

Supporting information

This supporting information belongs to the paper *Ion transport mechanisms in bipolar membranes for (photo)electrochemical water splitting*. It contains experimental details, extra sample analysis, derivation of Sherwood numbers and results on using Ba(OH)₂.

Experimental details

Flow cell setup

A flow cell was designed and built from two PTFE blocks, both having a cavity of 25x25 mm² and 0.30 mm deep to insert an electrode. A similar flow cell was used in previous research¹. Pt foil electrodes (Alfa Aesar, 0.025 mm thick) were used, on a support of graphite foil (Coidan Graphite Products, 0.30 mm). A PMMA spacer of 1.5 mm thick was put on top of the sample, with a silicon sheet in between to seal the sample edges, and defining an active electrode area corresponding to a circle with 2 cm diameter (3.14 cm² area). Both the anode and cathode side were prepared in this way, separated with a BPM (FumaSep FBM). Reference electrodes (Ag/AgCl, QIS) were inserted in the PTFE housing blocks, connecting to the catholyte and anolyte. The current was supplied through the C/Pt electrodes, and the BPM voltage was measured as the difference between the reference electrode potentials. No correction for ohmic losses was applied.

Electrolyte compositions

Buffer solutions at approximately pH 0, pH 2, pH 4, pH 7, pH 10, pH 12 and pH 14 are created. The composition of each solutions is shown in Table S1, together with the actual pH directly after preparing the solutions. Chemicals are obtained from Sigma Aldrich, with at least 98% purity. The salt concentration for all electrolytes is 1 M, except for pH 10, which has a 0.5 M borate/boric acid concentration. All alkaline solutions are stored with N₂ gas in the headspace and reservoirs were kept close during operation to minimize CO₂ capture in the solutions. The flow rate of the electrolytes in all cases is 0.63 cm/s (Re = 12.5).

Table 1: Electrolyte composition

Approximate pH	Composition	Measured pH
0	1 M H ₂ SO ₄	0.02
2	1 M KP _i (0.49 M H ₃ PO ₄ + 0.51 M KH ₂ PO ₄)	1.80
4	1 M Acetic acid + brought to pH 4 with KOH	4.00
7	1 M KP _i (0.55 M KH ₂ PO ₄ , 0.45 M K ₂ HPO ₄)	6.92
10	0.5 M HBO ₃ , + brought to pH 10 with KOH	10.00
12	1 M K ₂ HPO ₄ + 0.24 M KOH	11.91
14	1 M KOH	13.66

Electrochemical measurements

Two types of electrochemical measurements have been performed: 1) i-v curves with galvanodynamic scans, and 2) chronopotentiometry. A Princeton Applied Research (PARstat MC) was used to measure the membrane voltage and cell voltage simultaneously. The galvanodynamic scans are performed at least two times, in both directions. The data shown is obtained from the last scan,

going from high current density (20 mA/cm²) to low current density (-0.5 mA/cm²) to make sure that the BPM voltage is not underestimated, at a scan rate of 0.03 mA/cm²/s.

Ion sample measurements

To measure the ion cross-over, samples are taken after 16 hours of operation at 10 mA/cm². A volume of 12 mL is used at either side. The 16 hours of current operation corresponds to a charge transport of 1.25 meq/mL. Samples are analyzed with inductively coupled plasma mass spectrometry (ICP-MS) for the element K, Na, Li, P and S. The chloride concentration is derived from samples analyzed with ion chromatography (IC).

Samples analysis

Samples have been taken after 16 hours of operation to monitor ion cross-over. To analyze the effect of pH, we can compare the ion cross-over in case of pH 0-14 and pH 0-7. The ion cross-over of K⁺ and SO₄²⁻ is in both cases similar (within error margin), as demonstrated in Fig. S2. The cross-over of phosphate is insignificantly small, as expected.

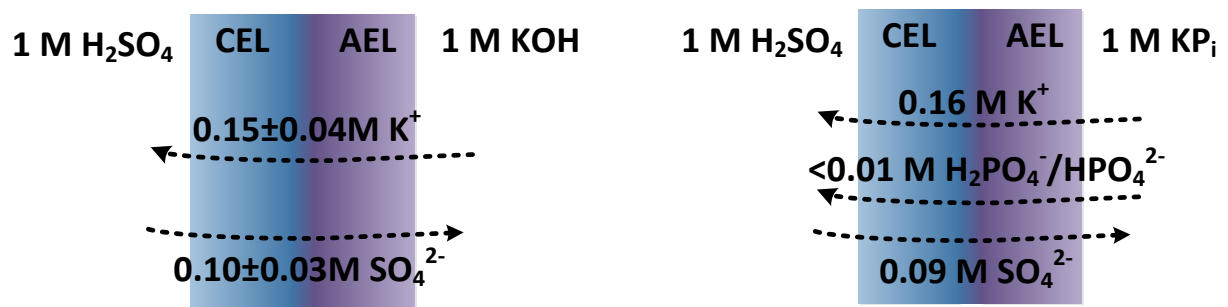


Fig. S1: ion cross-over after 16 hours of operation at 10 mA/cm², in which 1.25 meq/mL of charge is transported. For example, 0.15 M ion cross-over contributes 0.15/1.25 = 12% of the current density.

Sherwood numbers

The Sherwood number is defined as $Sh = \frac{k \cdot d_h}{D}$, being k the mass transport coefficient (m/s), d_h the hydraulic diameter (m) and D the diffusion coefficient (m²/s), and provides an indication for the total mass transport normalized to the diffusion flux. The mass transport ($k \cdot d_h$), and thus the Sherwood number, is directly proportional to the electrical current. For typical electrochemical cells, the flow velocity profile is fully developed after a short entrance length, but the concentrations profiles are not because the Schmidt number for salt solutions is in the order of 500. For these conditions, Sh is related to the Reynolds number (Re)^{2, 3}. For open channels (i.e., without a spacer netting), the Sherwood number is given by:

$$Sh = \text{for } Re < 1000 \text{ (Graetz equation)}$$

$$Sh = \frac{k \cdot d_h}{D} \text{ for } Re > 2000 \text{ (Colburn equation)}$$

Use of Ba(OH)₂

As an attempt to reduce ion cross-over, the use of multivalent ions is investigated. For hydroxide solutions, the options are very limited, because most multivalent cations (Ca²⁺, Mg²⁺) are weakly dissolvable in hydroxide form. The best soluble multivalent hydroxide salt is Ba(OH)₂, which has (at 20°C) a solubility of approximately 0.25 M. We have tested the use of 0.15 M Ba(OH)₂ as anolyte, in combination with 1 M HCl, 1 M HClO₄ and 1 M H₂SO₄.

The voltage over a complete cell (CoP cathode – BPM – NiFe anode) is significantly higher when using Ba(OH)₂ instead of KOH or NaOH, and the voltage is in all attempts unsteady. After autopsy of the membrane, a white color is visible on the membrane. Scanning electron microscope (SEM) and Energy dispersive X-ray (EDX) analysis reveal that BaSO₄ has precipitated in the membrane, which indicates that at least some of the Ba²⁺ can penetrate AEL of the BPM and SO₄²⁻ the AEL. BaSO₄ is known for a very low solubility. Another complication is precipitation of BaCO₃ when solutions are exposed to CO₂ in the air. In conclusion, multivalent hydroxides are not practical for use in (BPM) electrolysis.

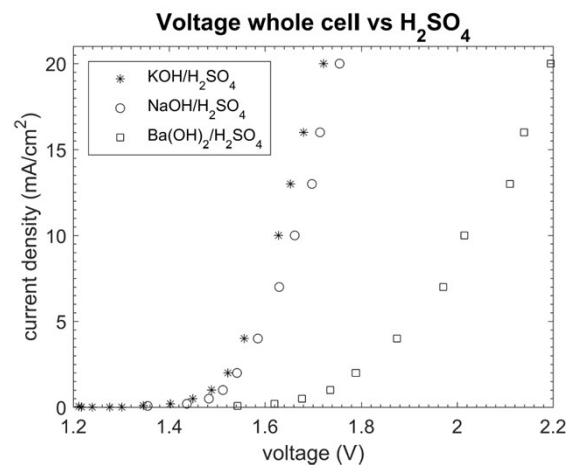


Fig. S2: *i-v* curves for Pt-BPM-Pt cell, in which the catholyte is always 1 M H₂SO₄, and the anolyte was varied between KOH, NaOH and Ba(OH)₂.

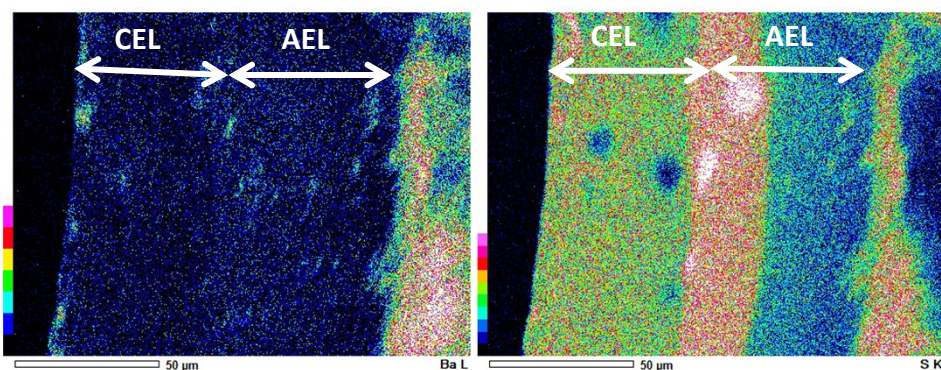


Fig. S3: EDX analysis of cross-section of BPM, for the elements Ba (left image) and S (right image). The CEL is at the left side of each picture, the AEL at the right side.

References

1. D. A. Vermaas and W. A. Smith, *ACS Energy Letters*, 2016, **1**, 1143-1148.
2. S. Pawlowski, P. Sizat, J. G. Crespo and S. Velizarov, *Journal of Membrane Science*, 2014, **471**, 72-83.
3. A. A. Sonin and M. S. Isaacson, *Industrial & Engineering Chemistry Process Design and Development*, 1974, **13**, 241-248.