyte. Both tanks continuously feed the reactants to an electrochemical cell. During discharge, H₂ is oxidized to H⁺ on a catalyst coated gas diffusion electrode (GDE). The generated H⁺ ions permeate through a proton-exchange membrane (PEM) to the liquid side and react with Br₂ to produce HBr. The overall electrochemical reaction is presented below [10]:

$$\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} \hspace{1cm} \text{Discharge} \hspace{1cm} E_{\text{therm}} = 1.098 \text{ V}$$  \hspace{1cm} (1)

H₂ + Br₂(aw) ⇌ 2 HBr (aq), E₀, calib = 1.098 V

The effect of the SPEEK/PVDF ratio and the number and type of electrospun layers in the final proton exchange membranes on the
membrane properties and performance was investigated. Results were compared to the properties and performance of SPEEK/PVDF blend membranes made by state-of-the-art solution-casting.

2. Experimental

2.1. Electrospinning SPEEK/PVDF blend nanofiber mats

SPEEK/PVDF blend nanofiber mats were prepared by electrospinning blend solutions with different ratios of SPEEK (IEC 2.07 meq g$^{-1}$, degree of sulfonation (DS) ~ 75%, Fumion® E-500, Fumatech, Germany) and the copolymer vinylidene difluorodehexafluoropropylene (Kynar powerflex® LBG, Arkema, France) in N,N-dimethylformamide (DMF, Acros Organics, 99%). Dope compositions are listed in Table 1.

Electrospinning was performed using a wire-electrospinning apparatus (Nanospider NS LAB, Elmarco, Czech Republic). The relative humidity and temperature of the electrospinning chamber was controlled (desiccant dehumidifier system (DDS) (ML270PLUS, Munters, The Netherlands)). The blend solutions were subsequently electrospun from a carrier moving along the working wire-electrode at a speed of 150 mm s$^{-1}$ with 80 kV applied voltage between the working and collecting electrode (working distance was set to 150 mm). Nanofibers were produced under 25 ± 1% relative humidity and 22 ± 0.5 °C. The distance between the collecting electrode and the substrate was 25 mm. Substrate collecting speed was fixed at 10 mm min$^{-1}$.

2.2. Preparation of SPEEK/PVDF blend membranes

2.2.1. Hot-pressing the electrospun SPEEK/PVDF blend nanofiber mats

Different membranes were prepared by stacking 12 layers of 25–30 μm thick electrospun mats. The nanofiber mats were appropriately arranged and stacked on top of each other following the composition summarized in Table 2. Afterwards, stacked layers were compressed together at 150 bar and 170 °C for 600 s to produce transparent, dense membranes with a thickness range of 50–60 μm. To avoid any deformation of the hot-pressed mats, the membranes were cooled down in the press with circulating cooling water at 150 bar for 180 s.

2.2.2. Solution-casting

Solution-cast SPEEK/PVDF membranes were prepared by dissolving the appropriate amounts of SPEEK and PVDF in DMF (Table 3). The blend solutions were cast on a glass plate using a doctor blade with a 200 μm fixed thickness at ambient conditions. The cast solutions were dried in an oven at 60 °C for 24 h and then dried at 140 °C for 48 h [24]. The final thickness of the prepared membranes was 50–60 μm.

Table 1

| SPEEK/PVDF ratio in solution (wt%/wt%) | Total polymer concentration (wt %) | SPEEK concentration (wt %) | PVDF concentration (wt %) |
|---------------------------------------|----------------------------------|---------------------------|---------------------------|
| 100/0                                 | 20                               | 20                        | 0                         |
| 80/20                                 | 20                               | 16                        | 4                         |
| 60/40                                 | 20                               | 12                        | 8                         |
| 50/50                                 | 20                               | 10                        | 10                        |

Table 2

| Membrane | Stacking arrangement of electrospun mats | Final membrane arrangement and composition |
|----------|------------------------------------------|-------------------------------------------|
| ES 100/0 | 12                                      | Hot-pressed electrospun mats |
| ES 90/10 | 3                                       | SPEEK/PVDF ratio (wt %/wt%) |
| ES 80/20 | 6                                       | 100/0 |

Table 3

| Cross-view of the repeating unit | Number of repeating units per membrane | Hot-pressed electrospun mats |
|----------------------------------|----------------------------------------|-----------------------------|
| ES 100/0                         | 12                                     | 100/0                       |
| ES 90/10                         | 3                                      | 90/10                       |
| ES 80/20                         | 6                                      | 80/20                       |
The IEC was determined using acid-base titration as described by Park et al. [20] and calculated using the following formula:

$$\text{Normalized IEC} = \frac{\text{IEC}}{\text{IEC}_{\text{dry}}}$$

Where N (mol L\(^{-1}\)) and V (L) are the normality and volume of the NaOH titrating solution, respectively. \(M_{\text{dry}}\) (g) is the dry mass of the membrane.

Membrane water uptake (%) was determined as follows. First, the sample was immersed in 4 M HBr for at least 24 h to ensure complete protonation. Then, the sample was washed multiple times with deionized water to remove the excess HBr and wiped with tissue paper to remove the adhered water. The wet weight (g) and thickness (µm) of the wiped samples were measured using an analytical balance and a screw micrometer, respectively. The dry weight was determined by drying the wet membrane in an oven at 60 °C for 24 h. The water uptake was calculated using the following formula:

$$\text{Water uptake} = \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100\%$$

Where \(W_{\text{wet}}\) (g) and \(W_{\text{dry}}\) (g) are the membrane weight before and after drying at 60 °C, respectively. To exclude the influence of membrane thickness, IEC and water uptake were normalized by the wet thickness [10]:

$$\text{Normalized IEC (meq g\(^{-1}\) cm\(^{-1}\))} = \frac{\text{IEC}}{t_{\text{wet}}}$$

$$\text{Normalized water uptake (g cm\(^{-2}\) h\(^{-1}\))} = \frac{\text{water uptake}}{100\% t_{\text{wet}}}$$

### 2.3.2. Ion exchange capacity and water uptake

IEC quantifies the number of functional groups of a given membrane. The IEC was determined using acid-base titration as described by Park et al. [20] and calculated using the following formula:

$$\text{IEC} = \frac{N \times V}{m_{\text{dry}}}$$

Where \(N\) (mol L\(^{-1}\)) and \(V\) (L) are the normality and volume of the NaOH titrating solution, respectively. \(m_{\text{dry}}\) (g) is the dry mass of the membrane.

The Br\(_3\) diffusion rate through the membrane was calculated using the following formula:

$$j = \frac{[\text{Br}_3^-] \times V \times M_w}{A \times t}$$

Where \([\text{Br}_3^-]\) (mol L\(^{-1}\)) is the Br\(_3^-\) concentration, \(V\) is the HBr solution volume (L), \(M_w\) is the molecular weight of Br\(_3^-\) (g mol\(^{-1}\)), \(A\) is the membrane area (cm\(^2\)) and \(t\) is the characterization time (h). Br\(_3^-\) diffusion rate was also normalized by the wet thickness [10]:

$$\text{Normalized Br}_3^- \text{ diffusion rate} = \frac{j}{t_{\text{wet}}}$$

### 2.3.3. Proton conductivity and Br\(_3^-\) diffusion rate

Through-plane proton conductivity of the membranes was determined by AC impedance spectroscopy measurement (SP-150 potentiostat, Bio-Logic, France) using a gold-stainless steel two-electrode cell with a radius of 1 mm (LEPMI, Grenoble INP, France). The membrane sample was immersed in 4 M HBr for 24 h before the measurement and washed thoroughly with deionized water before being clamped between two electrodes in a wet state.

AC impedance characterization was performed at constant voltage with 10 mV sinus amplitude and a frequency range of 10,000 Hz-0.2 Hz.

The formula for the calculation of proton conductivity is shown below:

$$\sigma = \frac{L}{(R_{\text{total}} - R_{\text{blank}})A}$$

Where \(\sigma\) (S cm\(^{-1}\)) is the through-plane proton conductivity, \(L\) (cm) is the wet thickness, \(R_{\text{blank}}\) (Ω) is the resistance of the cell without the membrane, \(R_{\text{total}}\) (Ω) is the resistance of the cell with the membrane and A (cm\(^2\)) is the electrodes active area.

The Br\(_3^-\) diffusion rate through the membrane was measured using an ex-situ titanium permeation cell (Elestor, The Netherlands) consisting of two compartments. Each compartment contained four layers of 0.4 mm carbon paper (Avcarb®, Avcarb Material Solutions, US) separated by the membrane under study (3.14 cm\(^2\) active area). The membrane was immersed in 4 M HBr for at least 12 h before the start of the experiment. One of the two compartments was continuously circulated with a 200 mL solution composed of 1 M Br\(_2\)/4 M HBr, while in the other half-cell a 200 mL solution of 4 M HBr was circulated as the carrier source (All ES membranes were positioned in the cell such that the surface made of hot-pressed 100/0 blend mat (Table 2) was faced towards 4 M HBr compartment.). The Br\(_3^-\) crossover rate from the bromine species source to the other compartment was monitored in a 6 h-long experiment, using UV-VIS spectroscopy (UV–Vis spectrophotometer EU-2600, Shanghai Onlab Instrument, China) at 266 nm wavelength to determine the concentration [11]. The solution outlet from the carrier compartment was connected to a small flow cell with a 0.2 mm thick slit (Starna BmbH, Germany) and the change in the absorption was continuously detected by the UV–Vis detector. The Br\(_3^-\) diffusion rate through the membrane was calculated by converting the absorption values to the Br\(_3^-\) concentration using a calibration curve. The following formula was used to calculate the Br\(_3^-\) diffusion rate \(j\) (g cm\(^{-2}\) h\(^{-1}\)):

$$j = \frac{[\text{Br}_3^-] \times V \times M_w}{A \times t}$$

Where \([\text{Br}_3^-]\) (mol L\(^{-1}\)) is the Br\(_3^-\) concentration, \(V\) is the HBr solution volume (L), \(M_w\) is the molecular weight of Br\(_3^-\) (g mol\(^{-1}\)), \(A\) is the membrane area (cm\(^2\)) and \(t\) is the characterization time (h). Br\(_3^-\) diffusion rate was also normalized by the wet thickness [10]:

$$\text{Normalized Br}_3^- \text{ diffusion rate} = \frac{j}{t_{\text{wet}}}$$

### 2.4. Membrane HBFB cell performance

The electrochemical performance of the prepared SPEEK/PVDF and commercial Nafion® (LC PFSA, 1.0 meq g\(^{-1}\), Fumasep® F-10100, Fumatech, Germany, 100 µm) membranes was investigated in an HBFB single cell made of titanium (Elestor, The Netherlands) with 3.14 cm\(^2\) active area. The cell liquid diffusion electrode (LDE) contained three layers of 0.4 mm carbon paper and an additional 0.4 mm carbon cloth (both Avcarb®, Avcarb Material Solutions, US) forming the interface layer with the membrane. The GDE contained a 1.0 mm porous titanium layer (Bekaert, The Netherlands) and a 0.2 mm carbon paper coated with 0.3 mg cm\(^{-2}\) platinum-iridium (Pt–Ir/C, IRD Fuel Cells, Denmark) as the catalyst layer. The membrane sample was laminated to the GDE at 4 bar and 135 °C for 480 s to increase the reaction surface area (All ES membranes were laminated to the GDE surface that consisted out of a hot-pressed 100/0 blend mat.). A Viton® O-ring (Eriks B.V., The Netherlands) was used as a sealing gasket for the gas side. 20 mL solution of 1.3 M Br\(_2\)/4 M HBr was used as electrolyte and passed through the cell at 25 °C with a flow rate of 200 mL min\(^{-1}\). Hydrogen gas was continuously fed to the anode at 2.5 bar with a rate of 1.1 mL min\(^{-1}\).

### 2.4.1. Polarization behavior

The polarization behavior was analyzed twice a day by three separate measurements per session. To ensure constant conditions in the cell,
both electrolytes were continuously circulated throughout the cell. The polarization behavior was monitored using an SP-150 potentiostat connected to a FlexP 0060 booster (Bio-Logic, France) in the voltage range of 0.7 V–1.2 V with a step size of 0.05 V and step time of 30 s. The electrical current was monitored every second and solely reported at the last second of each step. Current density (mA cm\(^{-2}\)) and power density (mW cm\(^{-2}\)) profiles were obtained during discharge and charge mode. The cell’s total ASR (including ohmic, charge transfer and mass transport ASRs) was calculated from the slope of the current-voltage curves.

2.4.2. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were performed at the end of each polarization behavior analysis at open-circuit voltage (OCV) using the potentiostat described before. AC was applied with a 10 mV sinus amplitude and a frequency range of 10,000–0.2 Hz. Fifteen data points (each including six measurements) were collected. The ohmic ASR was determined from the impedance intercept with the real axis in the Nyquist plot.

2.4.3. Cycling performance

Before the cycling tests, the HBFB cell was conditioned by charging it at 150 mA cm\(^{-2}\) up to 1.15 V. Cycling tests began at a constant current mode (150 mA cm\(^{-2}\)) with discharge and charge cut-off voltages of 0.7 V and 1.15 V, respectively. This voltage range was chosen to prevent detrimental effects on the cell, e.g. corrosion of the carbon and titanium, due to possible side reactions. The efficiency values were obtained using the following formulas:

\[
\text{Voltage efficiency (\%)} = \frac{\int_{V_{\text{discharge}}} V \, dt}{\int_{V_{\text{charge}}} V \, dt} \times 100\%
\]

\[
\text{Coulombic efficiency (\%)} = \frac{I_{\text{discharge}} \times t}{I_{\text{charge}} \times t} \times 100\%
\]

3. Results and discussion

3.1. Morphology and elemental analysis

SEM images of the electrospun SPEEK/PVDF blend nanofiber mats with different SPEEK/PVDF ratios are presented in Fig. 2.

Fig. 2 shows the electrospinning results using a 20 wt% total polymer concentration and the compositions as listed in Table 1. Electrospinning of pure SPEEK 100/0 and SPEEK/PVDF 60/40 gives the most homogeneous fiber mats where the fibers originating from the 100% SPEEK are slightly thinner. The mats prepared out of the 80/20 and 50/50 mixtures are more heterogeneous in nature and also show the presence of polymeric beads. Higher PVDF content results in higher solution viscosity and therefore, higher surface tension between the solution and the wire electrode [20,27]. This increases the thickness of the nanofibers [27]. The non-homogeneous 80/20 and 50/50 nanofiber mats are assumed to be formed due to an imbalance between the strain forced applied by the electric field and the viscosity of the solution [28]. For these reasons, only the pure SPEEK and the 60/40 wt% mixture are used for further research.

The elemental composition of the electrospun 60/40 SPEEK/PVDF blend nanofiber mat is depicted in Fig. 3.

Qualitative analysis results show that sulfur (indicating the presence of \(-\text{SO}_3\text{H}\) groups in SPEEK) and fluorine (representing the perfluorinated polymer PVDF) are homogeneously distributed (Fig. 3b and c). This is confirmed by the quantitative intensity profiles (Fig. 3d).

Similarly, the composition profiles for the hot-pressed and solution-cast membranes for a SPEEK/PVDF ratio of 80/20 are shown in Fig. 4.

The ES 80/20 cross-section (Fig. 4a1) presents a dense, pore-free...
membrane built of alternatively stacked and compressed electrospun 100/0 and 60/40 SPEEK/PVDF blend nanofiber mats. The alternating layers of 100/0 and 60/40 SPEEK/PVDF can be distinguished in the SEM image by their contrast difference caused by differences in inelastic interactions between the primary electron beam and the different polymer compositions. On the other hand, the cross-section of the SC 80/20 membrane (Fig. 4b1) shows large interfacial phase separation between SPEEK and PVDF. It contains large oval-shaped structures and voids (approx. 10–20 μm). The composition variations through the ES 80/20 membrane (Fig. 4a2-4) show that sulfur (SPEEK) and fluorine (PVDF) present wave-like signals over the layer thickness with some mixing which is the result of pressing. This proves that during the compression step, the individual electrospun layers do not fully intertwine. Also, the distribution of both sulfur and fluorine through the individual blend layers indicates the good compatibility and good interaction between SPEEK and PVDF [29]. In contrast, sulfur and fluorine are not homogeneously distributed but rather agglomerated as discrete areas in the SC 80/20 membrane (Fig. 4b2-4), indicating that SPEEK and PVDF do not mix on a molecular level. Fig. 4b2 indicates by the S-domains that the large oval-shaped structures are SPEEK agglomerates. During the cryogenic fracturing SPEEK agglomerates, depending on their position, end up in the top or bottom half. The agglomerates that end up in the opposite half leave holes as their footprint behind [27]. The PVDF rich areas form a continuous phase that surround the ionic clusters of SPEEK as in a matrix-like structure (Fig. 4b3). This clearly visible phase separation between SPEEK and PVDF is caused by the incompatibility between the highly hydrophobic PVDF and hydrophilic domains of SPEEK [29,30]. It is worth mentioning that while sulfur is detectable through the uneven surface of the cryogenic-fractured sample (Fig. 4b2), Fluorine, the lighter element, is harder to detect in the regions relatively distant to the X-ray detector (upper right and lower left corners in Fig. 4b1) due to its relatively lower content in the sample compared to SPEEK. As a result, they appear as dark regions (Fig. 4b3).

3.2. Membrane characterisation

Properties of the commercial PFSA membrane (~100 μm) are considered as a reference for the assessment of the electrospun and solution-cast SPEEK/PVDF blend membranes (~50–60 μm). Normalized IEC, normalized water uptake, through-plane proton conductivity and normalized Br₃ diffusion rate of the Nafion®, electrospun and solution-cast membrane samples are discussed below.

3.2.1. Normalized IEC and normalized water uptake

Normalized IEC and normalized water uptake of the commercial PFSA membrane and the SPEEK/PVDF blend membranes are presented in Fig. 5.

In general, both pure SPEEK and SPEEK/PVDF blend membranes show higher normalized IEC (Fig. 5a) and normalized water uptake (Fig. 5b) than the commercial PFSA membrane. The higher normalized IEC confirms a higher amount of charged groups per unit weight in SPEEK based membranes than in the PFSA membrane. Due to the hydrophilic nature of the –SO₃ groups, this translates into a higher normalized water uptake. The less pronounced separation of hydrophilic and hydrophobic domains in SPEEK compared to Nafion® [19] further enhances this difference in normalized water uptake. A decline in both
normalized IEC and normalized water uptake is observed when the PVDF content is increased. This is due to the hydrophobic nature of PVDF. At 0 wt% and 20 wt% PVDF content, electrospun and solution-cast blend membranes do not show huge deviations in their normalized IEC and normalized water uptake values and follow a similar pattern. This indicates that the preparation process does not affect the IEC and water uptake of the blend membranes and these properties are mainly governed by the SPEEK content [24,31].

3.2.2. Proton conductivity and normalized Br\textsubscript{3} diffusion rate

Fig. 6 shows the proton conductivity and normalized Br\textsubscript{3} diffusion rate of the commercial PFSA membrane and the SPEEK/PVDF blend membranes.

The proton conductivity of the PFSA membrane is higher than that of all SPEEK/PVDF membranes. Also, all electrospun membranes have higher conductivities than the solution cast membranes. To a certain extent, the relatively low proton conductivity of the SPEEK membranes relative to the PFSA membrane may stem from the aggregation of the hydrophilic SPEEK segments as isolated clusters [31] in contrast to percolating hydrophilic channels as in PFSA [10,19]. Moreover, the higher conductivity of the electrospun membranes relative to that of the solution-cast counterparts relates to the better interconnectivity and more homogeneous distribution of SPEEK over the full thickness of the membrane, which is further improved by the hot-pressing process [32,33] and is confirmed by the elemental composition (Fig. 4). Clearly, the phase separation between SPEEK and PVDF in the solution-cast membranes decreases the conductivity further. All blend membranes show a decline in proton conductivity with increasing the PVDF content. This decline is more pronounced for the solution-cast membranes compared to the electrospun ones. For example, SC 100/0 has more than 4 times higher conductivity than SC 80/20, while this change is almost negligible for ES 100/0 and ES 80/20 membranes. Even though SC 80/20 shows lower normalized water uptake (Fig. 5b), it exhibited more than 7 times lower proton conductivity than the ES 80/20 membrane. The poor conductivity of SC 80/20 can be explained by the existence of isolated SPEEK domains as a result of the polymer-polymer phase-separation [29,31]. On the other hand, ES 80/20 can conduct protons through the inter-connected SPEEK nanofiber pathways. Interestingly, ES 100/0 shows higher proton conductivity than SC 100/0. This is probably due to a better connection between the ionic groups of SPEEK molecular chains by experiencing high temperature and pressure during the hot-pressing, which can improve the passage of protons through the membrane [34].

Fig. 6b shows that an increasing PVDF content reduces the normalized Br\textsubscript{3} diffusion rate through the blend membranes. The diffusion rate of SC 80/20 is considerably lower than that of SC 100/0 due to the relatively inert character of PVDF. In comparison to PFSA, both the SC 80/20 and the ES 80/20 membranes represent comparable normalized Br\textsubscript{3} crossover rates. The slightly higher normalized Br\textsubscript{3} diffusion rate of ES 100/0 compared to SC 100/0 can be similarly explained by the increased connection between the hydrophilic domains of SPEEK which can result in higher bromine species crossover.

For a good HBFB performance, a high proton conductivity at a low bromine species crossover rate is necessary [10]. As such, alternatives for PFSA membranes should have at least a comparable if not better
balance between the \( \text{Br}_2 \) diffusion rate and the proton conductivity at a lower cost. So far, the obtained results show that the relatively thin electrospun blend membranes have comparable normalized \( \text{Br}_2 \) diffusion rates to the relatively thick PFSA membranes but at the expense of a 35%–42% lower proton conductivity (Fig. 6). Among the electrospun blend membranes, ES 80/20 and ES 90/10 are the first- and second-best samples concerning the balance between the proton conductivity and bromine species diffusion rate. Furthermore, with an approximately 40% lower wet thickness than the PFSA membrane, they significantly reduce the materials costs. The average cost of typically used PFSA membranes (~100 \( \mu \)m) for HBFB is ~€400 m\(^{-2}\) [21]. This is while the preparation cost of the ES 80/20 membrane (~50–60 \( \mu \)m), based on the amount of used polymers, is estimated to be ~€100 m\(^{-2}\) (solvent costs are considered comparable and production costs are not taken into account). These results along with the high normalized IEC and low normalized water uptake values obtained for these membranes justifies HBFB cell testing with ES 80/20 and ES 90/10 membranes.

3.3. HBFB cell performance

The electrochemical performance of the ES 90/10 and ES 80/20 membranes (~50–60 \( \mu \)m) was analyzed and compared to that of the commercial PFSA (~100 \( \mu \)m) membrane. The SC 80/20 membrane (~50–60 \( \mu \)m) was also studied to evaluate the role of electrospinning as a membrane preparation method.

3.3.1. Polarization behavior and EIS analysis

Fig. 7a shows the polarization behaviors of the tested membranes at HBFB cell discharge. The cell ASR values for the different membranes were obtained from the slope of the current-voltage profiles during charge and discharge (Fig. 7b). The cell ohmic ASR values were acquired from the in-situ EIS measurements using different membrane samples (Fig. 7b).

The ES 80/20 membrane presented the best performance with a maximum power density of 341 mW cm\(^{-2}\) and a current density of 487 mA cm\(^{-2}\) at 0.7 V discharge. The membrane is the only material in the electrochemical cell that has an ohmic component. Therefore, the in-situ ohmic ASR is a useful parameter for the evaluation of the membrane performance. The electrospun blend membranes show comparable ohmic, charge and discharge ASR values as the PFSA membrane. The SC 80/20 with a similar thickness to the ES membranes demonstrated much higher cell resistances and equally poor polarization behavior. The obtained ASR results show that the electrospun samples have equal (ohmic) resistance as the PFSA membrane at a given thickness.

3.3.2. Cycling performance

The HBFB cycling performance of the commercial PFSA at a current density of 150 mA cm\(^{-2}\) and a voltage range of 0.7–1.15 V was investigated as a reference (Fig. 8a). The best performing blend membrane in terms of membrane characteristics, HBFB polarization behavior and ohmic ASR is the ES 80/20 membrane. Therefore, this membrane was further compared to the commercial PFSA membrane for its HBFB cycling performance (Fig. 8b).

Low cell ohmic resistance (dominated by the membrane contribution) prolongs the discharge-charge duration, which enhances the voltage efficiency. On the other hand, a low bromine species crossover rate improves the coulombic efficiency. Thus, the combination of low membrane ASR and low \( \text{Br}_2 \) diffusion rate increases the energy efficiency of the cell [31]. During ten cycles, voltage, coulombic and energy efficiencies of the HBFB single cell are maintained above 60% with the commercial PFSA membrane (Fig. 8a). This is while these values are maintained above 80% with the ES 80/20 membrane during six cycles, but dramatically decrease until complete failure at the tenth cycle (Fig. 8b). The initial coulombic efficiency is higher than 100% for the ES 80/20 membrane. This stems from a shorter charging than the discharging period. The shorter charging duration is the consequence of liquid electrolyte crossover due to membrane degradation that led to less available bromine species in the liquid electrode and hence a loss in cell capacity [20]. Another indication of the gradual performance degradation of the ES 80/20 membrane is the increase in the cell’s ohmic ASR per cycle (Fig. 8b), whereas this value remained stable for the PFSA membrane over ten cycles (Fig. 8a). This performance decay of the electrospun membrane is attributed to 1) its relatively low thickness, which makes it vulnerable for electrolyte crossover, 2) an insufficient balance between the crossover rate of the bromine species and the proton-conductivity and 3) possible chemical/mechanical degradation of SPEEK by bromine species. This degradation is clearly visible in the gradual decrease in the cell ASR over the ten cycles (Fig. 8b), resulting in a gradual loss of ionic conductivity of SPEEK and an increase in bromine species cross over. Additionally, the observed dramatic drop in the efficiency profile (Fig. 8b) also indicates that an undesirable amount of electrolyte crossover to the gas electrode poisoned the Pt–Ir/C catalyst.

4. Conclusions

Novel dense membranes for cost-effective HBFB operation were prepared by blending SPEEK and PVDF. Blend solutions of SPEEK and PVDF were prepared at different polymer ratios and then converted to dense membrane sheets via 1) wire-electrospinning followed by hot-pressing or 2) solution-casting. Electrospinning improves the blend

---

**Fig. 7.** Polarization behavior and in-situ EIS measurement results of the HBFB single cell with the commercial PFSA (~100 \( \mu \)m) and the selected SPEEK/PVDF blend membranes (~50–60 \( \mu \)m): (a) Voltage and power density profiles based on the current density during discharge; (b) The cell total ASR obtained from the slope of the current-voltage profiles at discharge and charge and the ohmic resistance determined by in-situ EIS for each membrane.
membrane morphology due to fast vitrification that precludes polymer-polymer phase-separation. Contrary to solvent casting where isolated SPEEK domains are formed inside a PVDF skeleton, electrospinning provides a membrane with intertwined polymer networks, whereby ion-conductive SPEEK nanofiber pathways are being formed through a hydrophobic firming network of PVDF nanofibers. Furthermore, electrospinning positively affects the ex-situ properties and HBFB cell performance of the blend membrane compared to those prepared by solution-casting at similar composition. At an approximately 40% lower wet thickness than PFSA, ES 80/20 membrane shows comparable properties and improved HBFB single cell polarization behavior with more than 80% materials cost reduction. However, the relatively low thickness and insufficient chemical/mechanical stability of the ES 80/20 causes a rapid decay in the HBFB cycling performance.

These results promote an HBFB lifetime investigation with the wire-electrospun SPEEK/PVDF blend membranes and hence, open pathways to a long lifetime for low-cost hydrogen-bromine redox flow batteries.

CRediT authorship contribution statement

Sanaz Abbasi: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. Antoni Forner-Cuenca: Writing - review & editing. Wiebrand Kout: Writing - review & editing. Kitty Nijmeijer: Conceptualization, Supervision, Writing - review & editing. Zandrie Borneman: Conceptualization, Supervision, Writing - review & editing, Project administration, Funding acquisition.

Declaration of competing interest

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

Acknowledgment

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement no. 765289.

References

[1] Energy Insights McKinsey. https://www.mckinsey.com/industries/oil-and-gas/our-insights/global-energy-perspective-2019, 2019.

[2] Y. Zhang, J. Zhang, M.C.W. Kimnter-Meyer, X. Lu, D. Choi, J.P. Lemmon, J. Liu, Electrochemical energy storage for green grid, Chem. Rev. 111 (2011) 3577–3613, https://doi.org/10.1021/cr100290x.

[3] S. Chu, A. Majumdar, Opportunities and challenges for a sustainable energy future, Nature 488 (2012) 294–303, https://doi.org/10.1038/nature11475.

[4] T.A. Faunce, J. Prett, D. Su, S.J. Heane, F. Iacopi, On-grid batteries for large-scale energy storage: challenges and opportunities for policy and technology, MRS Energy Sustain 5 (2018) E11, https://doi.org/10.1557/mrs.2018.11.

[5] K.T. Cho, P. Ridgway, A.Z. Weber, S. Hausener, V. Battaglia, V. Srinivasan, High performance hydrogen/bromine redox flow battery for grid-scale energy storage, J. Electrochem. Soc. 159 (2012), https://doi.org/10.1149/2.08121jes, A1805-A1815.

[6] A. Forner-Cuenca, E.E. Penn, A.M. Oliveira, F.R. Brushett, Exploring the role of electrode microstructure on the performance of non-aqueous redox flow batteries, J. Electrochem. Soc. 166 (2019), https://doi.org/10.1149/2.06119jes, A2289-A2291.

[7] M. Skyllas-Kazacos, M.H. Chakrabarti, S.A. Hajimolana, F.S. Mjalli, M. Saleem, Progress in flow battery research and development, J. Electrochem. Soc. 158 (2011) R55, https://doi.org/10.1149/1.3595556.

[8] N. Singh, E.W. McFarland, Levelized cost of energy and sensitivity analysis for the hydrogen-bromine flow battery, J. Power Sources 288 (2015) 187–198, https://doi.org/10.1016/j.jpowsour.2015.04.114.

[9] K.T. Cho, P. Albertus, V. Battaglia, A. Kojic, V. Srinivasan, A.Z. Weber, Optimization and analysis of high-power hydrogen/bromine-flow batteries for grid-scale energy storage, Energy Technol. 1 (2013) 596–608, https://doi.org/10.1002/ente.201300108.

[10] Y.A. Hugo, W. Kout, F. Sikkema, Z. Borneman, K. Nijmeijer, Performance mapping of cation exchange membranes for hydrogen-bromine flow batteries for energy storage, J. Membr. Sci. 566 (2018) 406–414, https://doi.org/10.1016/j.memsci.2018.09.006.

[11] T.X. Wang, M.D. Kelley, J.N. Cooper, R.C. Beckwith, D.W. Margerum, Equilibrium, kinetic, and UV-spectral characteristics of aqueous bromine chloride, bromine, and chlorine species, Inorg. Chem. 33 (1994) 5872–5878, https://doi.org/10.1021/ic00103a040.

[12] J. Masud, T. Van Nguyen, N. Singh, E. McFarland, M. Ikenberry, K. Hohn, C.-J. Pan, Chlorine species, Inorg. Chem. 33 (1994) 5872–5878, https://doi.org/10.1021/ic00103a040.

[13] G. Gershinsky, P. Nanikashvili, R. Elazari, D. Zitoun, From the sea to hydrobromic acid: polydopamine layer as corrosion protective layer on platinum electrocatalyst, ACS Appl. Energy Mater. 1 (2018) 4678–4685, https://doi.org/10.1021/acsaeem.8b00808.

[14] M.C. Tucker, K.T. Cho, F.B. Spingler, A.Z. Weber, G. Lin, Impact of membrane characteristics on the performance and cycling of the Be2-H2 redox flow cell, J. Power Sources 284 (2015) 212–221, https://doi.org/10.1016/j.jpowsour.2015.03.010.

[15] J. Woo Park, R. Wyckz, G. Lin, P. Ying Chong, D. Powers, T. Van Nguyen, R. P. Dowd Jr., P.N. Pintuaro, Electro spun Nafion/PVDF single-fiber blended membranes for regenerative H2/Br2 fuel cells, J. Membr. Sci. 541 (2017) 85–92, https://doi.org/10.1016/j.memsci.2017.06.086.

[16] R. Baldwin, Electrochemical Performance and Transport Properties of a Nafion Membrane in a Hydrogen-Bromine Cell Environment, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH (USA), 1987.

[17] Y.A. Hugo, N. Mazur, W. Kout, F. Sikkema, Z. Borneman, K. Nijmeijer, Effect of bromine complexing agents on membrane performance in hydrogen/bromine flow batteries, J. Electrochem. Soc. 166 (2019), https://doi.org/10.1149/2.0901504jes. F455–F462.

[18] G. Gerhinskie, P. Nanikashvili, R. Elazari, D. Zitoun, From the sea to hydrobromic acid: polydopamine layer as corrosion protective layer on platinum electrocatalyst, ACS Appl. Energy Mater. 1 (2018) 4678–4685, https://doi.org/10.1021/acsaeem.8b00808.
[20] J.W. Park, R. Wycisk, P.N. Pintauro, Nafion/PVDF nanofiber composite membranes for regenerative hydrogen/bromine fuel cells, J. Membr. Sci. 490 (2015) 103–112, https://doi.org/10.1016/j.memsci.2015.04.044.

[21] G. Lin, P.Y. Chong, V. Yarlagadda, T.V. Nguyen, R.J. Wycisk, P.N. Pintauro, M. Bates, S. Mukerjee, M.C. Tucker, A.Z. Weber, Advanced hydrogen-bromine flow batteries with improved efficiency, durability and cost, J. Electrochem. Soc. 163 (2016), A5049–A5056.

[22] J. Park, R. Wycisk, P. Pintauro, V. Yarlagadda, T. Van Nguyen, Electrospun Nafion®/polyphenylsulfone composite membranes for regenerative hydrogen bromine fuel cells, Materials 9 (2016) 143, https://doi.org/10.3390/ma9030143.

[23] K.M. Forward, G.C. Rutledge, Free surface electrospinning from a wire electrode, Chem. Eng. J. 183 (2012) 492–503, https://doi.org/10.1016/j.cej.2011.12.045.

[24] Z. Li, J. Xi, H. Zhou, L. Liu, Z. Wu, X. Qiu, L. Chen, Preparation and characterization of sulfonated poly(ether ether ketone)/poly(vinylidene fluoride) blend membrane for vanadium redox flow battery application, J. Power Sources 237 (2013) 132–140, https://doi.org/10.1016/j.jpowsour.2013.03.016.

[25] B. Christgen, K. Scott, J. Dolfing, I.M. Head, T.P. Curtis, An evaluation of the performance and economics of membranes and separators in single chamber microbial fuel cells treating domestic wastewater, PLoS One 10 (2015), e0136108, https://doi.org/10.1371/journal.pone.0136108.

[26] F. Yalcinkaya, Preparation of various nanofiber layers using wire electrospinning system, Arab. J. Chem. 12 (2019) 5162–5172, https://doi.org/10.1016/j.ajche.2016.12.012.

[27] Y. Liao, R. Wang, M. Tian, C. Qiu, A.G. Fane, Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation, J. Membr. Sci. (2013) 425–426, https://doi.org/10.1016/j.memsci.2012.09.023, 30–39.

[28] X. Zong, K. Kim, D. Fang, S. Ran, B.S. Ho, B. Chu, Structure and process relationship of electrospun bioabsorbable nano fiber membranes, Polymer 43 (2002) 4403–4412, https://doi.org/10.1016/S0032-3861(02)00275-2.

[29] X. Liu, X. Meng, J. Wu, J. Huo, L. Cui, Q. Zhou, Microstructure and properties of novel SPEEK/PVDF-g-PSSA blends for proton exchange membrane with improved compatibility, RSC Adv. 5 (2015) 69621–69628, https://doi.org/10.1039/C5RA1894H.

[30] A. Bagheri, M. Javanbakht, H. Beydagi, P. Salarizadeh, A. Shabanikia, H. Salar Amoli, Sulfonated poly(etheretherketone) and sulfonated polyvinylidene fluoride-co-hexafluoropropylene based blend proton exchange membranes for direct methanol fuel cell applications, RSC Adv. 6 (2016) 39500–39510, https://doi.org/10.1039/C5RA0038J.

[31] H.-Y. Jung, J.-K. Park, Blend membranes based on sulfonated poly(ether ether ketone) and poly(vinylidene fluoride) for high performance direct methanol fuel cell, Electrochim. Acta 52 (2007) 7464–7468, https://doi.org/10.1016/j.electacta.2007.06.035.

[32] C. Kloes, M. Breitwieser, S. Vierllath, M. Klingeje, H. Cho, A. Buchler, J. Kerres, S. Thiele, Electrospin sulfonated poly(ether ketone) nanofibers as proton conductive reinforcement for durable Naion composite membranes, J. Power Sources 361 (2017) 237–242, https://doi.org/10.1016/j.jpowsour.2017.06.080.

[33] H.-Y. Li, Y.-L. Liu, Naion-functionalized electrospun polyvinylidene fluoride (PVDF) nanofibers for high performance proton exchange membranes in fuel cells, J. Mater. Chem. A 2 (2014) 3783–3793, https://doi.org/10.1039/C3TA14264G.

[34] C. Li, J. Liu, R. Guan, P. Zhang, Q. Zhang, Effect of heating and stretching membrane on ionic conductivity of sulfonated poly(phenylene oxide), J. Membr. Sci. 287 (2007) 180–186, https://doi.org/10.1016/j.memsci.2006.10.015.