

## Supporting Information

### Using reverse osmosis membranes to control ion transport during water electrolysis

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## Experimental

### Materials and methods

The electrodes used for electrochemical measurements were carbon-based electrodes with a supported platinum catalyst (ETEK 10 wt% Pt on Vulcan XC-72,  $0.35\text{mg cm}^{-2}$ ). Electrolytes consisted of 0.29 M, 0.62 M or 1 M solution of the salt (NaCl, NaClO<sub>4</sub> or KCl) in deionized water (DI,  $>18\text{ M}\Omega\text{ cm}$  at room temperature). Buffered electrolytes were prepared by dissolving NaCl or NaClO<sub>4</sub> in 1 M phosphate buffer (1 M PBS, pH 7). All chemicals were used as received from Sigma-Aldrich. The membranes used were two cation exchange membranes Selemion CMV (Sel; Asahi Glass, Japan), and Nafion 117 (Naf; Chemours) and two polyamide-based thin-film composite membranes (TFC) for seawater (SW; SW 30HR, DuPont) or brackish water (BW; BW 30LE, DuPont) reverse osmosis (RO). Different active layer orientations of the BW and SW membranes were used to compare their performance. When the active layer faced the cathode, the membranes are designated as BW/Cat and SW/Cat, and when they face the anode as BW/Ano and SW/Ano. The thickness of Selemion CMV was  $98 \pm 1\ \mu\text{m}$  with an ion exchange capacity of  $2.08\text{ meq g}^{-1}$ . The thickness of Nafion 117 was  $183\ \mu\text{m}$  with an ion exchange capacity of  $0.88\text{ meq g}^{-1}$ . The thicknesses of the RO membranes were  $123 \pm 5\ \mu\text{m}$  (BW) and  $130 \pm 4\ \mu\text{m}$  (SW). These properties of these membranes were based on reports by the manufacturer. All membranes were soaked in DI water for at least 2 days in a refrigerator at  $4\ ^\circ\text{C}$  without other treatments before use.

### Charge balance and proton transport example calculation

For a current density of  $40\text{ mA cm}^{-2}$  for 1 h, if the Faraday efficiency is 100 % for both H<sub>2</sub> and O<sub>2</sub>, the produced moles of H<sub>2</sub> ( $n_{CE}$ ) should be:

$$n_{CE} = \frac{\int_{i=1}^n I_i \Delta t}{2F} = 7.46 \times 10^{-4}\text{ mol}$$

and moles of O<sub>2</sub> ( $n_{CE}$ ) should be:

$$n_{CE} = \frac{\int_{i=1}^n I_i \Delta t}{4F} = 3.73 \times 10^{-4}\text{ mol}$$

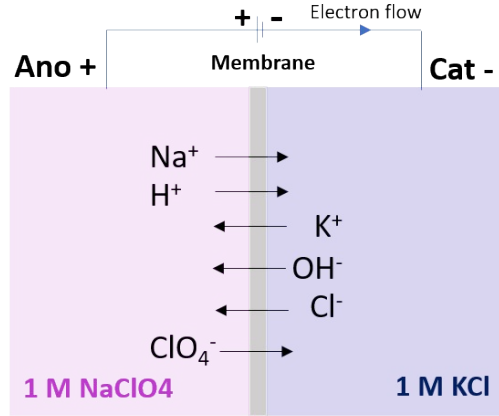
Therefore, the total water consumption is  $7.46 \times 10^{-4}$  mole, and the total volume of water consumption is:

$$V_{H_2O} = \frac{(7.4623 \times 10^{-4}\text{ mole})(18 \times 10^{-3}\text{ kg mol}^{-1})}{1 \times 10^3\text{ kg m}^{-3}} = 1.34 \times 10^{-2}\text{ mL}$$

The water volume change due to electrolysis:

$$\Delta V_{H_2O} = \frac{1.34 \times 10^{-2}\text{ mL}}{60\text{ mL}} \times 100\% = 0.0223\%$$

Therefore, the water volume change due to electrolysis was negligible. The total moles of ions transported through membrane can be calculated based on the average number of each ion from IC results and the solution volume of each chamber (30 mL).



**Schematic 1.** Illustration of ions transport through membrane under the applied constant current. All the hydrated ions are simplified as naked ions here.

The current density is summed up with contributions from each negative and positive ions species, as illustrated in Schematic 1. The cations moving from anolyte to catholyte and anions moving from catholyte to anolyte are considered as positive (+) to the current. In the opposite, the cations moving from catholyte to anolyte and anions moving from anolyte to catholyte are considered as negative (-) to the current. The H<sup>+</sup> and OH<sup>-</sup> transport in the opposite direction is considered in total as the net proton transport.

Selemion CEM and BW/Cat membranes were used as examples for the following calculations, where ion concentrations were averages obtained from multiple IC measurements. For Selemion CEM, the total ions transported through the membrane in the absence of current were:

$$\begin{aligned} \text{Moles of Na}^+ \text{ in Catholyte: } n_{Na^+} &= 26.3 \text{ mM} \times 30 \text{ mL} = 0.79 \text{ mmol of charge equivalents} \\ \text{Moles of K}^+ \text{ in Anolyte: } n_{K^+} &= 8.1 \text{ mM} \times 30 \text{ mL} = 0.24 \text{ mmol of charge equivalents} \\ \text{Moles of Cl}^- \text{ in Anolyte: } n_{Cl^-} &= 0.5 \text{ mM} \times 30 \text{ mL} = 0.015 \text{ mmol of charge equivalents} \\ \text{Moles of ClO}_4^- \text{ in Catholyte: } n_{ClO_4^-} &= 0.3 \text{ mM} \times 30 \text{ mL} = 0.009 \text{ mmol of charge equivalents} \end{aligned}$$

Therefore, the net ion transport is

$$n_{ion} = 0.79 - 0.24 + 0.015 - 0.009 = 0.56 \text{ mmol of charge equivalents}$$

For a current density of 40 mA cm<sup>-2</sup>, the total ions transport through the Selemion CEM membrane was:

$$\begin{aligned} \text{Moles of Na}^+ \text{ in Catholyte: } n_{Na^+} &= 62.0 \text{ mM} \times 30 \text{ mL} = 1.86 \text{ mmol of charge equivalents} \\ \text{Moles of K}^+ \text{ in Anolyte: } n_{K^+} &= 15.4 \text{ mM} \times 30 \text{ mL} = 0.462 \text{ mmol of charge equivalents} \end{aligned}$$

Moles of  $\text{Cl}^-$  in Anolyte:  $n_{\text{Cl}^-} = 0.6 \text{ mM} \times 30 \text{ mL} = 0.018 \text{ mmol}$  of charge equivalents  
 Moles of  $\text{ClO}_4^-$  in Catholyte:  $n_{\text{ClO}_4^-} = 0.4 \text{ mM} \times 30 \text{ mL} = 0.012 \text{ mmol}$  of charge equivalents

Therefore, the net ions transport is:

$$n_{\text{ion}} = 1.86 - 0.462 + 0.018 - 0.012 = 1.41 \text{ mmol of charge equivalents}$$

The net ions that contributed to current without deducting ion transport by diffusion is:

$$n_i = 1.41 \text{ mmol of charge equivalents}$$

The net ions contribute to current after deducting the ion transport due to diffusion is:

$$n_i' = 1.41 - 0.56 = 0.85 \text{ mmol of charge equivalents}$$

Similarly, for BW/Cat, the total ions transport through membrane under no current condition:

Moles of  $\text{Na}^+$  in Catholyte:  $n_{\text{Na}^+} = 1.0 \text{ mM} \times 30 \text{ mL} = 0.03 \text{ mmol}$  of charge equivalents

Moles of  $\text{K}^+$  in Anolyte:  $n_{\text{K}^+} = 0.6 \text{ mM} \times 30 \text{ mL} = 0.02 \text{ mmol}$  of charge equivalents

Moles of  $\text{Cl}^-$  in Anolyte:  $n_{\text{Cl}^-} = 0.98 \text{ mM} \times 30 \text{ mL} = 0.03 \text{ mmol}$  of charge equivalents

Moles of  $\text{ClO}_4^-$  in Catholyte:  $n_{\text{ClO}_4^-} = 0.81 \text{ mM} \times 30 \text{ mL} = 0.02 \text{ mmol}$  of charge equivalents

Therefore, the net ion transport is

$$n_{\text{ion}} = 0.03 - 0.02 + 0.03 - 0.02 = 0.02 \text{ mmol of charge equivalents}$$

Under the current density of  $40 \text{ mA cm}^{-2}$ , the total ions transport through BW/Cat membrane:

Moles of  $\text{Na}^+$  in Catholyte:  $n_{\text{Na}^+} = 19.3 \text{ mM} \times 30 \text{ mL} = 0.6 \text{ mmol}$  of charge equivalents

Moles of  $\text{K}^+$  in Anolyte:  $n_{\text{K}^+} = 2.9 \text{ mM} \times 30 \text{ mL} = 0.09 \text{ mmol}$  of charge equivalents

Moles of  $\text{Cl}^-$  in Anolyte:  $n_{\text{Cl}^-} = 15.3 \text{ mM} \times 30 \text{ mL} = 0.46 \text{ mmol}$  of charge equivalents

Moles of  $\text{ClO}_4^-$  in Catholyte:  $n_{\text{ClO}_4^-} = 1.8 \text{ mM} \times 30 \text{ mL} = 0.05 \text{ mmol}$  of charge equivalents

Therefore, the net ion transport is:

$$n_{\text{ion}} = 0.6 - 0.09 + 0.46 - 0.05 = 0.9 \text{ mmol of charge equivalents}$$

The net ions contribute to current is:

$$n_i = 0.9 \text{ mmol of charge equivalents}$$

The net ions contribute to current by deducting the ions diffusion is:

$$n_i' = 0.9 - 0.02 = 0.88 \text{ mmol of charge equivalents}$$

Total charges needed to carry  $40 \text{ mA cm}^{-2}$  current density for 1 h is:

$$Q = I t = 40 \frac{\text{mA}}{\text{cm}^2} 3600 \text{ s} = 144 \text{ C cm}^{-2}$$

Total moles of net electron transfer is:

$$n_t = \frac{144 \frac{C}{cm^2} 1 cm^2}{96485 \frac{C}{mole}} = 1.49 \text{ mmol of charge equivalents}$$

Therefore, the net proton transport to carry current for Selemion CEM is:

$$n_{H^+} = 1.49 \text{ mmol} - 1.41 \text{ mmol} = 0.08 \text{ mmole}$$

After diffusion ions reduction:

$$n_{H^+}' = 1.49 \text{ mmole} - 0.85 \text{ mmol} = 0.64 \text{ mmole}$$

The net proton transport to carry current for BW/Cat is:

$$n_{H^+} = 1.49 \text{ mmole} - 0.9 \text{ mmol} = 0.6 \text{ mmole}$$

After diffusion ions reduction:

$$n_{H^+}' = 1.49 \text{ mmole} - 0.88 \text{ mmol} = 0.61 \text{ mmole}$$

Considering the diffusion process is affected when applying the electric field, it is difficult to differentiate the portion of ion transport from diffusion versus that due to the electric field. Therefore, the moles of proton transport through Selemion CEM is in the range of 0.08 ~ 0.64 mmol and the moles of proton transport through BW/Cat is in the range of 0.59 ~ 0.61 mmol.

If all the protons generated at anode stay in the anolyte (with the assumption of 100 % Faraday efficiency), that means there will be 1.49 mmol of protons in the anolyte after applying 40 mA cm<sup>-2</sup> for 1 h, so the theoretical pH of the final anolyte should be:

$$pH = -\log [H^+] = -\log \left[ \frac{1.49 \text{ mmole}}{30 \text{ ml}} \right] = -\log [0.0497 \text{ M}] = 1.304$$

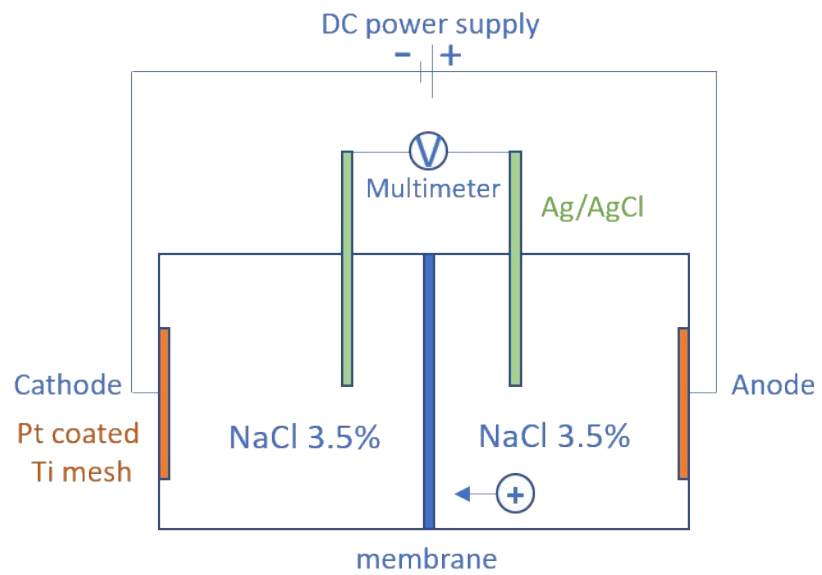
Considering the proton transport through the membrane (calculated above), the anolyte pH should be:

For Selemion CEM:

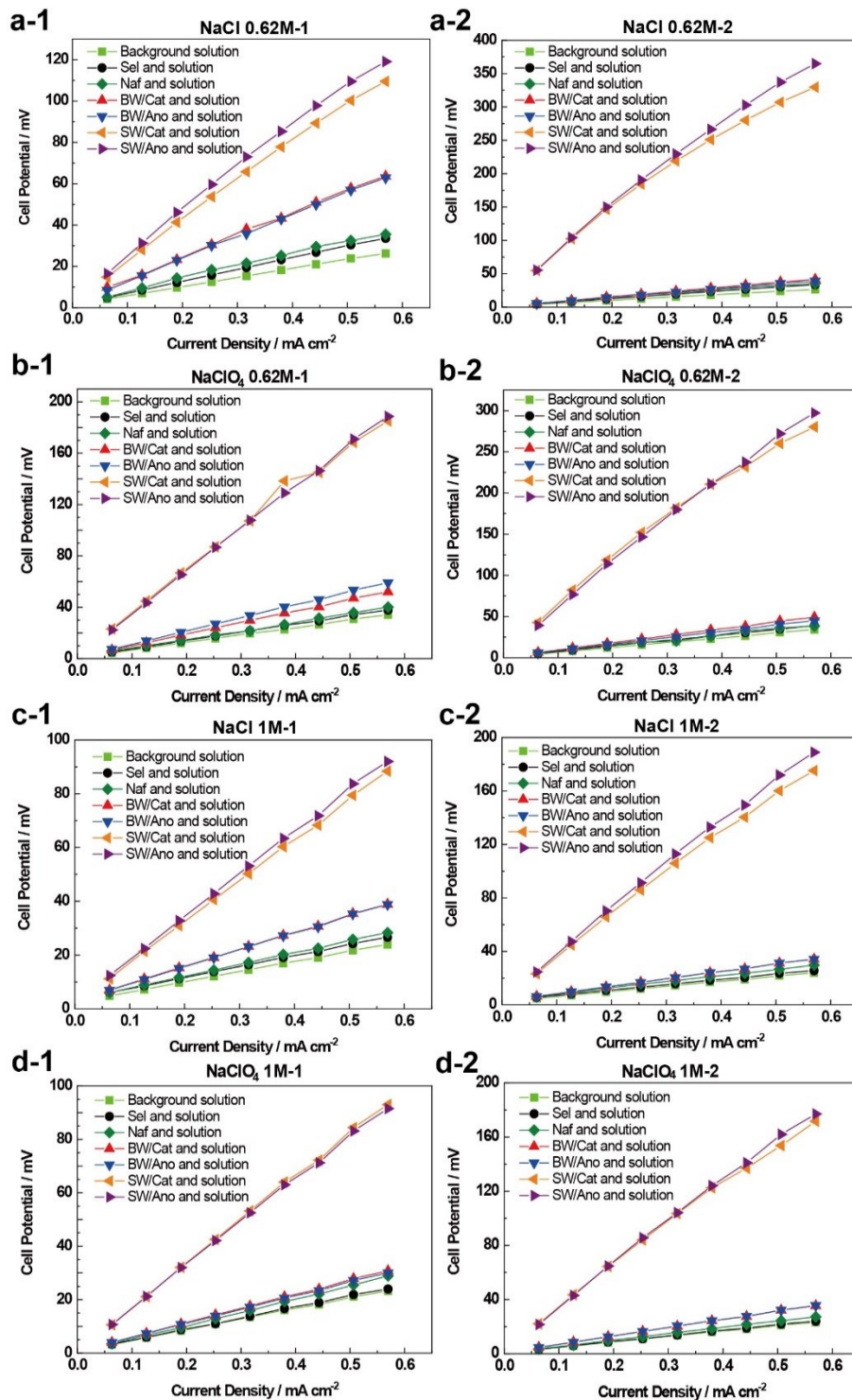
$$\begin{aligned} pH &= -\log \left[ \frac{1.49 \text{ mmole} - 0.08 \text{ mmol}}{30 \text{ ml}} \right] = -\log [0.0468 \text{ M}] = 1.328 \\ &= -\log \left[ \frac{1.49 \text{ mmole} - 0.64 \text{ mmol}}{30 \text{ ml}} \right] = -\log [0.0283 \text{ M}] = 1.548 \text{ diffusion deduction} \end{aligned}$$

For BW/Cat:

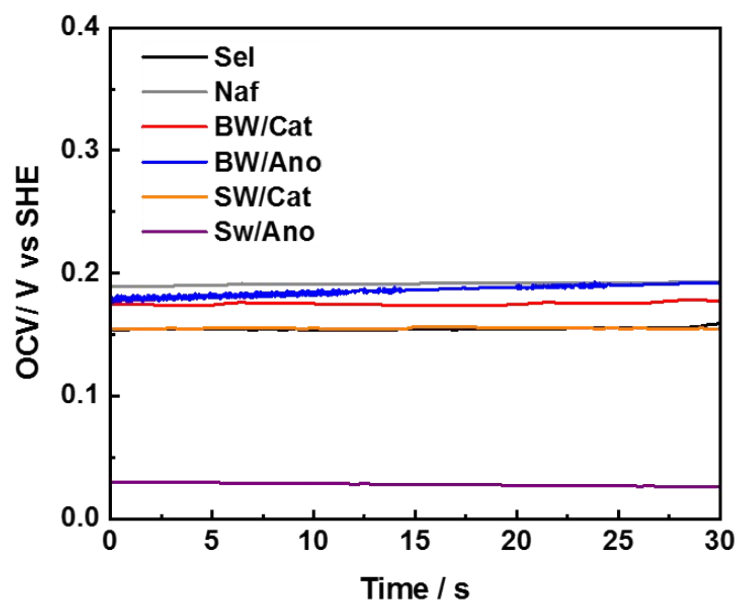
$$\begin{aligned} pH &= -\log \left[ \frac{1.49 \text{ mmole} - 0.6 \text{ mmol}}{30 \text{ ml}} \right] = -\log [0.0297 \text{ M}] = 1.527 \\ &= -\log \left[ \frac{1.49 \text{ mmole} - 0.61 \text{ mmol}}{30 \text{ ml}} \right] = -\log [0.0293 \text{ M}] = 1.533 \text{ diffusion deduction} \end{aligned}$$



**Figure S1.** Experimental setup for measuring the membrane resistance with the same salt solution (e.g., 3.5% NaCl) on each side of the membrane.



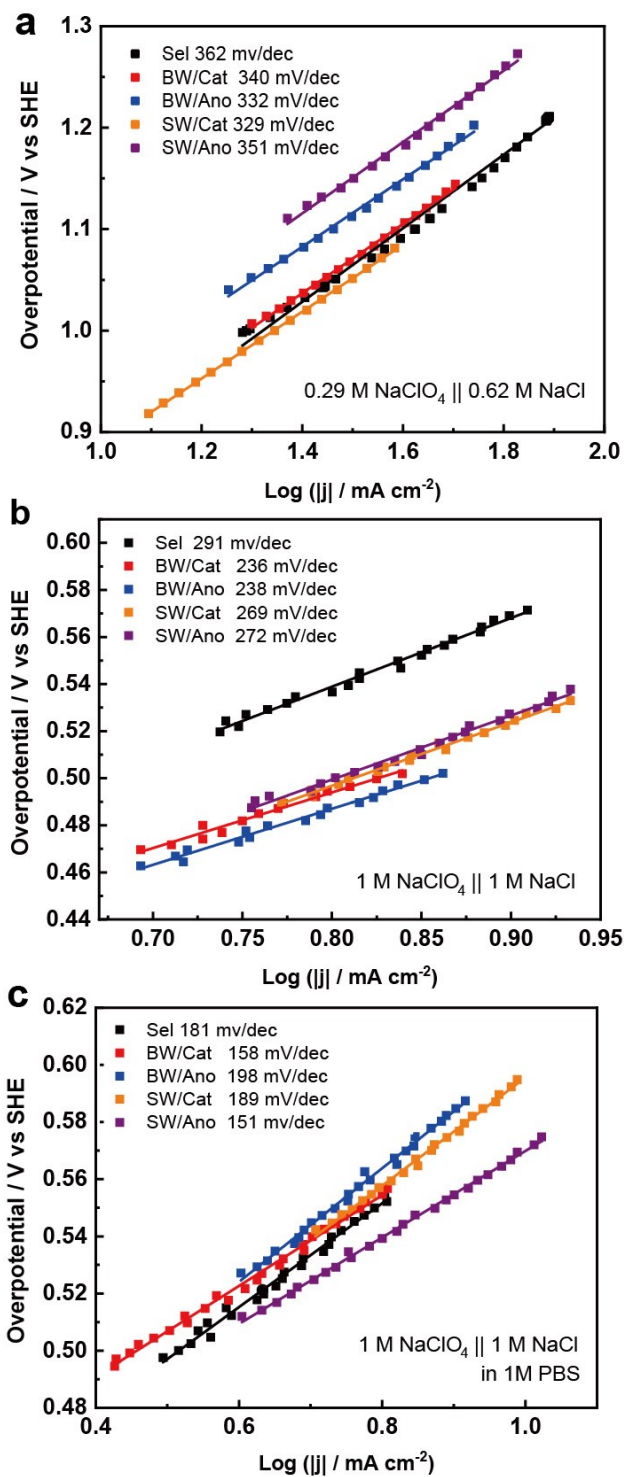
**Figure S2.** Raw data for membrane resistance measurements using the Selmion CEM, Nafion 117, BW, or SW, conducted in NaCl or NaClO<sub>4</sub> (0.62 M or 1 M on either side of the membrane as indicated). Each type of membrane was tested with two different pieces for one condition.



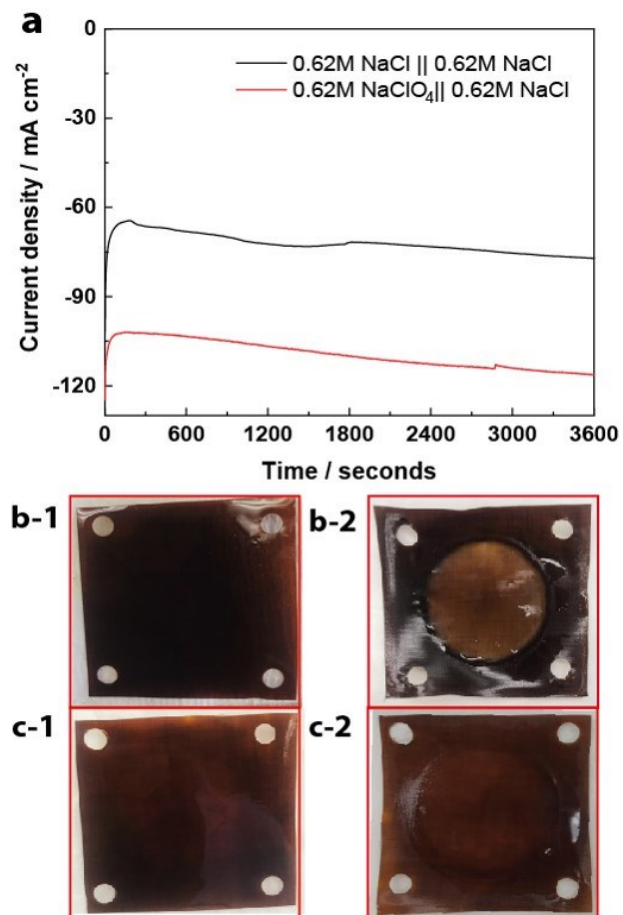
**Figure S3.** Open circuit voltage recorded for 30 seconds before linear sweep voltammetry ( $5 \text{ mV s}^{-1}$ , between  $0 \text{ V}$  and  $-1.4 \text{ V}$  vs. SHE) measurement for different membranes.

In order to control the LSV, open circuit potential (OCP) of each working electrode was monitored before each test (**Figure S3**). The similar OCPs in each test indicated that the over potential for each system could be directly obtained from LSV results without an OCP correction.

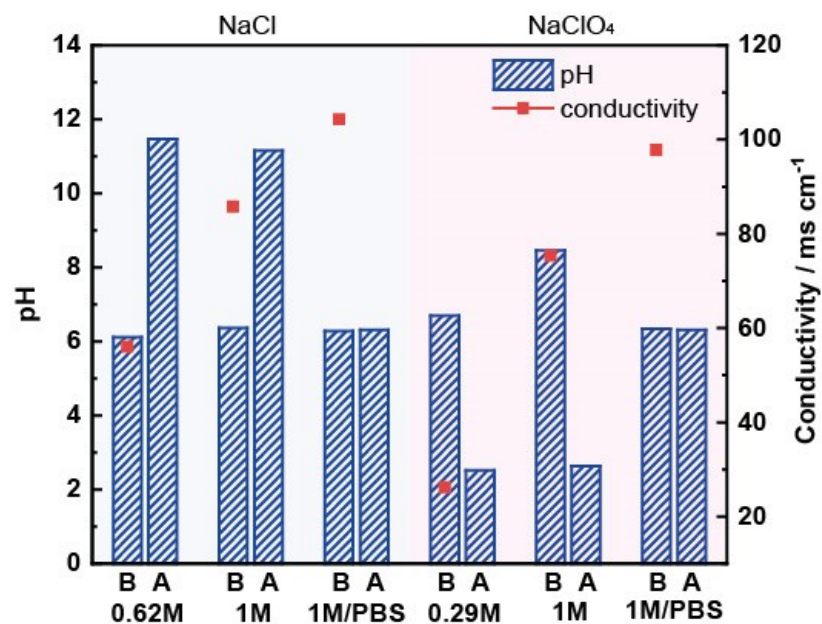




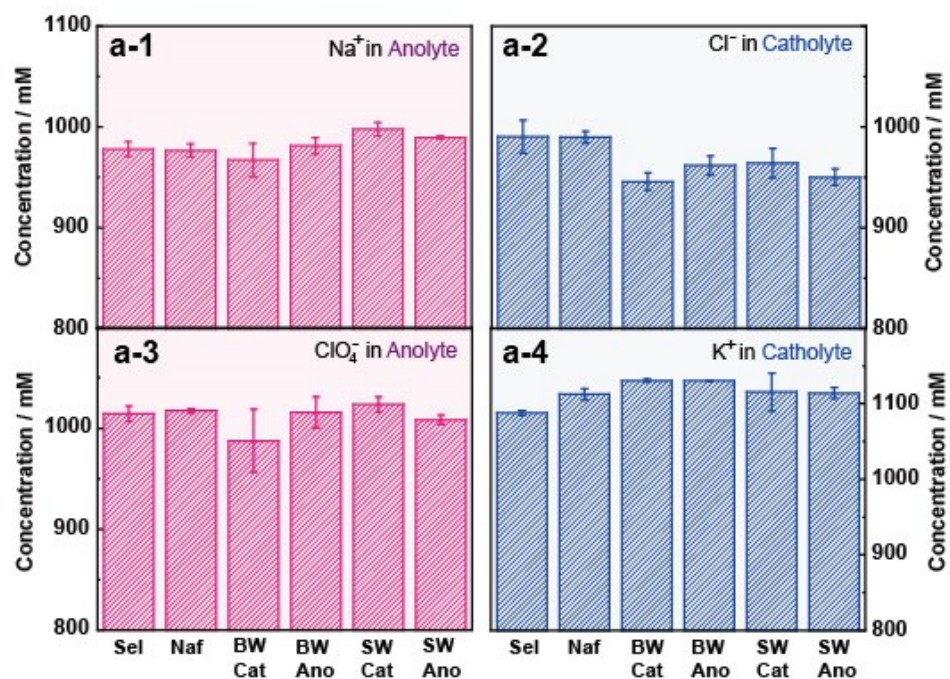
**Figure S4.** Corresponding Tafel plots with different membranes under different electrolyte conditions: (a) 0.29 M NaClO<sub>4</sub> anolyte and 0.62 M NaCl catholyte, (b) 1 M NaClO<sub>4</sub> anolyte and 1 M NaCl catholyte, and (c) 1 M NaClO<sub>4</sub> anolyte and 1 M NaCl catholyte in 1M PBS.



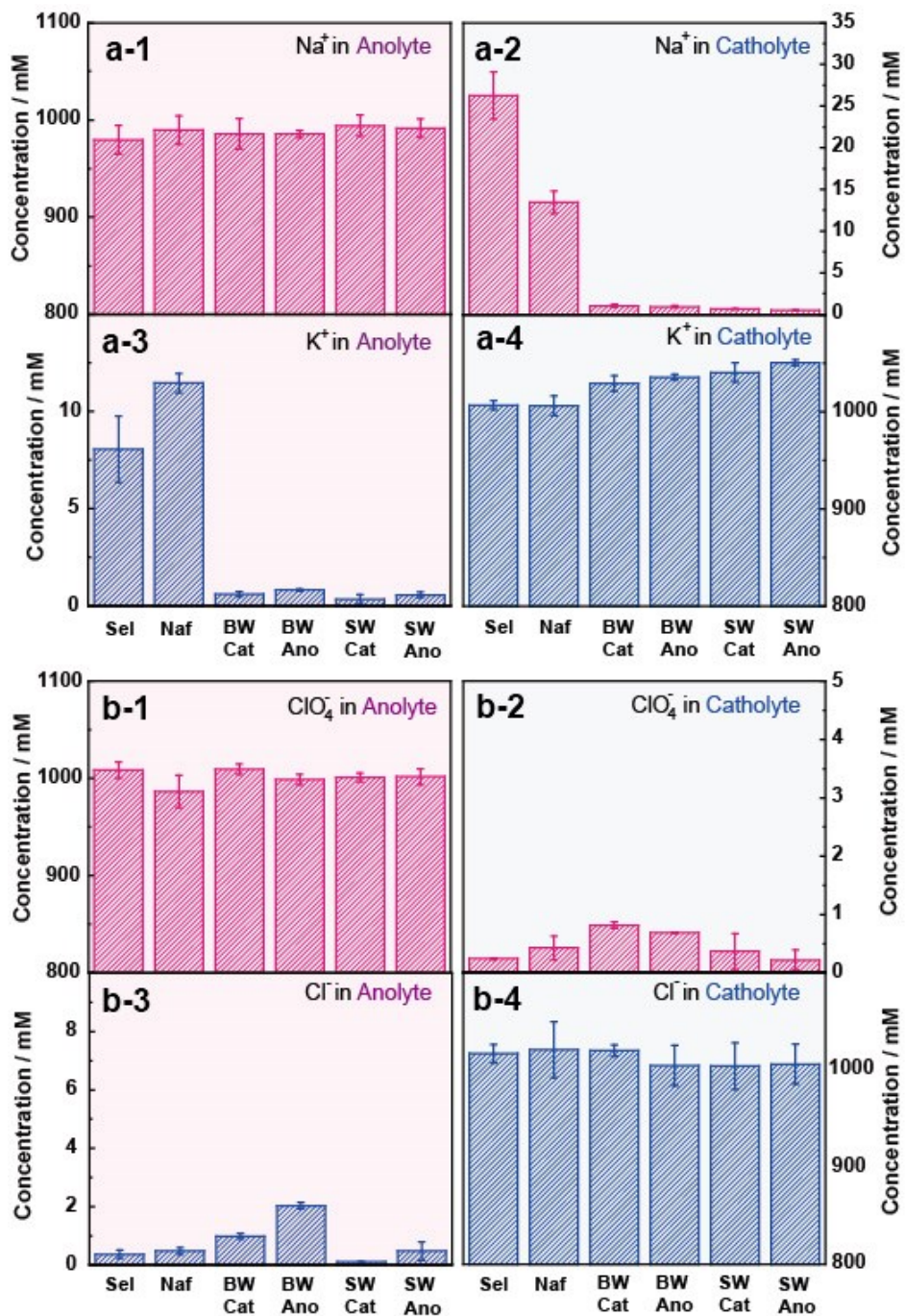
**Figure S5.** Chronoamperometry (CP) results by applying  $-1.2$  V vs SHE with Selemion CEM in 0.62 M NaCl (3.5%) as synthetic seawater for the catholyte, and 0.62 M NaCl (3.5%) or 0.62 M NaClO<sub>4</sub> for the anolyte. The differences in the CEM colors under these different conditions are shown before and after the 1 h CP tests.



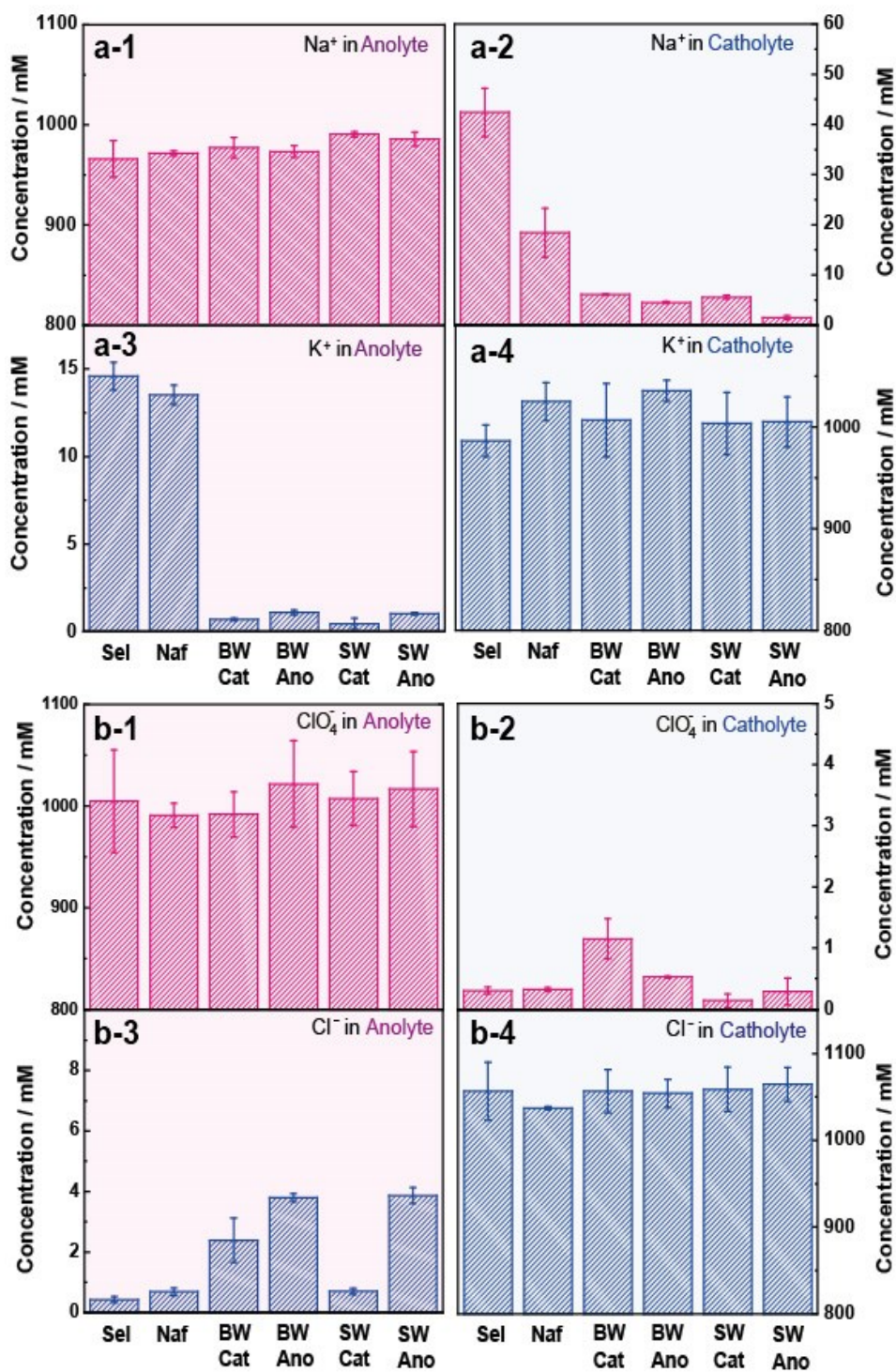
**Figure S6.** pH and conductivity summary of each solution before (B) and after (A) linear sweep voltammetry scans ( $5 \text{ mV s}^{-1}$ , between  $0 \text{ V}$  and  $-1.4 \text{ V}$  vs. SHE).



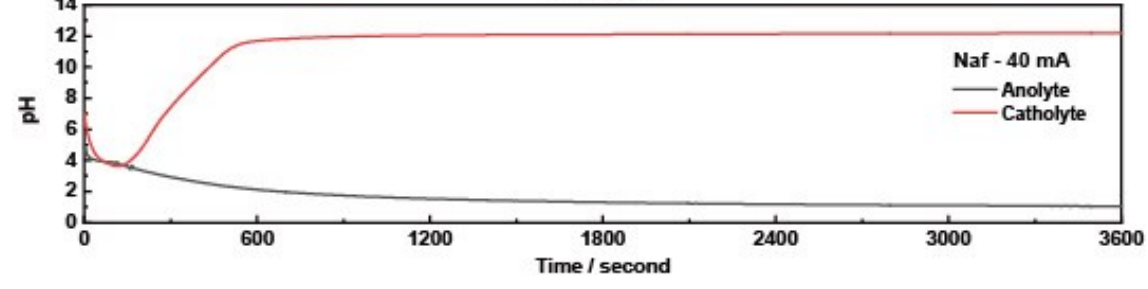
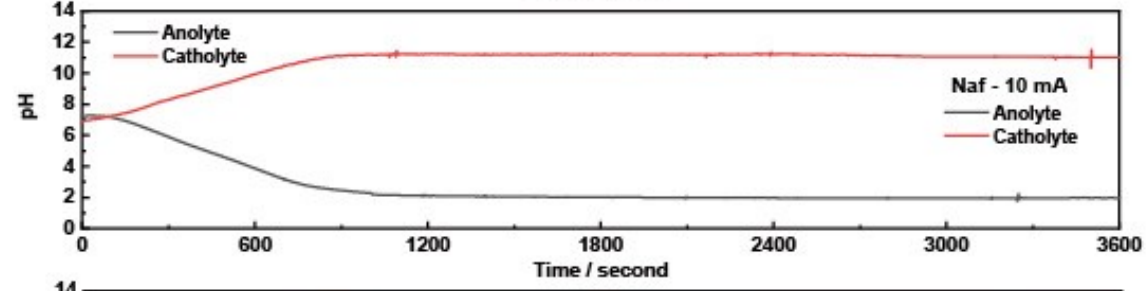
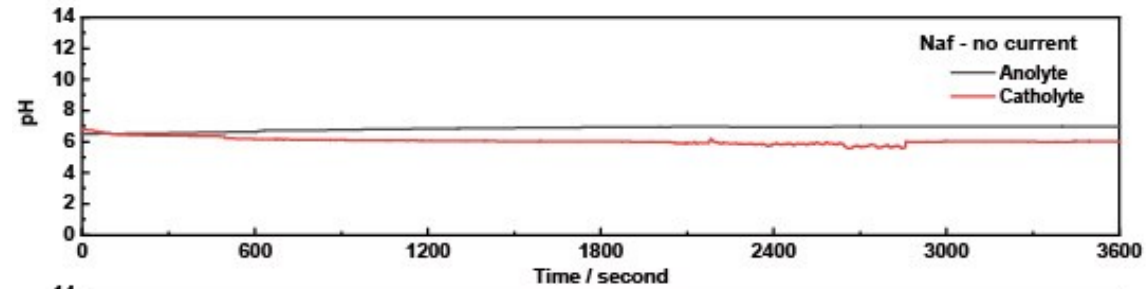
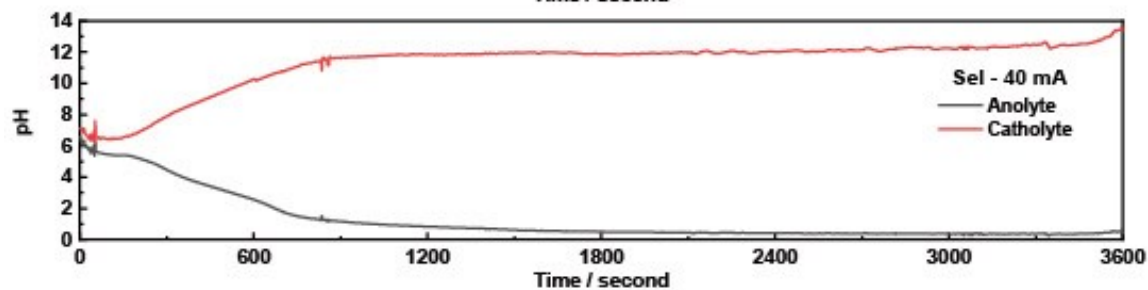
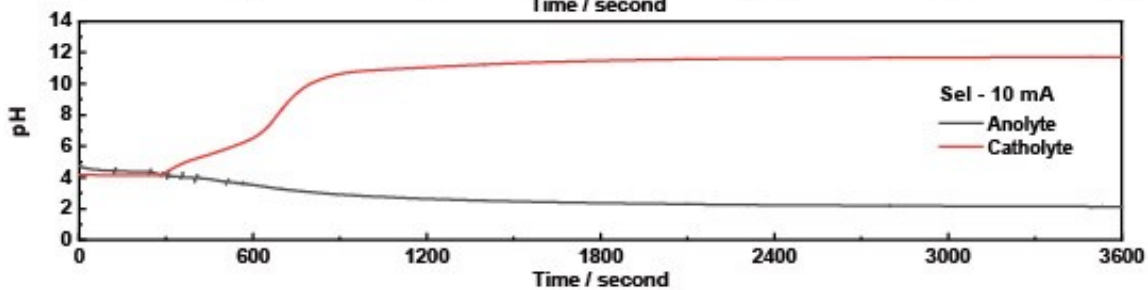
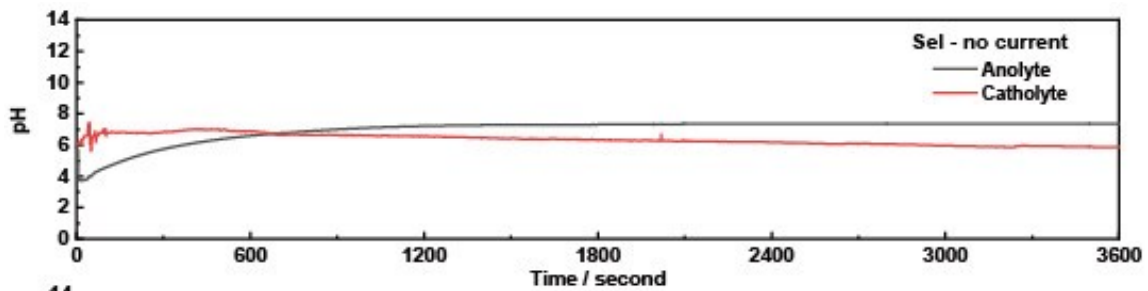
**Figure S7** Concentration of cations and anions in the indicated analytes or catholytes using different membranes with an applied current of  $40 \text{ mA cm}^{-2}$  after 1 hour, with  $1 \text{ M NaClO}_4$  as anolyte and  $1 \text{ M KCl}$  as catholyte.

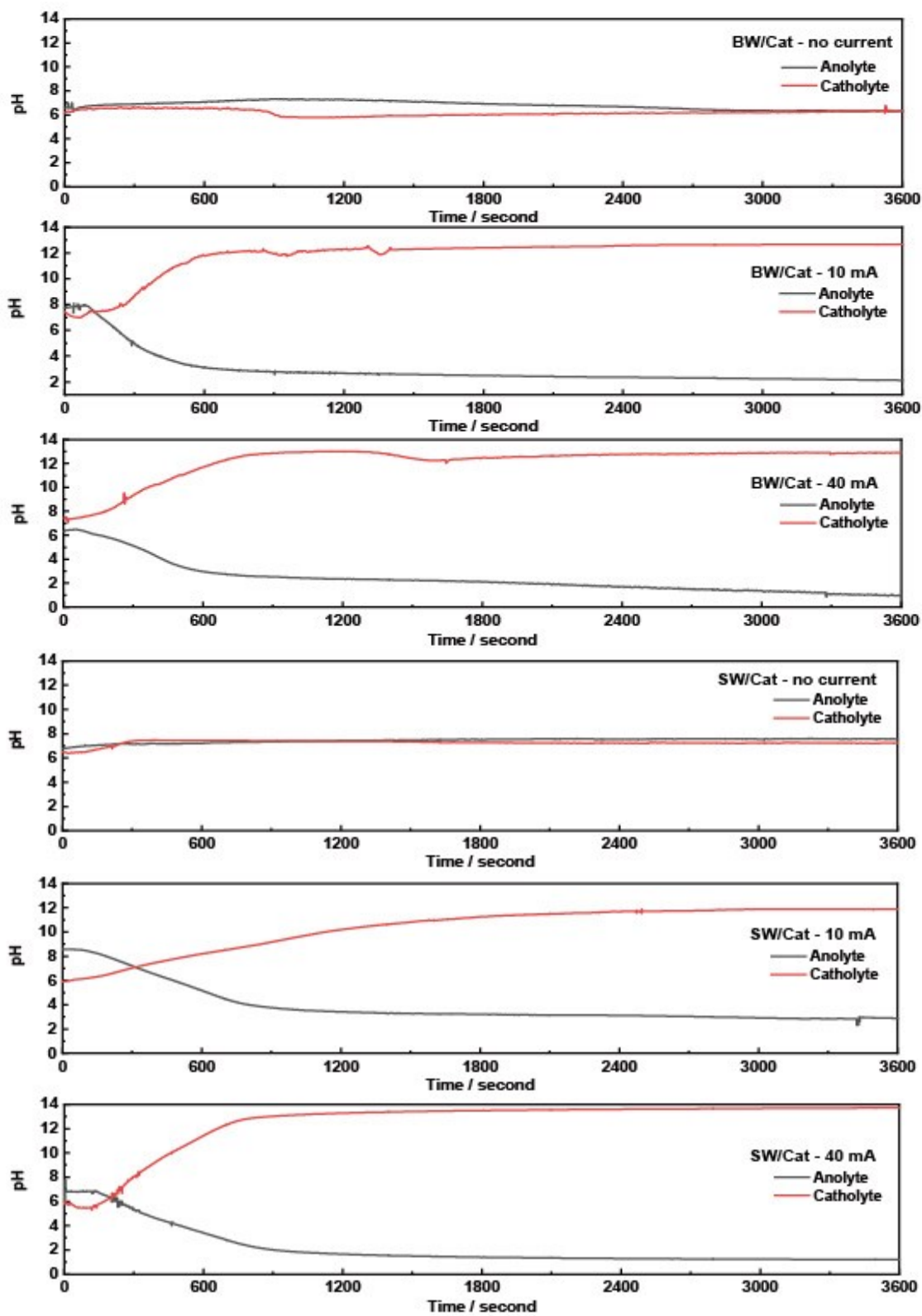


**Figure S8.** Concentration of cations and anions in the indicated anolytes or catholytes using different membranes without current after 1 hour (control), with 1 M NaClO<sub>4</sub> as anolyte and 1 M KCl as catholyte.



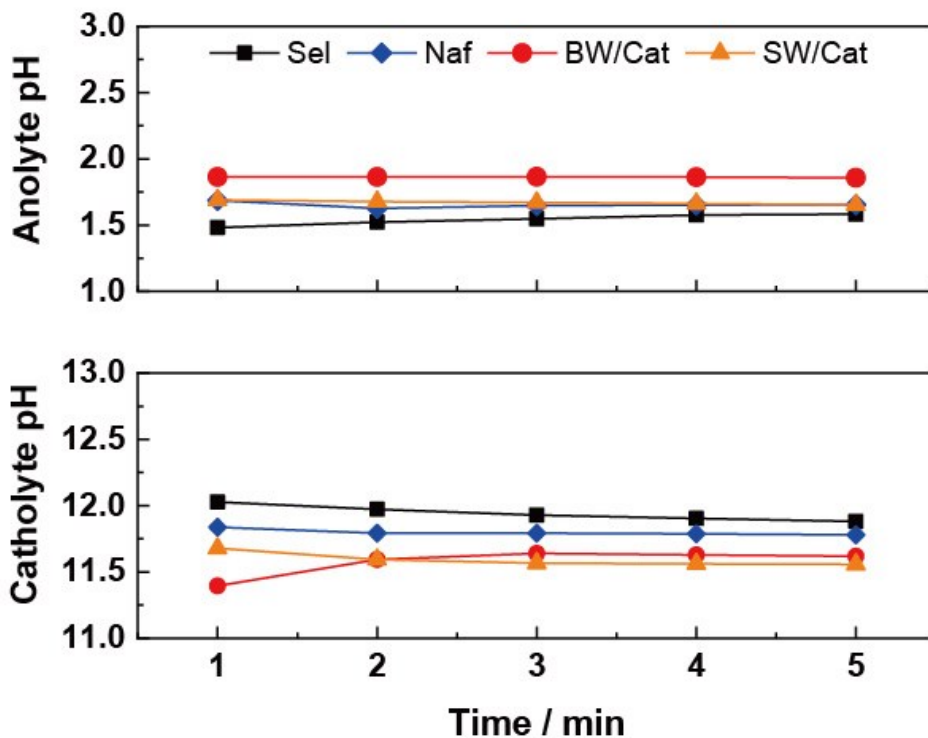
**Figure S9.** Concentration of cations and anions in the indicated anolytes or catholytes using different membranes with an applied current of  $10 \text{ mA cm}^{-2}$  after 1 hour, with  $1 \text{ M NaClO}_4$  as anolyte and  $1 \text{ M KCl}$  as catholyte.





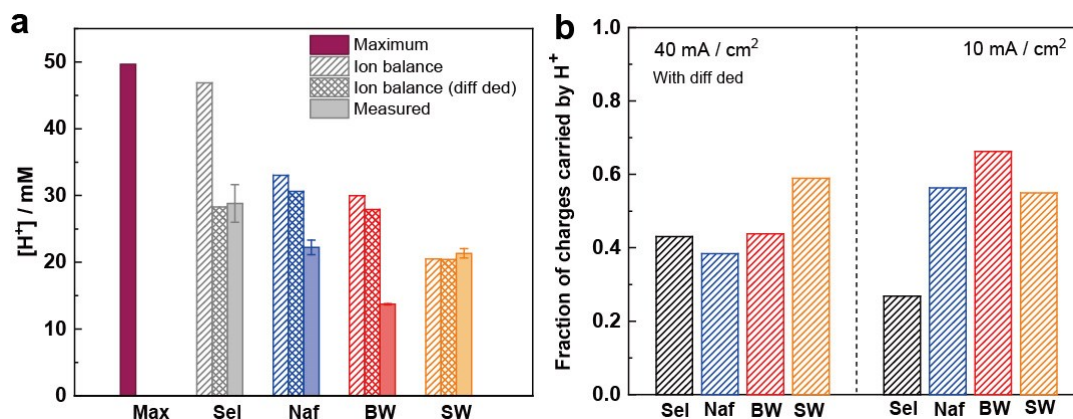
**Figure S10.** Inline pH vs time measurement results for each membrane with no applied current, 10 mA cm<sup>-2</sup> and 40 mA cm<sup>-2</sup> for 1 hour with 1 M NaClO<sub>4</sub> as anolyte and 1 M KCl as catholyte.

During salt crossover tests, the pH was monitored over time using inline pH meter for all the different membranes under each test condition (**Figure S10**). However, comparisons of the final pH were not in agreement with the inline measurements suggesting that accuracy of the inline pH measurements were slightly affected by the electrical field when the constant current was applied.<sup>1</sup> Thus, the results in Figure S10 show a general trend but not the absolute value of the pH. The final pH was measured by collecting the anolyte and catholyte solution to record for 5 min (**Figure S11**) to get an average pH, and this pH was used for ion balance comparison.

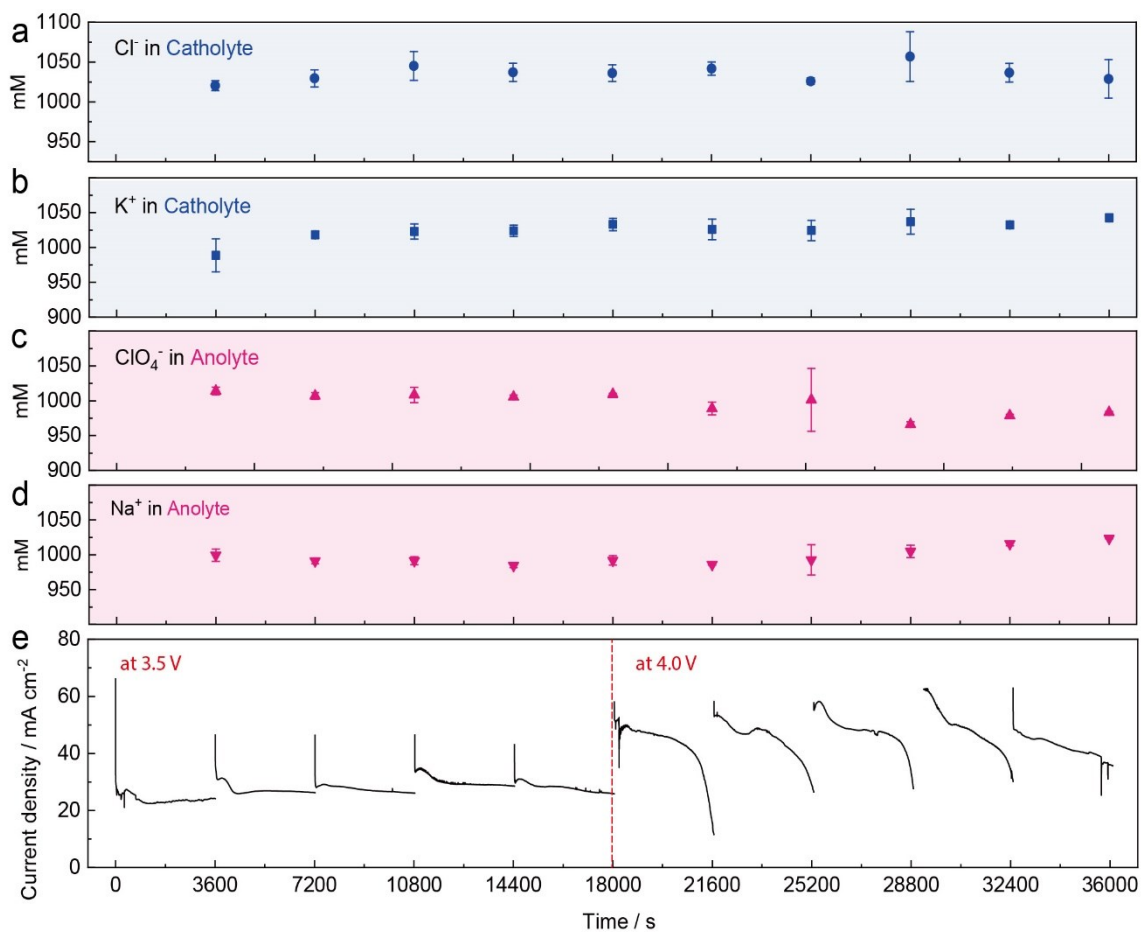


**Figure S11.** pH recorded for final anolyte and catholyte with different membranes after applied current density of  $40 \text{ mA cm}^{-2}$  for 1 hour, with 1 M  $\text{NaClO}_4$  as anolyte and 1 M  $\text{KCl}$  as catholyte. The electrolyte was mixed well after the inline measurement.





**Figure S12.** (a) Proton concentrations in the anolyte for different conditions, assuming a 100% Faradaic efficiency ( $40 \text{ mA cm}^{-2}$  for 1 h): maximum proton concentration calculated for no proton transport through membrane (Max); proton concentrations remaining based on measured ion transport of other salt species (without diffusion deduction; Ion balance) and assuming ion diffusion not due to passive ion diffusion [with diffusion deduction; Ion balance (diff ded)]; and proton concentrations converted from measured pH values at the end of the experiment (Measured). (b) The fraction of charge carried by protons transport through different membranes to sustain  $40 \text{ mA cm}^{-2}$  and  $10 \text{ mA cm}^{-2}$  for 1 h, with deduction of ions diffusion (1 M  $\text{NaClO}_4$  anolyte and 1 M KCl catholyte).



**Figure S13.** The concentration of cations and anions using BW membranes after applying constant potentials of 3.5 V for the first 5 cycles, and then 4.0 V for a total of 10 cycles, with 1 hour for each cycle: (a) Cl<sup>-</sup> concentration in catholyte, (b) K<sup>+</sup> in catholyte, (c) ClO<sub>4</sub><sup>-</sup> in anolyte, and (d) Na<sup>+</sup> in anolyte. Chronoamperometry (CP) results showing the current in the cells due to applying 3.5 V for the first 5 cycles and 4.0 V for the next 5 cycles.

**Table S1** Statistical analysis summary of salt crossover based on final concentrations after each 1-h cycle. The slopes,  $R^2$  and p values are based on the linear regressions shown in Figure 6 at different applied potential (3.5 V or 4.0 V).

<b>At 3.5 V</b>	<b>K<sup>+</sup> in Anolyte</b>	<b>Na<sup>+</sup> in Catholyte</b>	<b>Cl<sup>-</sup> in Anolyte</b>	<b>ClO<sub>4</sub><sup>-</sup> in Catholyte</b>
<b>Fitting Slope + SD</b>	$2.71 \times 10^{-6}$ $\pm 3.48 \times 10^{-6}$	$5.34 \times 10^{-4} \pm$ $1.32 \times 10^{-4}$	$1.22 \times 10^{-4}$ $\pm 1.64 \times 10^{-5}$	$1.57 \times 10^{-5}$ $\pm 6.84 \times 10^{-6}$
<b>R<sup>2</sup></b>	0.16833	0.84587	0.94874	0.63835
<b>P value</b>	0.49266	0.02698	0.005	0.10488
<b>At 4.0 V</b>	<b>K<sup>+</sup> in Anolyte</b>	<b>Na<sup>+</sup> in Catholyte</b>	<b>Cl<sup>-</sup> in Anolyte</b>	<b>ClO<sub>4</sub><sup>-</sup> in Catholyte</b>
<b>Fitting Slope + SD</b>	$1.43 \times 10^{-5}$ $\pm 2.26 \times 10^{-5}$	$7.06 \times 10^{-4} \pm$ $4.35 \times 10^{-5}$	$6.62 \times 10^{-5}$ $\pm 2.82 \times 10^{-5}$	$1.55 \times 10^{-5}$ $\pm 5.01 \times 10^{-6}$
<b>R<sup>2</sup></b>	0.11835	0.98875	0.64664	0.76232
<b>P value</b>	0.57046	$5.08 \times 10^{-5}$	0.10094	0.5322

## References

- 1 Veselinović, D. & Velikić, Z. The pH measurement with glass electrode in an electromagnetic field. *Journal of the Serbian Chemical Society*. **81**, 8, doi:10.2298/jsc160407082v (2016).