Supporting Information

Electrochemical and Hydraulic Analysis of Thin-Film Composite and Cellulose Triacetate Membranes for Seawater Electrolysis Applications

Rachel Taylor[1], Le Shi[2], Xuechen Zhou[2], Ruggero Rossi[2], Cristian Picioreanu[3], and Bruce E. Logan[1,2]

[1]Department of Chemical Engineering, The Pennsylvania State University, University Park, PA, USA.

[2]Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA, USA.

[3]Water Desalination and Reuse Center (WDRC), Biological and Environmental Science and Engineering Division (BESE), King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia
*Corresponding author. Email: blogan@psu.edu; Tel.: +1-814-863-7908

Resistance Measurements

For the membrane electric resistance measurements, the membrane was placed in a cubic cell with a cylindrical chamber containing either 0.6 M or 1 M NaCl (Figure S1 and Figure S2). Two Ag/AgCl reference electrodes were placed on either side of the membrane and inside tubing connected to Luggin capillaries. The anode and cathode were both Pt/Ti mesh electrodes placed at either end of the cylindrical chamber, 10 cm apart. A potentiostat was used to apply low current densities (0.07 to 3 mA/cm^2) to the cell, and the reference electrodes measured the potential drop across the membrane. The second hole next to the one holding the reference electrode is used to facilitate removal of the liquid following an experiment.
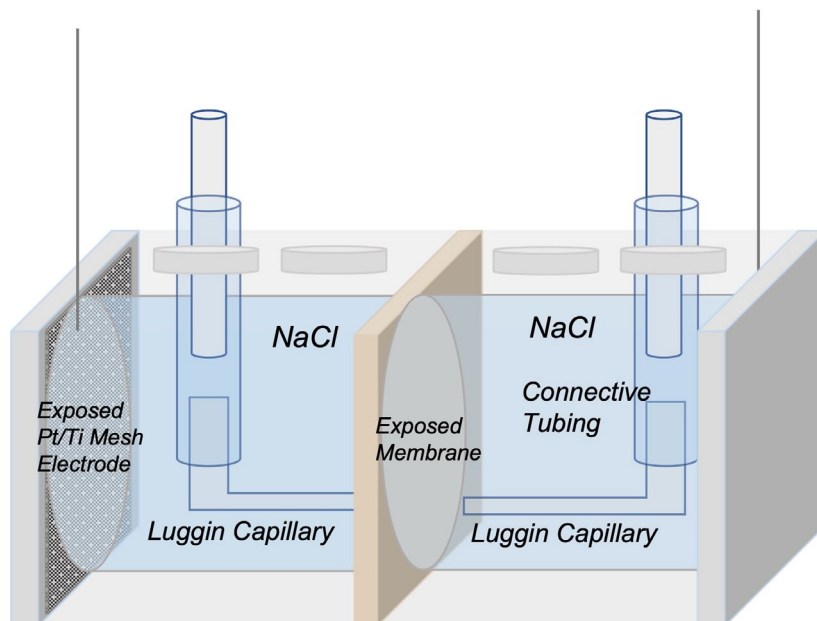

Figure S2. Schematic of cubic cell with cylindrical chamber used for membrane electric resistance measurements. The size of each component is not to scale.
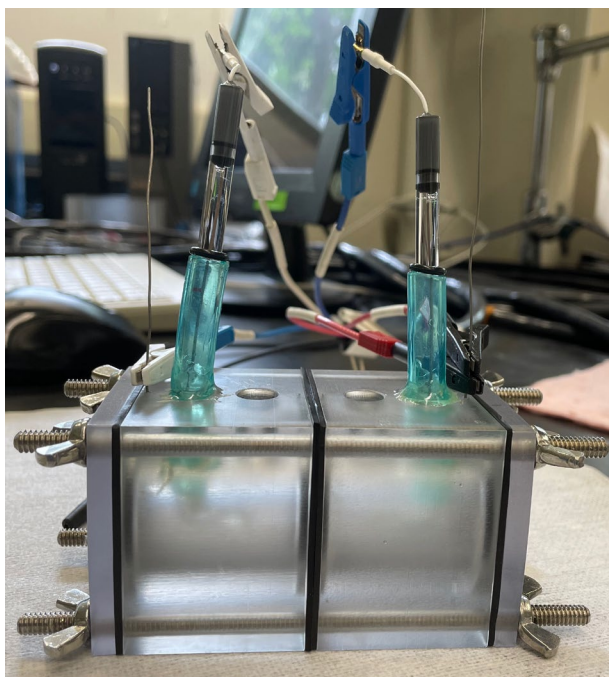
30

Figure S2. Photograph of apparatus used for membrane resistance measurements

31   EC-Lab software recorded the potential drop between the reference electrodes at each applied
32   current (Figure S3 and Figure S4). The results were linear, confirming that the current densities
33   applied were in the ohmic region of a polarization curve, and the energy requirement to facilitate
34   the desired current density is solely dictated by the ohmic contributions of the cell. From this
35   data, the resistance between the reference electrodes can be extracted as the proportionality
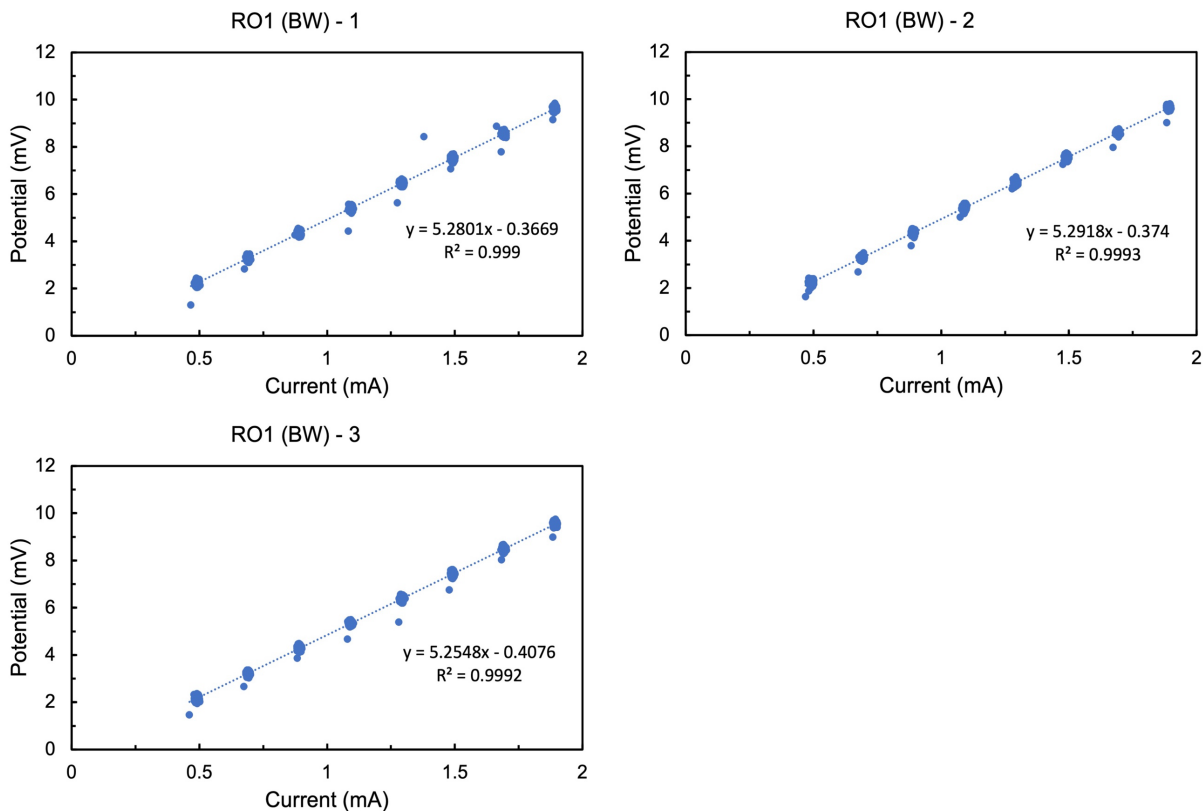36   constant between the potential vs. current plots.
37

Figure S3. Potential versus current data for 3 pieces of RO1 (BW) membrane cut from a larger flat sheet membrane.

In the ohmic region, potential (U) in units of V, is linearly related to the current (I) in units of A, and the slope of the line is the resistance (R) in units of Ω. Therefore, the total resistances of the membrane + solution, $R_{mem+sol}$, in units of Ω is the following for the three pieces of RO1 (BW) membrane:

RO1 (BW) – 1: 5.28 Ω
RO1 (BW) – 2: 5.29 Ω
RO1 (BW) – 3: 5.25 Ω

To find the area resistance, multiply the resistances by the exposed area of the membrane, 7.55 cm^2:

RO1 (BW) – 1: $(5.28\ \Omega)(7.55\ cm^2) = 39.86\ \Omega\ cm^2$
RO1 (BW) – 2: $(5.29\ \Omega)(7.55\ cm^2) = 39.94\ \Omega\ cm^2$
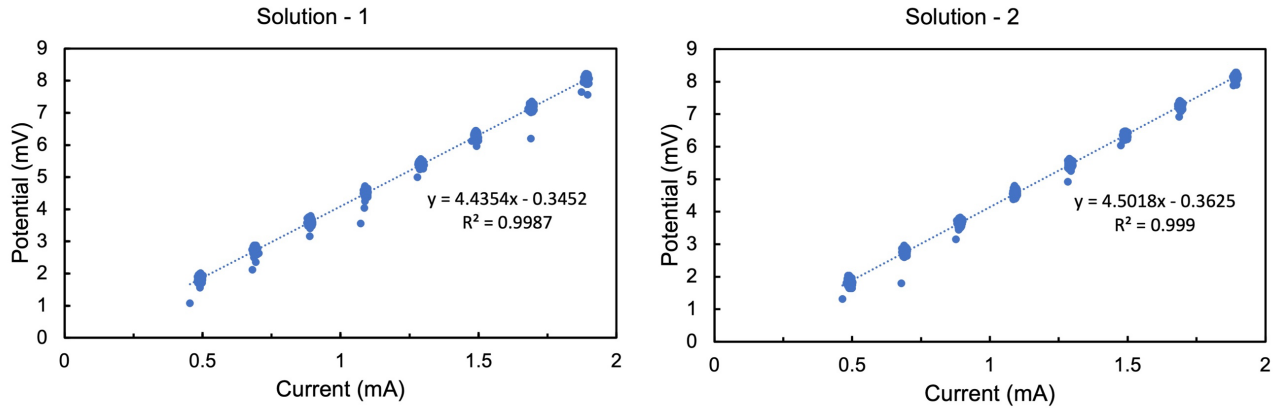RO1 (BW) – 3: $(5.25\ \Omega)(7.55\ cm^2) = 39.64\ \Omega\ cm^2$

Figure S4. Potential vs. current data for 1M NaCl solution between reference electrodes.

56   The solution resistances R_{sol} are the following:

58   Solution – 1: 4.44 Ω cm^2
59   Solution – 2: 4.50 Ω cm^2

61   The area resistances are the following:

63   Solution – 1: $(4.44\ \Omega)(7.55\ cm^2) = 33.52\ \Omega\ cm^2$
64   Solution – 2: $(4.50\ \Omega)(7.55\ cm^2) = 33.98\ \Omega\ cm^2$

66   Average $R_{mem+sol}$: 39.81 Ω cm^2
67   Average R_{sol}: 33.75 Ω cm^2

69   The membrane resistance is calculated as:

71
$$R_{mem} = R_{mem+sol} - R_{sol} = 39.81\ \Omega\ cm^2 - 33.75\ \Omega\ cm^2 = 6.06\ \Omega\ cm^2$$

74   **Total Thickness Measurements:**

76   The total thicknesses of three RO membranes, one NF membrane, and one FO membrane were
77   measured using an outside micrometer (Mitutoyo Kawasaki, Japan) (Figure S5). When the
78   membrane total thickness was compared to electric resistance, there was no significant
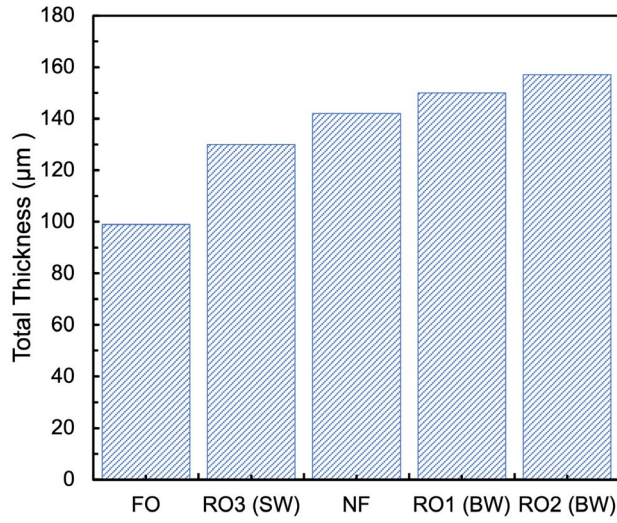79   correlation between the two ($R^2 = 0.06$).

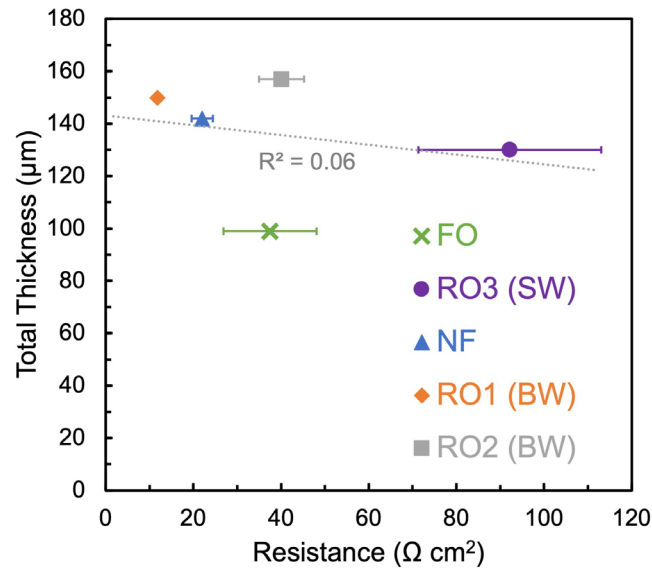**Figure S5.** Total thickness measured using an outside micrometer.

82

Figure S6. Total thickness plotted against membrane resistance.

Membrane Water Flux using Manufacturer's Specification Sheets

To better understand the differences between the reverse osmosis membranes we selected for further studies, we used manufacture's published data to learn about the membrane performance in filtration experiments (Table S1). We calculated the permeate fluxes in LMH using the published gallons per day (gpd) of permeate and membrane active area [1-3] (Table S2).

Table S1. Reported gallons per day of permeate, membrane active area, and NaCl rejection for three RO membranes studied. Using this data, the permeate flux was calcuated for each membrane in LMH.

Membrane	Reported gallons per day (gpd)	Reported Membrane Active Area (ft^2)	Calculated Flux (gfd)	Calculated Flux (LMH)	Reported Rejection
RO1 (ACM5, Trisep)	800	26	30.8	52.3	98.5%
RO2 (BW-XLE, DuPont)	14,000	440	31.8	54.1	99.0%
RO3 (SWC4, Hydranautics)	5,200	370	14.1	23.9	99.8%

The following is an example of how we used the published data to calculate the permeate flux in LMH:

RO1 (ACM5, Trisep):

GFD = 800 gpd / 26 ft^2 = **30.8 gfd**
LMH = 30.8 gfd * 1.7 (LMH/gfd) = **52.3 LMH**

The results are summarized as follows:

Table S2. Flux in LMH and NaCl rejection of three RO membranes used in electrochemical and hydraulic studies in this work.

Membrane	Permeate Flux (LMH)	Rejection
RO1 (ACM5, Trisep)	52.3	98.5%
RO2 (BW-XLE, DuPont)	54.1	99.0%
RO3 (SWC4, Hydranautics)	23.9	99.8%

Water Electrolyzer Experiments

During electrolysis, protons generated at the anode and hydroxide ions generated at the cathode will cause large pH gradients across the reactor. After electrolyzing saltwater for two hours in the zero-gap flow cell using each of the three RO membranes, one NF membrane, and one FO membranes, the pH was measured in the anolyte and catholyte. (Figure S7).
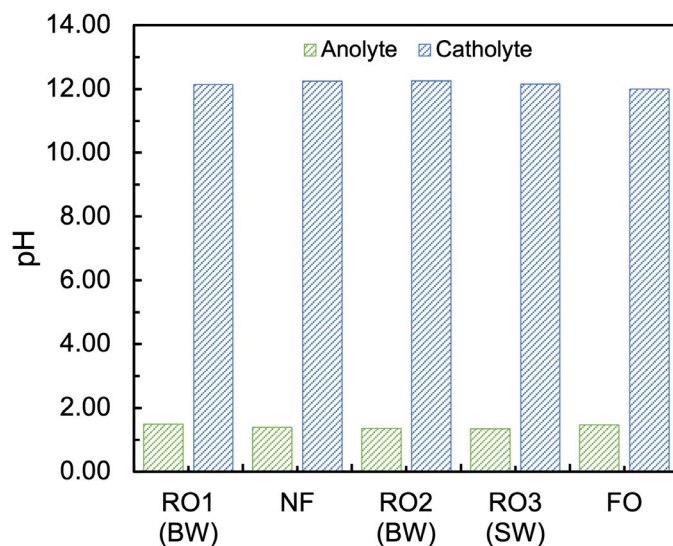
114

Figure S7. Anolyte and Catholyte pH after 2 hours of electrolysis with a saltwater (NaCl, 1 M) catholyte and contained catholyte (NaClO$_4$, 1 M) in a zero-gap flow cell. The pH was measured with a SevenMulti dual pH and conductivity meter (Mettler Toledo, Switzerland).

115   **Ion Crossover Experiments**
116
117   After electrolyzing saltwater in the cubic cell with a cylindrical chamber for 1 hour using each of
118   the selected membranes (3 RO, 1 NF, 1 FO), the pH was measured in the anolyte and catholyte.
119   The same large pH gradients observed in the zero-gap flow cell (Figure S7) were observed in the
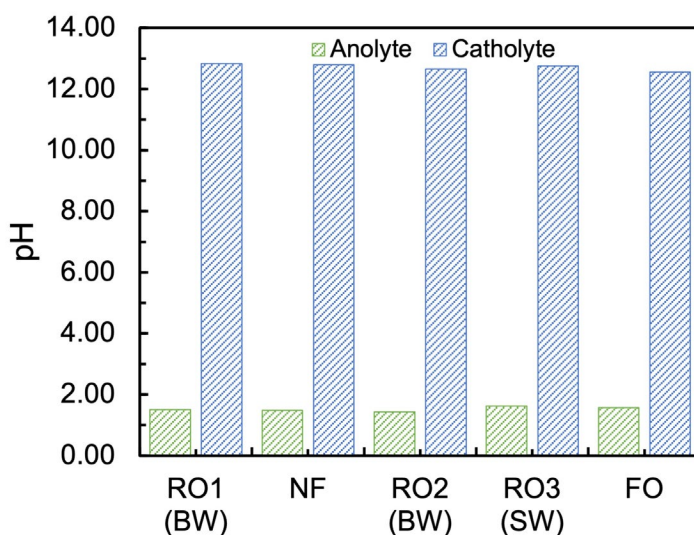120   cubic cell with a cylindrical chamber (Figure S8).
121

Figure S8. Anolyte and Catholyte pH after 1 hour of electrolysis with a saltwater (NaCl, 1 M) catholyte and contained anolyte (NaClO$_4$, 1 M) in a cubic reactor. The pH was measured with a SevenMulti dual pH and conductivity meter (Mettler Toledo, Switzerland).

122
Calculating Fraction of Charge Carried by Water Ions (H$^+$ and OH$^-$)

123

124

125 Ions carry charge in the direction of the potential gradient to maintain a set current density. The
126 moles of ions required to carry a constant current density of 20 mA/cm^2 can be calculated, which
127 is shown below. The fraction of charge carried by salt ions can be determined from the ion
128 crossover data collected during electrolysis in the cylindrical chamber. Sodium and chloride ions
129 are transported in the direction of the electric field, so they contribute to the 20 mA/cm^2 current
130 density between the anode and cathode. Potassium and perchlorate transport across the
131 membrane due to diffusion only, moving in the opposite direction of the potential gradient.
132 Therefore, more ions must be transported in the direction of the potential gradient to counteract
133 the loss of charge transfer due to potassium and perchlorate crossover.

134

135 The moles of charge carried by protons or hydroxide ions can be deduced by comparing the
136 moles of ions which must be transported across the membrane to maintain a current density of 20
137 mA/cm^2 to the amount of salt ions which crossed over the membrane in the direction of the
138 potential gradient. Knowing the fraction of charge which was carried across each membrane by
139 protons and hydroxide ions will give insight into the selective ion transport of each membrane.

140

141 For a current density of 20 mA/cm^2, the moles of charge transferred to carry the current for one
142 hour is:

143

144
$$n_t = \frac{I\,t\,A_e}{F} = \frac{\left(20\,\frac{\text{mA}}{\text{cm}^2}\right)(3600\text{ s})(1.68\text{ cm}^2)}{\left(96485\,\frac{\text{C}}{\text{mol}}\right)} = 1.25\text{ mmol charge equivalents}$$

145

146 The moles of charge carried by salt ions over 1 hour can be subtracted from the total moles of
147 charge transferred to determine the moles carried by water ions (H$^+$ + OH$^-$). Water loss during 1
148 hour of electrolysis at 20 mA/cm^2 is negligible, so the volume in the anolyte and catholyte is
149 considered constant, 31 mL [4]. The following ion crossover concentrations are average
150 concentrations.

151

152 The contribution of salt ion and water ions to charge transfer, and the fraction of charge carrier
153 that is water ions is calculated the following way for each membrane:

154

155 **RO1 (BW):**

156

157 Moles of Na$^+$ in Catholyte: $n_{Na^+} = (4.42\text{ mM})(\,31\text{ mL}) = 0.14$ mmole charge equiv.
158 Moles of ClO$_4^-$ in Catholyte: $n_{ClO_4^-} = (0.47\text{ mM})(31\text{ mL}) = 0.01$ mmole charge equiv.
159 Moles of K$^+$ in Anolyte: $n_{K^+} = (0.59\text{ mM})(31\text{ mL}) = 0.02$ mmole charge equiv.
160 Moles of Cl$^-$ in Anolyte: $n_{Cl^-} = (22.99\text{ mM})(31\text{ mL}) = 0.71$ mmole charge equiv.

161

162 Net salt ion charge contribution towards current density:

163

164
$$n_s = n_{Na^+} + n_{Cl^-} - n_{K^+} - n_{ClO_4^-} = 0.14 + 0.71 - 0.02 - 0.01 = 0.82\text{ mmole}$$

165

166 Moles of charge carried by water ions:

167

168
$$n_w = n_t - n_s = 1.25 - 0.82 = 0.43 \text{ mmole charge equiv.}$$

169

170 Fraction of charge carried by water ions (transport number):

171

172
$$t_{H^+} = \frac{0.43 \text{ mmole}}{1.25 \text{ mmole}} = 0.34$$

173

174 **RO2 (BW):**

175

176   Moles of Na^+ in Catholyte: $n_{Na^+} = (5.30 \text{ } mM)(31 \text{ } mL) = 0.16$ mmole charge equiv.
177   Moles of ClO_4^- in Catholyte: $n_{ClO_4^-} = (0.36 \text{ } mM)(31 \text{ } mL) = 0.01$ mmole charge equiv.
178   Moles of K^+ in Anolyte: $n_{K^+} = (0 \text{ } mM)(31 \text{ } mL) = 0$ mmole charge equiv.
179   Moles of Cl^- in Anolyte: $n_{Cl^-} = (20.95 \text{ } mM)(31 \text{ } mL) = 0.65$ mmole charge equiv.

180

181 Net salt ion charge contributing towards current density:

182

183
$$n_s = n_{Na^+} + n_{Cl^-} - n_{K^+} - n_{ClO_4^-} = 0.16 + 0.65 - 0 - 0.01 = 0.8 \text{ mmole}$$

184

185 Charge carried by water ions:

186

187
$$n_w = n_t - n_s = 1.25 - 0.8 = 0.45 \text{ mmole charge equiv.}$$

188

189 Fraction of charge carried by water ions (transport number):

190

191
$$t_{H^+} = \frac{0.45 \text{ mmole}}{1.25 \text{ mmole}} = 0.36$$

192

193 **RO3 (SW):**

194

195   Moles of Na^+ in Catholyte: $n_{Na^+} = (9.81 \text{ } mM)(31 \text{ } mL) = 0.30$ mmole charge equiv.
196   Moles of ClO_4^- in Catholyte: $n_{ClO_4^-} = (0.44 \text{ } mM)(31 \text{ } mL) = 0.01$ mmole charge equiv.
197   Moles of K^+ in Anolyte: $n_{K^+} = (0 \text{ } mM)(31 \text{ } mL) = 0$ mmole charge equiv.
198   Moles of Cl^- in Anolyte: $n_{Cl^-} = (10.46 \text{ } mM)(31 \text{ } mL) = 0.32$ mmole charge equiv.

199

200 Net salt ion charge contributing towards current density:

201

202
$$n_s = n_{Na^+} + n_{Cl^-} - n_{K^+} - n_{ClO_4^-} = 0.30 + 0.32 - 0 - 0.01 = 0.61 \text{ mmole}$$

203

204 Charge carried by water ions:

205

206
$$n_w = n_t - n_s = 1.25 - 0.61 = 0.64 \text{ mmole charge equiv.}$$

207

208 Fraction of charge carried by water ions (transport number):

209

$$t_{H^+} = \frac{0.64 \text{ mmole}}{1.25 \text{ mmole}} = 0.51$$

NF:

Moles of Na^+ in Catholyte: $n_{Na^+} = (27.34 \, mM)(31 \, mL) = 0.85$ mmole charge equiv.
Moles of ClO_4^- in Catholyte: $n_{ClO_4^-} = (4.28 \, mM)(31 \, mL) = 0.13$ mmole charge equiv.
Moles of K^+ in Anolyte: $n_{K^+} = (0.04 \, mM)(31 \, mL) = 0.001$ mmole charge equiv.
Moles of Cl⁻ in Anolyte: $n_{Cl^-} = (6.5 \, mM)(31 \, mL) = 0.20$ mmole charge equiv.

Net salt ion charge contributing towards current density:

$$n_s = n_{Na^+} + n_{Cl^-} - n_{K^+} - n_{ClO_4^-} = 0.85 + 0.20 - 0.001 - 0.13 = 0.92 \text{ mmole}$$

Charge carried by water ions:

$$n_w = n_t - n_s = 1.25 - 0.92 = 0.33 \text{ mmole charge equiv.}$$

Fraction of charge carried by water ions (transport number):

$$t_{H^+} = \frac{0.33 \text{ mmole}}{1.25 \text{ mmole}} = 0.26$$

FO:

Moles of Na^+ in Catholyte: $n_{Na^+} = (49.52 \, mM)(31 \, mL) = 1.54$ mmole charge equiv.
Moles of ClO_4^- in Catholyte: $n_{ClO_4^-} = (7.32 \, mM)(31 \, mL) = 0.23$ mmole charge equiv.
Moles of K^+ in Anolyte: $n_{K^+} = (7.52 \, mM)(31 \, mL) = 0.23$ mmole charge equiv.
Moles of Cl⁻ in Anolyte: $n_{Cl^-} = (5.45 \, mM)(31 \, mL) = 0.17$ mmole charge equiv.

Net salt ion charge contributing towards current density:

$$n_s = n_{Na^+} + n_{Cl^-} - n_{K^+} - n_{ClO_4^-} = 1.54 + 0.17 - 0.23 - 0.23 = 1.25 \text{ mmole}$$

Charge carried by water ions:

$$n_w = n_t - n_s = 1.25 - 1.25 = 0 \text{ mmole charge equiv.}$$

Fraction of charge carried by water ions (transport number):

$$t_{H^+} = \frac{0 \text{ mmole}}{1.25 \text{ mmole}} = 0$$

Literature cited

[1]   "TriSep ACM5 Low Energy RO Membrane," in "Product Specification - Trisep ACM5," TriSep, 2021. [Online]. Available: https://www.lenntech.com/Data-sheets/Trisep-2540-ACM5-TSF-L.pdf

[2]   DuPont, "FilmTech XLE-440 Element," in "Product Data Sheet," 2020. [Online]. Available: https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/RO-FilmTec-XLE-440-PDS-45-D01513-en.pdf

[3]   Hydranautics, "SWC4-LD," Hydranautics Nitto Group Company, 2018.

[4]   L. Shi, R. Rossi, M. Son, D.M. Hall, M.A. Hickner, C.A. Gorski, and B.E. Logan, Using reverse osmosis membranes to control ion transport during water electrolysis, Energy Environ. Sci. 13 (2020) 3138-3148. https://doi.org/10.1039/d0ee02173c.