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# 1 Electrochemical impedance spectroscopy as a 2 performance indicator of water dissociation in 3 bipolar membranes

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## 10 **Abstract**

11 A bipolar membrane (BPM) can be used to maintain a pH difference in an electrolysis cell,  
12 which provides freedom to independently optimize the environments and catalysts used for paired  
13 redox reactions. A BPM consists of two physical layers, of which one is selective for the exchange of  
14 cations and the other for anions. The water dissociation reaction (WDR) splits water into protons and  
15 hydroxide ions under an electric field that concentrates at the interface of the two membrane layers.  
16 However, salt ions in commonly used electrolytes influence this WDR when they are present at the  
17 interface. Using electrochemical impedance spectroscopy (EIS), we observed the rate of water  
18 dissociation decrease in the presence of salt ions while also observing the diffusion and migration of  
19 these salt ions, showing a clear link between the peaks observed in EIS and ion crossover. In addition,  
20 we show how EIS can be used to in-situ monitor the stability and ageing of a BPM, revealing that  
21 degradation of the BPM is more prominent in extreme pH electrolyte pairs compared to non-extreme  
22 electrolyte pairs. The in-situ monitoring of the WDR and stability of a BPM are vital methods for  
23 adequate and consistent comparison of novel designs of BPM-based systems, where EIS allows for  
24 discriminating BPM characteristics from other components even during operation.

## 25 **Introduction**

26 The increasing concentration of greenhouse gases such as CO<sub>2</sub> in our atmosphere has  
27 destabilized Earth's climate, as confirmed by the most recent report from the Intergovernmental Panel  
28 on Climate Change (IPCC).<sup>1</sup> The consequences of a 1 °C increase of the global mean temperature  
29 compared to pre-industrial levels are already evident, requiring immediate actions to reduce our global  
30 CO<sub>2</sub> emissions and mitigate further dire consequences. With rapidly decreasing prices of renewable  
31 energy and an increasing electrification of the energy sector, a promising approach to close the carbon

32 cycle with the production of valuable products is needed. This can be achieved by synthesizing  
33 chemicals and fuels using renewable energy via water electrolysis or the electrocatalytic reduction of  
34 carbon dioxide (CO<sub>2</sub>ER).

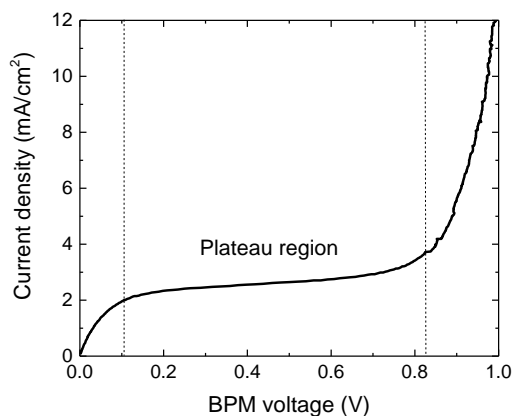
35         When considering either of these electrochemical routes at an industrially relevant scale, it is  
36 important to have a system run at a high energy efficiency. In other words, the applied potential should  
37 be as close as possible to the thermo-neutral cell potential for the combined oxidation and reduction  
38 reactions. The importance of high energy efficiency arises from the relatively high contribution of  
39 electricity costs in electrochemical systems<sup>2</sup>, which makes achieving a high efficiency a necessity to  
40 compete with current chemical production means, where nearly all the fuels and commodity chemicals  
41 originate from fossil-based resources. However, the state-of-the-art electrolysis of water or CO<sub>2</sub> still  
42 has a low energy efficiency at high current densities due to large overpotentials for the relevant  
43 reduction-oxidation reactions, ohmic losses across the electrolyte and potential drops across an ion  
44 exchange membrane that separates the anode and cathode compartments.<sup>3-5</sup> Making matters more  
45 difficult, catalysts for the reduction and oxidation reactions perform better—i.e., have a higher stability  
46 and lower overpotential—in different electrolytes with different pHs, thereby making a total system  
47 difficult to optimize with a single electrolyte.<sup>6,7</sup>

48         To integrate different electrolytes into a single electrochemical cell, a bipolar membrane  
49 (BPM) can be implemented. Recently, several studies have successfully observed stable operation and  
50 lower cell potentials using independent electrolyte pairs for water oxidation coupled to water  
51 reduction or CO<sub>2</sub>ER using a BPM.<sup>7-10</sup> A BPM consists of two physical layers, one which is selective for  
52 the exchange of cations (cation exchange layer, CEL) and the other for anions (anion exchange layer,  
53 AEL). Under an applied potential or pH gradient across the BPM, the interface between these layers  
54 enhances the dissociation of water into protons and hydroxide ions, described by the water  
55 dissociation reaction (WDR).<sup>11-13</sup> At this membrane-membrane interface, a catalyst can be deposited  
56 to further improve the kinetics of the WDR. A great deal of research on understanding and improving  
57 the characteristics of a BPM focuses on the interface between the anion-cation exchange layers.<sup>14-16</sup>

58         The ion-exclusivity of a BPM, with two different layers and their fixed charges, should in theory  
59 be impermeable for any charged species transported through both layers. Since the ion-exclusivity is  
60 imposed by finite fixed charges of the membrane layers, a (limited) co-ion exchange will occur between  
61 the two different solutions. In monopolar membranes, co-ions are described as ions with the same  
62 charge as the fixed charges in the membrane layer. However, for the BPM, co-ions have a more  
63 ambiguous definition because of the different polarity in the two membrane layers. Here, we define  
64 co-ions as ionic salt species that do not participate in the WDR, i.e., all ions except for H<sup>+</sup> and OH<sup>-</sup>. It is

65 important to note that a CEL and an AEL in contact with electrolytes with very high or very low pH such  
66 as KOH and H<sub>2</sub>SO<sub>4</sub>, respectively, theoretically do not contain co-ions in the membrane layers. The  
67 contribution to the ionic current, equal to the electrical current through the cell, of each individual ion  
68 species is described by the transport number.<sup>17</sup> As this ionic current in the BPM is composed of a  
69 movement of co-ions and charge transport due to water dissociation, migration of co-ions lowers the  
70 efficiency of the water dissociation reaction<sup>18</sup> and thus negatively affects the overall cell efficiency.

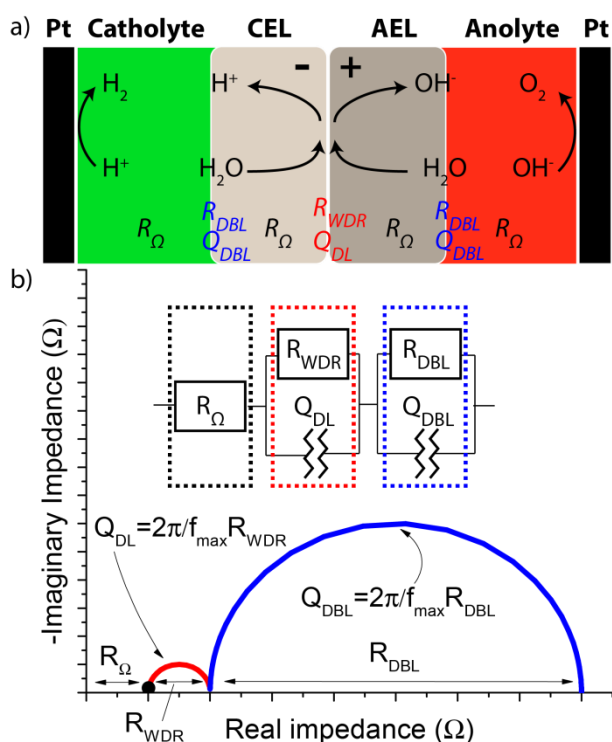
71 Recent studies have shown the dependency of electrolyte pH and composition surrounding  
72 the BPM on the voltage response across the BPM in the presence of an applied current.<sup>13</sup> Depending  
73 on the electrolytes used, the i-V curve typically contains a sharp increase of the voltage at a certain  
74 current density. After this initial increase, a plateau at a relatively constant current density,  $j_{plateau}$ , is  
75 observed until reaching the membrane voltage of water dissociation (0.829 V), where the current  
76 increases sharply with applied potential (see Figure 1). However, in contrast to monopolar membranes,  
77 which also show activity towards the WDR above a limiting current density,<sup>19</sup> bipolar membranes have  
78 shown that charge transport can be dominated by the WDR below the plateau current density under  
79 certain conditions.<sup>20</sup> At higher current densities, the water dissociation efficiency increases  
80 further.<sup>12,18,21,22</sup> It is necessary to probe the electronic behavior of the interfacial layer to better  
81 understand the conditions that determine the WDR, and the relation with the i-V curve and the plateau  
82 region.



83  
84 **Figure 1: Typical i-V curve of a bipolar membrane in a salt electrolyte, with the plateau region between a BPM voltage of**  
85 **0.1 to 0.8 V. A galvanodynamic scan was applied at a scan rate -0.01 mA cm<sup>-2</sup> s<sup>-1</sup> with 5M NaCl in both compartments.**

86 One way to probe the WDR is via electrochemical impedance spectroscopy (EIS), which  
87 differentiates the various components of the BPM as electrical features that can be derived from  
88 impedance responses upon a varying frequency.<sup>17</sup> In this way, factors such as the finite conductivity of  
89 the membrane layers and electrolyte solutions are measured as an ohmic resistor, the diffusion

90 boundary layer is shown as a constant phase element, and the sudden changes in charge density at  
 91 the BPM interfaces are shown as electrical double layers.<sup>23–28</sup> In this work, EIS is used to examine the  
 92 equivalent circuit elements that represent a BPM separating two different pairs of electrolytes at  
 93 various current densities, as schematically shown in Figure 2. The results show that EIS is a useful tool  
 94 to monitor ion transport in BPMs, which is composed of products of the WDR and crossover of co-ions  
 95 through the BPM. Furthermore, a decrease of impedance features linked to decreased co-ion transport  
 96 through the BPM was observed when the current exceeded  $j_{plateau}$ . These findings are important to  
 97 understand the role of co-ions in supporting and inhibiting the WDR at currents below the plateau  
 98 current density. In addition, EIS was able to monitor the stability of the BPM and its individual  
 99 components during operation in an electrochemical cell by performing EIS before and after  
 100 galvanostatic experiments. These experiments showed a degradation in the membrane layers as well  
 101 as the WDR performance for a case with a pH difference of 14, but relatively stable conditions for a  
 102 case with less extreme electrolytes.



103  
 104 **Figure 2: (a) Schematic representation of individual components of the impedance response of a BPM in an**  
 105 **electrochemical cell, with (black) Ohmic losses of membrane and solution, (red) membrane-membrane interface where**  
 106 **WDR occurs, and (blue) diffusion boundary region with a constant phase element. (b) The equivalent circuit used to**  
 107 **describe the impedance results is shown with the corresponding Nyquist plot.**

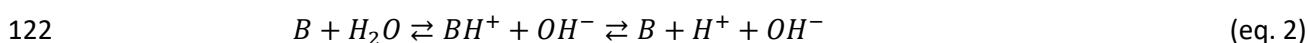
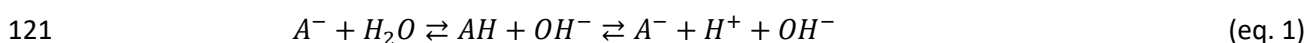
108

## 109 **Theory**

### 110 **Water dissociation reaction**

111 A bipolar membrane has three electrochemical interfaces: two membrane-solution interfaces  
112 (CEL/catholyte and AEL/anolyte) and one internal interface (CEL/AEL). The latter is the membrane-  
113 membrane interface where the water dissociation reaction occurs when a reverse bias is applied to  
114 the system, with the negatively charged layer opposing the negative charged cathode.

115 The reaction rate of the WDR is  $5 \times 10^7$  times faster in a BPM than in aqueous electrolyte, which  
116 is enhanced by the electrochemical properties of a BPM.<sup>14</sup> There are multiple theories describing the  
117 WDR<sup>14</sup>: some focus on the Donnan equilibrium,<sup>29</sup> some on the second Wien effect,<sup>30</sup> and others on  
118 proton transfer reactions with fixed charges.<sup>31,32</sup> In the latter theory, which has the most realistic  
119 simulated reaction rates, weak acids and bases catalyze the WDR, shown in the following reaction  
120 schemes:



123 Here  $AH$  and  $B$  are a weak acid and base, respectively. Both membrane layers perform one reaction  
124 dominantly, e.g. the cation exchange layer with negatively charged species would preferentially  
125 perform reaction (1), while the anion exchange layer with positively charged species preferentially  
126 performs reaction (2). To avoid the reverse reaction, separation of both  $H^+$  and  $OH^-$  via membrane  
127 charges with opposite charge is required, which implies that the WDR is most effective near the  
128 CEL/AEL interface.<sup>33</sup> A catalyst present at the interface between the AEL and CEL improves the kinetics  
129 of these reactions as well by lowering the activation energy—in this case, the reaction of (1) or (2),  
130 producing protons and hydroxide ions.<sup>14</sup>

### 131 **Electrochemical impedance spectroscopy**

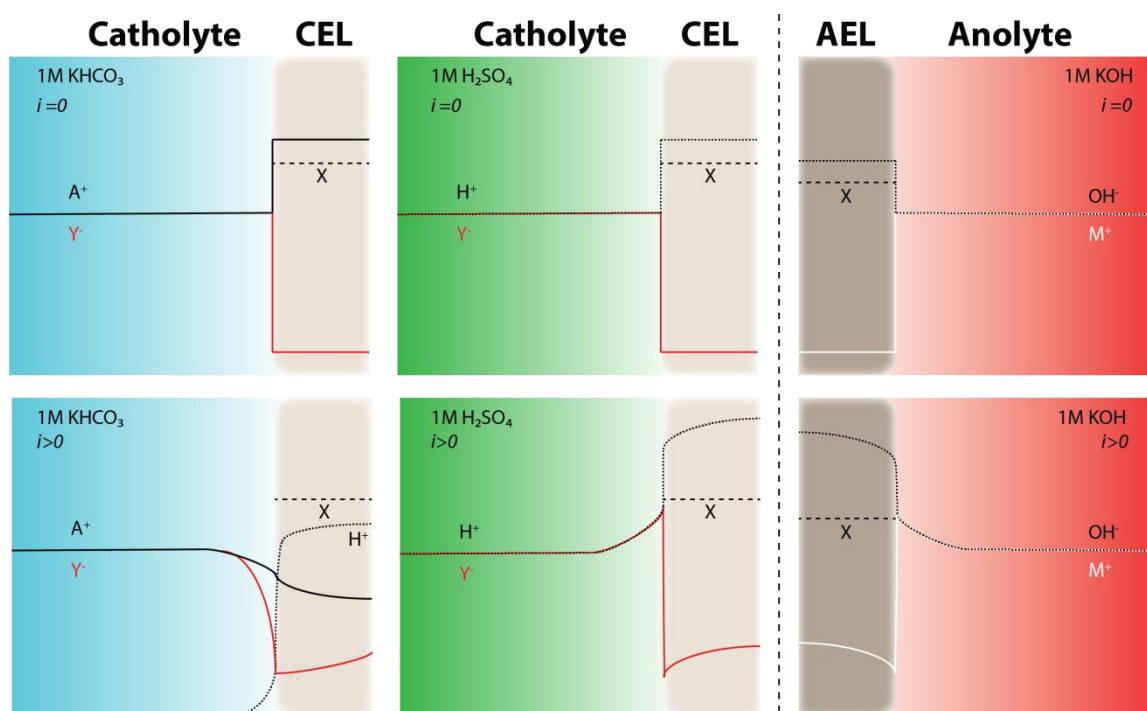
132 Electrochemical impedance spectroscopy can be used to examine the electronic responses of  
133 individual components of a membrane by varying the applied frequency.<sup>17</sup> An introduction of the  
134 theory behind the EIS data and interpretations is provided in the supporting information. Figure 2(b)  
135 shows the proposed equivalent circuit describing the three components of a BPM. The first component  
136 is  $R_\Omega$ , related to the conductivity of the combined membrane layers. This component follows Ohm's  
137 law ( $V = IR$ ), and since there is no capacitive effect in  $R_\Omega$ , it is independent of frequency. The  
138 resistance can be determined from a Nyquist plot by measuring the distance between the origin and  
139 the start of the first semicircle. This value also includes the Ohmic losses of the electrolytes from the  
140 membrane to the reference electrodes.

141 The second component of the equivalent circuit describes the WDR, and the kinetics of this  
142 reaction are in the form of a resistance ( $R_{WDR}$ ). In parallel with the resistor is the electric double layer  
143 of the internal interface, represented as a non-ideal capacitor ( $Q_{DL}$ ). This RQ-network shows the typical  
144 semicircle of a charge transfer reaction,<sup>17</sup> in this case to produce protons and hydroxide ions.  $R_{WDR}$  is  
145 equal to the width of the semicircle, and  $Q_{DL}$  is the inverse of the angular velocity ( $\omega = 2\pi f$ ) of the  
146 peak height and  $R_{WDR}$ . Since a BPM typically has a non-uniform current distribution, the system  
147 cannot be described with an ideal capacitor. Instead, a constant phase element is used, including a  
148 non-ideality factor  $n$ , lying between 0 and 1, with  $n = 0$  being a resistor and  $n = 1$  an ideal capacitor.<sup>23</sup>  
149 Hurwitz and Dibiani (2003) described the water dissociation component of their equivalent circuit in  
150 combination with a component related to the proton gradient near the membrane-membrane  
151 interface.<sup>27</sup> However, in our and their experiments, there is no indication that this gradient component  
152 is required for successful fitting of the results, and it is therefore considered to be a part of the water  
153 dissociation component.

154 The third component relates to the diffusion boundary layer between the membrane layers  
155 and electrolytes. When ions are transported out of the membrane layer and surrounded by mobile  
156 charges with the same charge, they enter an electroneutral solution with which they differ in  
157 concentration. This effect happens due to the Donnan exclusion in the membrane layer, which is the  
158 source of the Donnan potential between the diffusion layer of the electrolyte solution and the  
159 membrane layer.<sup>34,35</sup> This is especially true when the concentration of the protons or hydroxide ions is  
160 low in the electrolyte (e.g. in a bicarbonate electrolyte). Similar to the second component, the  
161 resistance that the transported ions encounter ( $R_{DBL}$ ) is in parallel with a non-ideal capacitor,  
162 represented by a constant phase element ( $Q_{DBL}$ ). These two elements both show non-linear behavior  
163 upon a variation of current. First, the resistance is created by concentration polarization at the  
164 membrane-electrolyte interface. Since impedance is the ratio of the voltage, which is described by the  
165 Donnan potential  $\Delta\Phi_{Donnan} = \ln(C_i/\bar{C}_i)$  with  $\bar{C}_i$  the concentration of species  $i$  in the membrane and  
166 the current, the resistance is non-linear dependent upon a varying current. This is because of the  
167 logarithmic behavior as well as the non-linear behavior of  $C_i/\bar{C}_i$  in non-steady state.<sup>36</sup> Second, the non-  
168 ideal capacitor, which is created by the change in charges at these interfaces, is also a function of  
169 concentration. Since the change in charge of all species in this region is not linear, the DBL is not  
170 linear<sup>37</sup>, as shown in Figure 3 which gives a schematic representation of the concentration profile of  
171 three electrolytes of the membrane-solution interface. For example, for a CEL the concentration of the  
172 cations is equal to the sum of the concentrations of the fixed charges and the anions, which are present  
173 due to non-ideality of the membrane layer. Once a current is applied, cations migrate out of the CEL  
174 towards the cathode, and protons replenish the membrane layer to maintain electroneutrality. This is

175 visible when  $\text{KHCO}_3$  is used as catholyte (left in Figure 3). Due to the different diffusion coefficients in  
 176 the membrane layer and electrolyte, a diffusion boundary layer is formed once a current is applied,  
 177 which is dominated by the main carrier of the current, e.g.  $\text{OH}^-$  in the case of the AEL.

178 Most literature has focused on the first two components, since the third component is typically  
 179 found at lower frequencies ( $<1$  Hz) and requires a stable setup to perform long term measurements to  
 180 reduce noise.<sup>24,25,27</sup> In addition to the experimental data present in the literature, also modelling has  
 181 been performed of the electrochemical impedance response by Alcaraz *et al.* based on the Nernst-  
 182 Planck and Poisson equations, describing the membrane-membrane interface as a pn-junction.<sup>38</sup> The  
 183 model does not include the diffusion boundary layers at the electrolyte-membrane interface, which is  
 184 a limitation for comparing the results with this work. Yan *et al.* studied a BPM at lower frequency in  
 185 their supplementary information; however, they described the third component as a Gerischer  
 186 impedance coupling the diffusion boundary layer to a chemical reaction.<sup>39</sup> In our work, the EIS results  
 187 from two different electrolyte pairs across a BPM are shown, indicating that the co-ion plays a role in  
 188 the diffusion boundary layer as well as in the WDR component of the equivalent circuit.



189  
 190 **Figure 3: Concentration profiles of electrolytes near ion exchange layer, in the diffusion boundary layer. Assuming that**  
 191 **no ion exchange occurs when no current is applied, there is no DBL when  $i=0$ . If  $i>0$ , migration component results in an**  
 192 **increased concentrations of present ions. At the membrane-solution interface, there is the double layer where no**  
 193 **electroneutrality occurs, with  $X$  concentration of fixed charges,  $A^+$  and  $M^+$  concentration of cations and  $Y^-$  concentration**  
 194 **of anions.**

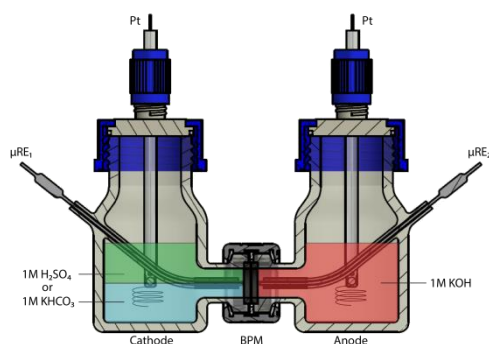
195



196 **Methods**

197 In this work, we compare two different electrolyte combinations across a BPM during  
198 electrolysis to determine the effect of co-ions on the water dissociation reaction. One electrolyte pair  
199 theoretically contains no co-ions in the membrane layer ( $\text{H}_2\text{SO}_4$  as the catholyte and  $\text{KOH}$  as the  
200 anolyte), because  $\text{SO}_4^{2-}$  and  $\text{K}^+$  will be excluded from the CEL and AEL, respectively, based on ion-  
201 selectivity of the membrane layers. For simplicity, this case will be designated as the ‘no co-ions<sub>mem</sub>’  
202 case, where the ‘mem’ indicates that this is only the case in ideal membrane layers. Another electrolyte  
203 pair,  $\text{KHCO}_3$  and  $\text{KOH}$ , does contain a co-ion in the CEL in the form of  $\text{K}^+$ , and is designated as the ‘co-  
204 ions’ case. Bicarbonate is often used as an electrolyte for the  $\text{CO}_2$  reduction reaction due to its buffer  
205 capacities and optimal pH to partially suppress the hydrogen evolution reaction.<sup>40</sup> Therefore this  
206 electrolyte was chosen to assess its compatibility with a BPM for use in a  $\text{CO}_2\text{ER}$  system. Specifications  
207 of the chemicals and materials used are described in the supporting information.

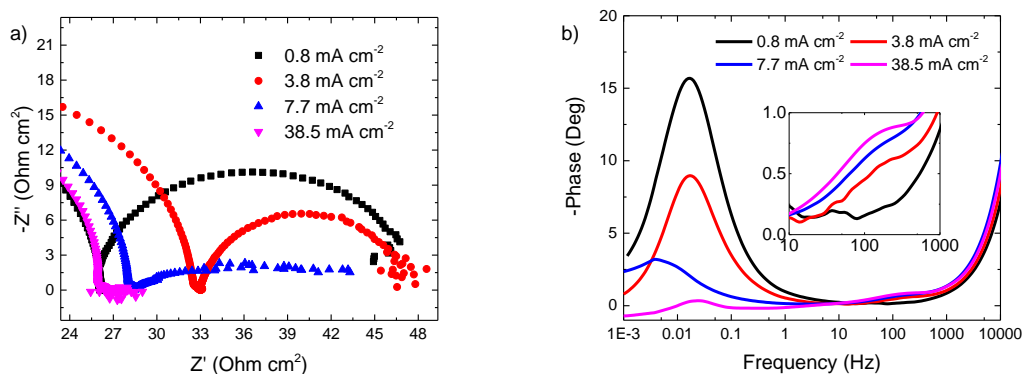
208 A commercially available Fumatech BPM was used in all experiments, which were performed  
209 with a SOLARTRON potentiostat (EnergyLab XM) in galvanostatic mode and three cycles of frequency  
210 to reduce noise. The frequency was varied from 10 kHz to 1 mHz. Bode plots shown here are smoothed  
211 with a Lowess method. EIS measurements were performed in a 4-electrode setup (Figure 4) with two  
212  $\text{Ag}/\text{AgCl}$  reference electrodes placed on both sides of the BPM, and the effective distance is therefore  
213 approximately 0.5 mm from the bipolar membrane in an aqueous H-cell configuration. The membrane  
214 has a surface area of  $1.33 \text{ cm}^2$ . Working and counter electrodes are made of Pt-wires and each have a  
215 surface area of  $2.83 \text{ cm}^2$ . Ageing experiments were performed in a flow cell (see Figure SI2), with a  
216 membrane and electrode surface area of  $10 \text{ cm}^2$ . Analysis of the impedance data was performed with  
217 ZView 2 (Scribner), and the fitting was performed with the equivalent circuit shown in Figure 2, which  
218 will be used to indicate the performance of the individual components of the BPM discussed in the  
219 results.



220  
221 **Figure 4: Schematic illustration of impedance setup in H-cell configuration with the two used electrolytes ( $\text{H}_2\text{SO}_4$  and**  
222  **$\text{KHCO}_3$ ) in the catholyte, separated from the anolyte ( $\text{KOH}$ ) by a BPM.**

## 223 Results & discussion

224 Nyquist plots for the case of co-ions ( $\text{KHCO}_3$  vs.  $\text{KOH}$ ) were obtained as a function of current  
225 density, shown in Figure 5(a). As the current density increased, the diameter of the semicircle  
226 decreased, showing a lower resistance across the membrane. The variation of the origin of the  
227 semicircle is due to the changing of the position of the reference electrode in each experiment, and  
228 does not affect the resistive features associated with the semicircle itself. Bode plots were also  
229 obtained as a function of current density, as shown in Figure 5(b) where two major features can be  
230 seen in the form a phase shift. A peak in the phase shift indicates an increase of the imaginary  
231 impedance, indicative for a capacitive effect. At low current densities, a large peak is present below 1  
232 Hz, and a minimum in the phase shift can be seen around 100 Hz. As the current density is increased,  
233 the peak below 1 Hz decreases significantly, while a subtle peak emerges between 10 and 500 Hz,  
234 shown in the inset of Figure 5(b). In addition, another increase of the phase shift is visible at  
235 frequencies above 1000 Hz; however, this increase is independent of the applied current. Furthermore,  
236 it is a high frequency dispersion or stray capacitance of the reference electrodes, which is caused by  
237 the limited exchange capacity of the glass frit at high frequencies and appears as a capacitance effect  
238 in the Bode plot. Additionally,  $1\text{M Na}_2\text{SO}_4$  vs.  $\text{Na}_2\text{SO}_4$  was tested, similar to the case of the co-ions does  
239 this electrolyte combination also contain co-ions at the membrane-membrane interface and showed  
240 similar behavior as for  $1\text{M KHCO}_3$  vs.  $\text{KOH}$  (see Figure S15).

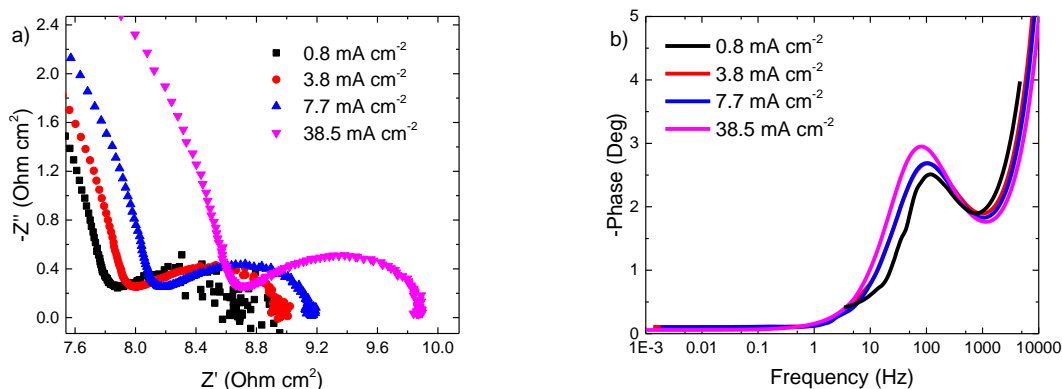


241

242 **Figure 5: Presence of co-ions ( $1\text{M KHCO}_3$  vs.  $\text{KOH}$ ) in function of DC current with an amplitude of 50% of the direct**  
243 **current. (a) Nyquist plot and (b) Bode plot with varying frequency.**

244 EIS experiments were also performed at different current densities in the no  $\text{co-ions}_{\text{mem}}$  case  
245 ( $\text{H}_2\text{SO}_4$  vs.  $\text{KOH}$ ) and reveal a completely different behavior compared to the prior case. Nyquist plots  
246 similarly show a changing origin of the semicircle, but no variation in the radius of the semicircle with  
247 increasing current density, shown in Figure 6(a). The Bode plot shows no peak in phase shift below 1  
248 Hz and only a peak between 10 and 1000 Hz is observed, which does not change significantly with

249 different current densities, as shown in Figure 6(b). At higher frequencies, a stray capacitance is visible,  
 250 similar to the case with no co-ions<sub>mem</sub>.

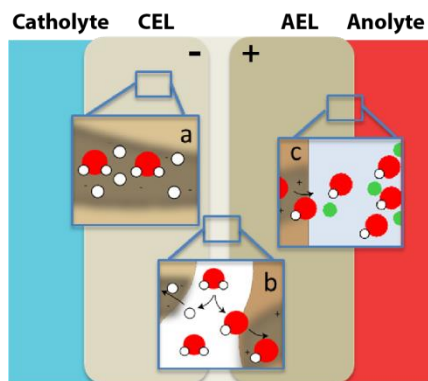


251

252 **Figure 6: Impedance results of the no co-ions<sub>mem</sub> case (1M H<sub>2</sub>SO<sub>4</sub> vs. KOH) in function of DC current with an amplitude of**  
 253 **50% of the direct current. (a) Nyquist plot and (b) Bode plot with varying frequency.**

254 When the data from Figures 5 and 6 is compared, the previously described equivalent circuit  
 255 can be matched to specific frequency ranges and physical phenomena. The first component of the  
 256 equivalent circuit, related to the Ohmic resistance ( $R_{\Omega}$ ), depends primarily on the conductivity of the  
 257 membrane, relating to the mobility of ions in the membrane layers as shown schematically in Figure  
 258 7(a). It is important to note that EIS does not allow the ability to determine  $R_{\Omega}$  without including the  
 259 conductivity of the electrolyte, which should be limited due to the relatively short distance between  
 260 the reference electrodes and the membrane. The second component of the equivalent circuit is related  
 261 to the water dissociation reaction, shown schematically in Figure 7(b). Based on the presence of two  
 262 peaks in the co-ions case (1M KHCO<sub>3</sub> vs. KOH), and only one peak in the no co-ion case (1M H<sub>2</sub>SO<sub>4</sub> vs.  
 263 KOH), it is likely that the shared peak in the frequency range between 10 and 1000 Hz (for this specific  
 264 membrane) is related to the water dissociation reaction that occurs in both cases above  $j_{plateau}$ . This  
 265 peak is represented in the equivalent circuit with a resistor ( $R_{WDR}$ ) and a constant phase element  
 266 ( $Q_{DL}$ ) in parallel. The peaks are fitted with ZView2, and an example of the fitting curve is given in Figure  
 267 S14. For the no co-ions<sub>mem</sub> case, Table 1 shows the fitted R and Q values, alongside the position of the  
 268 phase shift peaks. The slight variation in the fitted values corresponds with the limited change in the  
 269 kinetics of the WDR that may be related to ageing of the BPM, as will be discussed later. In the case of  
 270 H<sub>2</sub>SO<sub>4</sub> vs. KOH, the local environment at the catalytic active sites remains similar since the bulk  
 271 electrolyte contains the same mobile species at these different currents, consisting mostly of fixed  
 272 charges, water and protons or hydroxide ions, depending on the membrane layer. The role of the flux  
 273 of ions produced at the membrane-membrane interface does not affect the WDR peak, since the flux  
 274 has to match the consumption of ions at the electrode. The amount of crossover of co-ions at 50

275 mA/cm<sup>2</sup> is 1.5% (see Table SI1), while the rest of the current transported towards the electrodes comes  
 276 from the WDR.



277  
 278 **Figure 7: Schematic representation of (a) Ohmic losses, (b) water dissociation reaction, and (c) diffusion boundary layer.**

279 **Table 1: Impedance data of the no co-ion case (1M H<sub>2</sub>SO<sub>4</sub>-KOH), with the WDR semicircle fitted via an equivalent circuit.**  
 280  $f_{WDR}$  is the frequency at which the phase shift ( $\theta_{WDR}$ ) is maximised.  $R_{WDR}$ ,  $Q_{DL}$  and  $n_{WDR}$  are resistance, constant phase  
 281 element and fitting parameter of the WDR semicircle.

$j$ mA cm <sup>-2</sup>	$-\theta_{WDR}$ Deg	$f_{WDR}$ Hz	$R_{WDR}$ $\Omega$ cm <sup>2</sup>	$Q_{DL}$ mF cm <sup>2</sup>	$n_{WDR}$ -
0.8	2.51	116.5	0.91	7.80	0.85
3.8	2.68	107.8	1.07	6.50	0.85
7.7	2.69	100.0	1.08	7.15	0.85
38.5	2.95	79.6	1.29	7.41	0.85

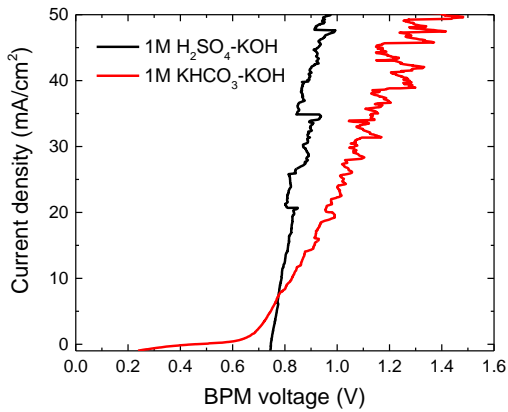
282  
 283 Table 2 and 3 show the fitted RC-values for the co-ions case (1M KHCO<sub>3</sub> vs. KOH) for the WDR  
 284 and DBL peak, respectively. In this case, both peaks are dependent on the applied current. The lower  
 285 n-value of the WDR capacitor indicates that the capacitor is less ideal than the no co-ions<sub>mem</sub> case.  
 286 Furthermore, when a current is applied below the plateau current density,  $j_{plateau}$ , e.g. in the case of  
 287 0.8 mA cm<sup>-2</sup>, no WDR peak is visible. Indeed, analysis from an ion-coupled plasma optical emission  
 288 spectrometer (ICP-OES) showed a 100% co-ion crossover (see Table SI2), implying that below  $j_{plateau}$   
 289 no net WDR occurs. At higher currents, a lower capacitance in the electrical double layer is observed,  
 290 trending towards similar values as in the case with no co-ions<sub>mem</sub>. In addition, the resistance of the  
 291 WDR converges towards similar values for both electrolyte pairs as the current densities increases,  
 292 indicating that the conditions near the membrane-membrane interface are the same at those  
 293 conditions. At these higher currents, fewer co-ions—in this case K<sup>+</sup>—are present at the interface, which  
 294 corresponds more to the situation of the case of no co-ions<sub>mem</sub>. The increase in  $R_{WDR}$  compared to the  
 295 no co-ions<sub>mem</sub> case is clarified via Figure 8, which shows the i-V curve (red) of a BPM in the co-ion case  
 296 (1M KHCO<sub>3</sub> vs. KOH). In this figure, a plateau current density is observed between 0.4 and 0.8 V of the  
 297 BPM potential.

298 **Table 2: Impedance data of the co-ion case (1M KHCO<sub>3</sub>-KOH), with WDR semicircle fitted via an equivalent circuit.  $f_{WDR}$  is**  
 299 **the frequency at which the phase shift ( $\theta_{WDR}$ ) is maximised.  $R_{WDR}$ ,  $Q_{DL}$  and  $n_{WDR}$  are resistance, constant phase element**  
 300 **and fitting parameter of the WDR semicircle.**

$j$ mA cm <sup>-2</sup>	$-\theta_{WDR}$ Deg	$f_{WDR}$ Hz	$R_{WDR}$ $\Omega$ cm <sup>2</sup>	$Q_{DL}$ mF cm <sup>2</sup>	$n_{WDR}$ -
0.8	-	-	-	-	-
3.8	0.55	146.8	1.95	3.64	0.60
7.7	0.64	108.0	1.69	6.50	0.60
38.5	0.80	125.9	1.30	9.10	0.70

301 **Table 3: Impedance data of the co-ions case (1M KHCO<sub>3</sub> vs. KOH), with DBL semicircle fitted via equivalent circuit.  $f_{DBL}$  is**  
 302 **the frequency at which the phase shift ( $\theta_{DBL}$ ) is maximised.  $R_{DBL}$ ,  $Q_{DBL}$  and  $n_{DBL}$  are resistance, constant phase element**  
 303 **and fitting parameter of the DBL semicircle.**

$j$ mA cm <sup>-2</sup>	$\theta_{DBL}$ Deg	$f_{DBL}$ Hz	$R_{DBL}$ $\Omega$ cm <sup>2</sup>	$Q_{DBL}$ F cm <sup>2</sup>	$n_{DBL}$ -
0.8	15.68	0.017	22.35	0.91	0.95
3.8	8.97	0.017	13.00	1.39	1.00
7.7	3.19	0.004	-	-	-
38.5	0.34	0.025	0.52	~19.5	0.70



304 **Figure 8: i-V curves of a BPM for the co-ion case (1M KHCO<sub>3</sub> vs. KOH) in red and for the no-co-ion case (1M H<sub>2</sub>SO<sub>4</sub> vs KOH)**  
 305 **in black. Both curves are obtained with a galvanodynamic scan at a scan rate -0.1 mA cm<sup>-2</sup> s<sup>-1</sup> with the flow cell.**  
 306

307 The third component of the equivalent circuit is related to the diffusion boundary layer at the  
 308 electrolyte-membrane interface, and is only visible at frequencies below 1 Hz, as shown in Figure 5  
 309 experimentally and Figure 7(c) schematically. The EIS data obtained from the fitted DBL semicircle for  
 310 the co-ion case is shown in Table 3. Quantifying the resistance is useful to determine the energy loss  
 311 of this component as it is noticeable during direct current operation, whereas the  $Q_{DBL}$  is not  
 312 noticeable during direct current operations. However,  $Q_{DBL}$  is still a good measure for the build-up of  
 313 charge caused by the change of transport numbers of the ions that move across in the membrane layer  
 314 compared to the bulk solution.<sup>23</sup> At lower current densities, diffusion and migration are of the same  
 315 order of magnitude, indicating that ion transport is not dominated by either of them, and co-ions with

316 their respective charge are present at the interfaces. As a result of the presence of these co-ions, a  
317 lower capacitance is noticed at lower current densities (see Table 2).

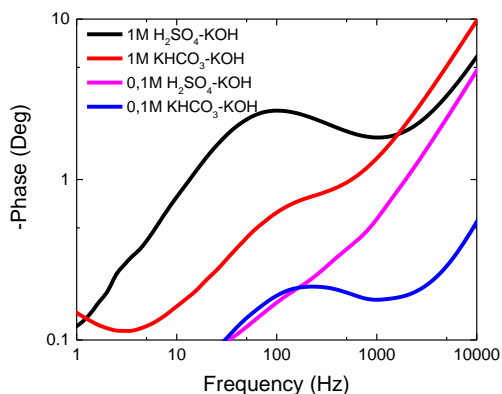
318 Both for the WDR and the DBL peak, the decrease in the capacitance at higher current densities  
319 for the co-ions case (1M  $\text{KHCO}_3$  vs. KOH) can possibly be explained by changes in concentrations of  
320 species at the respective interfaces. One hypothesis to explain this is that the supporting electrolyte is  
321 more conducting at higher current densities, as  $\text{H}^+$  and  $\text{OH}^-$  are the most mobile ions. In addition, the  
322 buffer capacity of the electrolyte near the BPM may decrease due to the change in local pH, as  
323 simulated by Ke *et al.*<sup>41</sup> This decrease in buffer capacity results in a lower capacitance since the charge  
324 can no longer be stored near the BPM.<sup>42</sup> At higher current densities, there will be relatively less  
325 transport of co-ions at steady state because of the direction of the migration component, which  
326 transports the co-ions away from the BPM. Combined with the change of local pH, this reduces the  
327 difference in transport numbers of the ions ( $\text{H}^+$  and  $\text{OH}^-$  for these high currents) that are transported  
328 in the membrane layer compared to the bulk solution. In the no co-ions<sub>mem</sub> case (1M  $\text{H}_2\text{SO}_4$  vs. KOH),  
329 this difference in transport number at the membrane-electrolyte interface is rather small, since the  
330 concentration of protons is similar to the concentration in the bulk solution. Similar trends are  
331 observed when negative currents are applied for the case of no co-ions<sub>mem</sub> ( $\text{H}_2\text{SO}_4$  vs. KOH), while a  
332 plateau also appears in the i-V curve around  $-35 \text{ mA cm}^{-2}$  along with a DBL component in the Bode plot  
333 (see Figure SI1). Although this mechanism is not yet fully understood, it does imply that the equivalent  
334 circuit shown in Figure 1(d) is generalizable for different combinations of pHs surrounding the BPM, as  
335 well as different concentrations that will be discussed in the following section.

### 336 **Concentration effect**

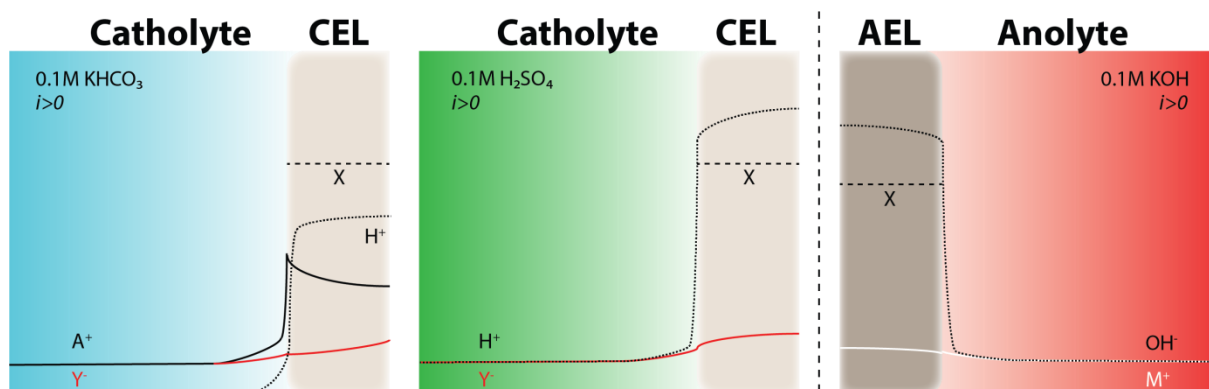
337 In order to understand the effect of the concentrations of ions in and around the BPM, EIS  
338 data were obtained for electrolyte pairs as a function of electrolyte concentration. When the  
339 concentration of  $\text{H}_2\text{SO}_4$ -KOH was lowered from 1M to 0.1M, for the no co-ions<sub>mem</sub> case, the WDR peak  
340 is reduced in size, as shown in Figure 9 and Table SI3 with the fitted results. However, no WDR peak is  
341 visible for 0.1M  $\text{KHCO}_3$  vs. KOH, as the peak might be hidden within the stray capacitance.

342 From the i-V curve of the 0.1M  $\text{H}_2\text{SO}_4$ /KOH case (Figure SI3), the kinetics of the WDR seems to  
343 be lowered compared to the higher concentration case. Also, the WDR capacitance has reduced (Table  
344 SI3), indicating that fewer mobile charge species are present in the membrane-membrane interface.  
345 This is schematically shown in Figure 10, with the concentrations profile of three electrolytes with a  
346 concentration of 0.1M when a current is applied to the system. The flux of ions will create a DBL at the  
347 membrane-solution interface, which is smaller than in the case of a 1M concentration (Figure 3). Since  
348 there is a lower concentration of co-ions in the bulk, the concentration gradient is also lower, reducing

349 the driving force for ions with a similar charge as the fixed charges to diffuse into the membrane layer.  
 350 Because of electroneutrality, this then leads to a lower concentration of the ions of opposing charge,  
 351 which reduces the charge at the membrane-membrane interface.



352  
 353 **Figure 9: Bode plot of 1M and 0.1M electrolyte concentrations across the BPM. Curves were obtained at  $7.7 \text{ mA cm}^{-2}$  with**  
 354 **50% amplitude.**

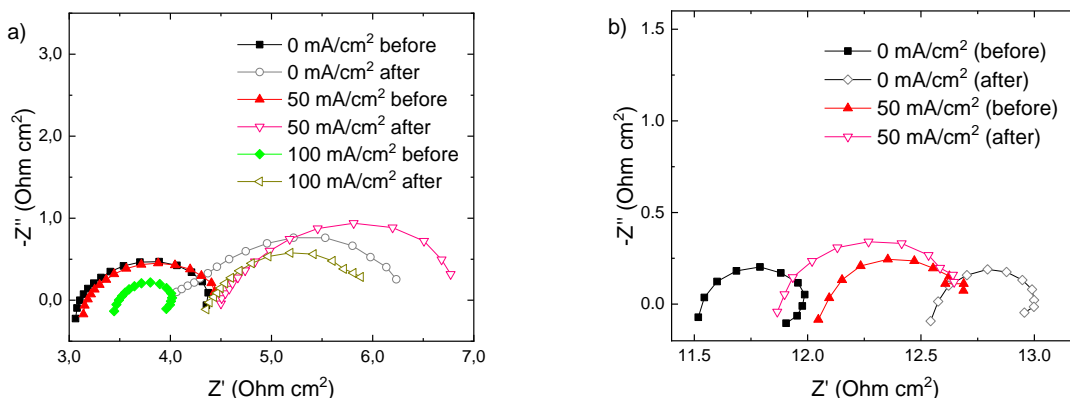


355  
 356 **Figure 10: Qualitative estimation of concentration profiles for diluted salt concentrations in the electrolyte.**

357 **Ageing of BPM**

358 In this section, we introduce electrochemical impedance spectroscopy as a tool to in-situ  
 359 observe the ageing of a BPM and membranes in general. When a BPM is used in industrial applications,  
 360 high activity and durability are of high importance. The performance of the BPM should also be  
 361 measurable in operation, which is possible by applying a small perturbation to the DC current or  
 362 voltage, resulting in the typical EIS graphs presented above. Differentiating between the individual  
 363 components, such as conductivity of the membrane or kinetics of the WDR, reveals which methods  
 364 can be used to prolong the lifetime of the membrane, e.g. lowering the current or replacing the  
 365 electrolyte(s), or, if that is no longer sufficient, renewing the BPM.

366 For this purpose, a BPM was tested in a flow cell (see Figure SI2) of 10 cm<sup>2</sup> with a flow rate of  
 367 0.07 cm<sup>3</sup> s<sup>-1</sup> in 1M H<sub>2</sub>SO<sub>4</sub> vs. 1.3M KOH. An impedance measurement was performed at the beginning  
 368 of the experiment with an applied direct current of 20 mA/cm<sup>2</sup> and an EIS amplitude of 5 mA/cm<sup>2</sup>.  
 369 After this, for 5 days a DC current of 0, 50, and 100 mA/cm<sup>2</sup> was applied, respectively. Immediately  
 370 after this experiment, the same EIS measurement was repeated. Similarly, 0 and 50 mA/cm<sup>2</sup> were  
 371 tested for 1M KHCO<sub>3</sub> vs. NaOH. Both experiments for all current densities are shown in Figure 11.



372  
 373 **Figure 11: Ageing of a BPM over 5 days (a) at 0, 50 and 100 mA/cm<sup>2</sup> in 1M H<sub>2</sub>SO<sub>4</sub> and 1.3M KOH and (b) at 0 and 50**  
 374 **mA/cm<sup>2</sup> in 1M KHCO<sub>3</sub> and 1M NaOH in a flow cell with 60 rpm. EIS performed with a frequency range between 10 kHz**  
 375 **and 0.4 Hz. Lower frequencies are not shown because of the noise limitations of the flow cell (e.g., due to gas bubbles) in**  
 376 **that frequency range.**

377 For the experiment with no current applied, only a slow exchange of co-ions via diffusion was  
 378 observed, driven by the concentration gradient across the BPM. For the no co-ions<sub>mem</sub> case (H<sub>2</sub>SO<sub>4</sub> vs.  
 379 KOH), analysis from ICP-OES showed an exchange of 10% K<sup>+</sup> from the anolyte towards the catholyte  
 380 after 5 days of open-circuit operation. Once a current was applied, the crossover increased to 20% and  
 381 32% for 50 and 100 mA/cm<sup>2</sup>, which was 11% and 13.5% of the applied current, respectively. The  
 382 crossover of SO<sub>4</sub><sup>2-</sup> was minor compared to K<sup>+</sup>, as can be seen in Table SI1. The increase of the crossover  
 383 can be described by the extra migration component that is related to the electric field gradient on the  
 384 system, which transports K<sup>+</sup> through the membrane towards the cathode that attracts positive charged  
 385 ions. These high crossover numbers indicate that this membrane is not ideal for systems that are  
 386 sensitive to fouling from neighboring co-ions. This strong degradation is not visible in the co-ions case  
 387 (Figure 11(b)). Alongside the strong degradation of the membrane in extreme conditions, there is a  
 388 strong need for further membrane development using the discussed techniques in order to successful  
 389 implement BPMs in current technologies and reduced energy costs.

390



391 **Table 5: Impedance data of WDR semicircles after stability measurements.**

Electrolyte	Current density mA cm <sup>-2</sup>	State	$R_{WDR}$ $\Omega$ cm <sup>2</sup>	$Q_{WDR}$ F cm <sup>2</sup>	$n_{WDR}$ -
1M H <sub>2</sub> SO <sub>4</sub> -KOH	0	Before	1.30	0.35	0.80
	0	After	2.10	0.30	0.80
	50	Before	1.30	0.55	0.75
	50	After	2.40	0.26	0.85
	100	Before	0.52	0.25	0.90
	100	After	1.70	0.52	0.75
1M KHCO <sub>3</sub> -NaOH	0	Before	0.50	0.40	0.85
	0	After	0.45	0.55	0.85
	50	Before	0.60	0.55	0.85
	50	After	0.85	0.55	0.85

392

393 When the system is subject to an applied current density of 50 mA/cm<sup>2</sup> for 5 days, the increase  
 394 in the potential over the BPM is around 170 mV. EIS results (Figure 11(a), two measurements in red),  
 395 show the individual increases of the membrane components can be determined. The Ohmic resistance  
 396 increased from 3.2  $\Omega$  cm<sup>2</sup> to 4.2  $\Omega$  cm<sup>2</sup>, which corresponds to a voltage loss of 50 mV. This extra Ohmic  
 397 resistance loss is associated to the bulk of the membrane layers, which is known from literature to  
 398 occur via charge leaching at high pH.<sup>43</sup> The difference in the width of the two semicircles resulted in  
 399 another 50 mV increase. The remaining extra potential of the 170 mV can be attributed to the finite  
 400 membrane selectivity, which causes ion crossover, lowering the conductivity and resulting in an extra  
 401 Ohmic loss. Other effects have a minimal impact on the ageing including the diffusion boundary  
 402 component, which is neglected since this component is negligible for the no co-ions<sub>mem</sub> case (H<sub>2</sub>SO<sub>4</sub> vs.  
 403 KOH), and the pH remained nearly constant throughout the experiment.

404 The increase in the WDR resistance after ageing is noteworthy, especially since it is not  
 405 accompanied by an increase in the capacitive component in the equivalent circuit. The capacitor is  
 406 represented as a double layer in the internal interface because of the strong polarized environment.  
 407 There are two possible explanations for the decrease in the kinetics. The first is the reduced activity of  
 408 the catalyst at the interface, which performs reactions (1) and (2), due to lowered number of fixed  
 409 charges via recombination—where positive and negative fixed charges recombine to form a neutral  
 410 component. The importance of the catalyst loading has been studied earlier in relation with required  
 411 voltage, and in general the lower the catalyst loading, the higher voltage is required.<sup>11,39</sup> The second  
 412 explanation is the widened interface thickness, which was proven in literature to have an import  
 413 impact on the voltage.<sup>15</sup> Here, the integration of the layers at the membrane-membrane interface  
 414 separated in time. Therefore, the interfacial catalyst and the electronic properties of the interface itself

415 should be main focus points in the future developments and minimization of operational losses in  
416 BPMs.

## 417 **Conclusions**

418 In this work, a bipolar membrane was examined using electrochemical impedance  
419 spectroscopy, which makes it possible to differentiate electronic information among the different  
420 components of the membrane. In particular, the interface between the two membrane layers was of  
421 interest. At this interface, the water dissociation reaction occurs, which dissociates water into protons  
422 and hydroxide ions under an applied potential. However, depending on the electrolyte(s) surrounding  
423 the membrane, the i-V curves behaves differently. Therefore, two cases were studied, one without co-  
424 ions and the other with co-ions. It was demonstrated that the individual components, such as the  
425 kinetics of the water dissociation reaction and the capacitance of the diffusion boundary layer, can be  
426 identified using EIS, contributing to understanding of electrochemical elements within the BPM. EIS  
427 shows that at low current densities below the plateau current density, a different behavior exists,  
428 which is dominated by co-ion transport. The co-ions case showed a plateau at a low current density,  
429 where co-ions seem to be responsible for the charge transport (shown with ICP-OES analysis) and no  
430 WDR peak is visible in the impedance measurement. At higher current densities for  $\text{KHCO}_3/\text{KOH}$ , and  
431 at all (positive) current densities for the  $\text{H}_2\text{SO}_4/\text{KOH}$  case, impedance spectra show a clear capacitive  
432 element that is ascribed to the WDR. Finally, EIS has proven to be a useful tool to monitor the ageing  
433 of a BPM and to determine which component is affected most by the ageing, which is important to  
434 design and implement BPMs in electrochemical cells for industrial applications.

## 435 **Conflicts of interest**

436 There are no conflicts to declare.

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