Supporting information

Title: Electrochemical impedance spectroscopy as a performance indicator for water dissociation in bipolar membranes

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Materials

The H-cell used in the experiments was designed by Ben in ‘t Veen and produced by Shell. The Pt wires used as work and counter electrode were produced by Heraeus with a diameter of 300 µm, with a Pt electrode sputtered on a Ti substrate and a Ni electrode of analytical grade. The flow cell, MicroFlowCell, was purchased from Electrocell (Denmark). The micro reference electrodes of type LF-1-100 are manufactured by Innovative Instruments Inc. and have a polyetheretherketone (PEEK) body with a diameter of 1 mm. The commercial BPM, Fumasep FBM-PK, used in this study was produced by Fumatech GmbH (Germany). H_2SO_4 (95-97% purity), KOH (45 wt% in H_2O) and $KHCO_3$ (99.7% purity) were purchased from Sigma Aldrich. NaOH (Baker analyzed, J.T. Baker) was purchased from Boom.

Electrochemical impedance spectroscopy

By performing the impedance measurements in galvanostatic mode, i.e. applying a fixed direct current (DC), a positive potential difference across the BPM is measured. Upon the application of this current, an alternating current is applied around this direct current. This secondary current has the form of a sinusoidal wave ($I = I_0 sin(\omega t)$) with the applied current shown as the amplitude, I_0, of the wave and the angular frequency, $\omega = 2\pi f$, which depends on the applied frequency, f. The impedance is then determined by the ratio of the measured voltage versus the applied current. Hereby, it is important to minimize the ratio of noise versus data by increasing the amplitude I_0 without exceeding the local linear region, which is important to avoid distortion of the impedance data. This region can be assessed by performing galvanodynamic scans as shown in Figure 1. At lower current densities, the amplitude is rather small to avoid ending up in the plateau region, resulting in a higher noise vs data ratio, explaining the scattering in for example in Figure 6. Data obtained from impedance measurements are often shown in a Nyquist plot, where the negative imaginary impedance is plotted as a function of the real impedance on the x-axis and in a Bode plot (examples shown in Figure 5), where the phase shift is plotted as a function of the applied frequency. An increase on the negative axis of the phase shift indicates a capacitive effect and is shown as a semi-circle on a Nyquist plot.

Negative currents in no co-ions$_{mem}$ case (H_2SO_4-KOH)

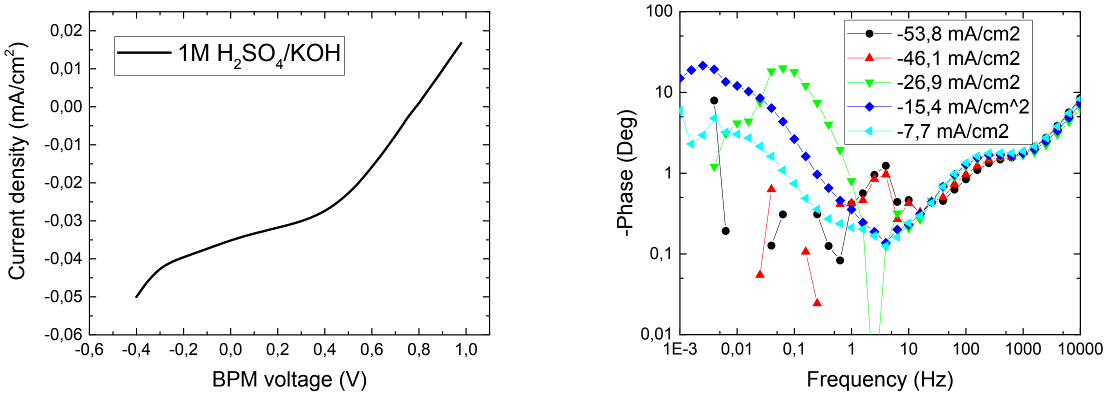

Figure SI1: (a) i-V curve of H_2SO_4-KOH in H-cell, and (b) impedance plots at negative currents of a BPM in H_2SO_4-KOH, lower current densities suffered from noise in the lower frequency region (<1 Hz).

Co-ion crossover

Table SI1: Co-ion crossover data, with values obtained after ageing measurements (5 day experiments).

		S [g/l]	K [g/l]	Na [g/l]		S [g/l]	K [g/l]	Na [g/l]
0 mA/cm²	1M KHCO3	<0.1	40.2	4.39	1 M NaOH	<0.1	3.9	18.48
50 mA/cm²	1M KHCO3	<0.1	50.8	10	1M NaOH	<0.1	0.2	19
		S [g/l]	**K [g/l]**	**Na [g/l]**		**S [g/l]**	**K [g/l]**	**Na [g/l]**
0 mA/cm²	1M H2SO4	35	4.9	<0.1	1.3M KOH	0.5	50	0.34
50 mA/cm²	1M H2SO4	39	11	<0.1	1.3M KOH	0.7	55	0.35
100 mA/cm²	1M H2SO4	46	18	0.13	1.3M KOH	0.9	62	0.42

Table SI2: Co-ion crossover of $KHCO_3$ and NaOH at currents below plateau current density (1 mA/cm²) applied for 45 min.

		S [g/l]	K [g/l]	Na [g/l]		S [g/l]	K [g/l]	Na [g/l]
1 mA/cm²	1M KHCO3	<0.1	41.8	0.71	1M NaOH	<0.1	0.4	21.52
REF	1M KHCO3	<0.1	37.1	0.12	1M NaOH	<0.1	<0.1	21.96

If one wants to know the relative crossover through the bipolar membrane (BPM), the crossover value, expressed in mol per liter, should be divided by the total amount of protons consumed. The total amount of protons can be calculated by dividing the total charge by the Faraday constant ($F = 96485\ C/mol$). For example, for 50 mA/cm² in 5 days in the flow cell, the total consumption of protons is 2.23 mol protons. Using a 100 ml reservoir, the concentration is 22.3 M H^+. If the exchange of K^+ in those 5 days is 11 g/l, with an atomic mass of 39.09 g/mol, the concentration in the catholyte is 0.46 mol/l, which is 10% crossover of the exchanged current. If a similar calculation is performed for SO_4^{2-}, the reported value of 13% is found.

Flow cell setup

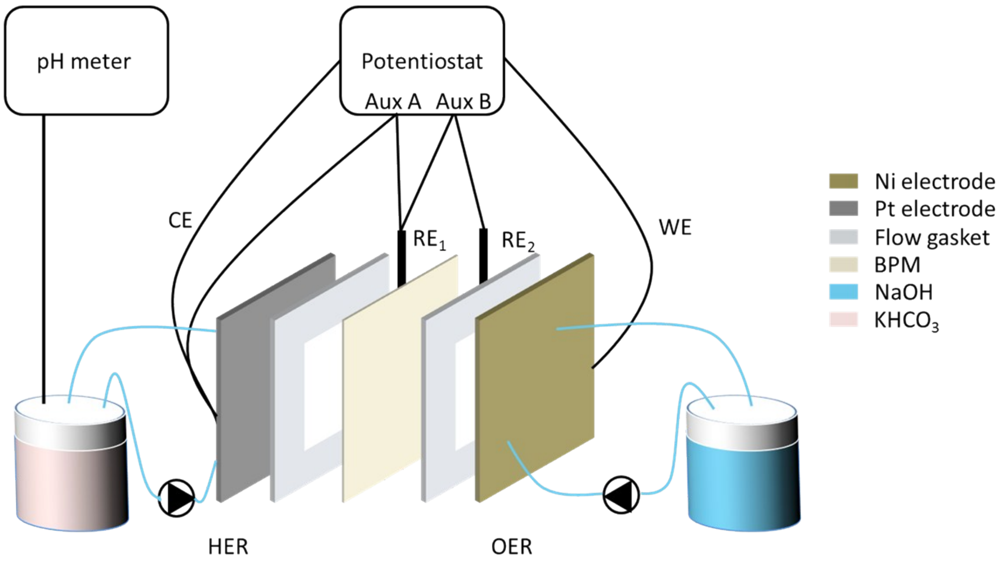

Figure SI2: Flow cell schematic for studying the aging of BPMs for a longer duration.

i-V curve of H2SO4-KOH at 1M and 0.1M

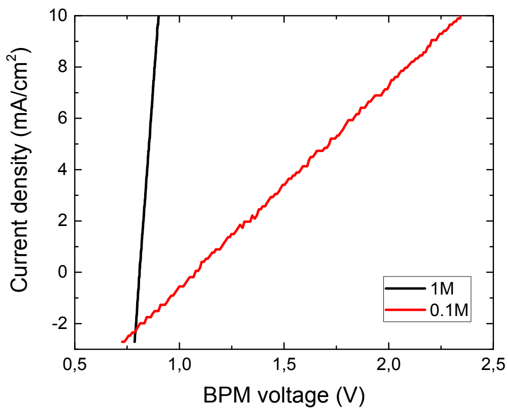

Figure SI3: i-V curves of 1M and 0.1M of H_2SO_4 vs. KOH.

Table SI3: Impedance data to observe concentration effect of the two investigated cases. All measurements are performed at 7.7 mA/cm².

Electrolyte	$-\theta_{WDR}$ Deg	f_{WDR} Hz	R_{WDR} Ω cm²	Q_{DL} mF cm²	n_{WDR} -
1M H_2SO_4-KOH	2.69	100.0	1.08	7.15	0.85
0.1M H_2SO_4-KOH	0.23	184.8	1.30	3.90	0.82
1M $KHCO_3$-KOH	0.64	108.0	1.69	6.50	0.60
0.1M $KHCO_3$-KOH	-	-	-	-	-

Fitting curve

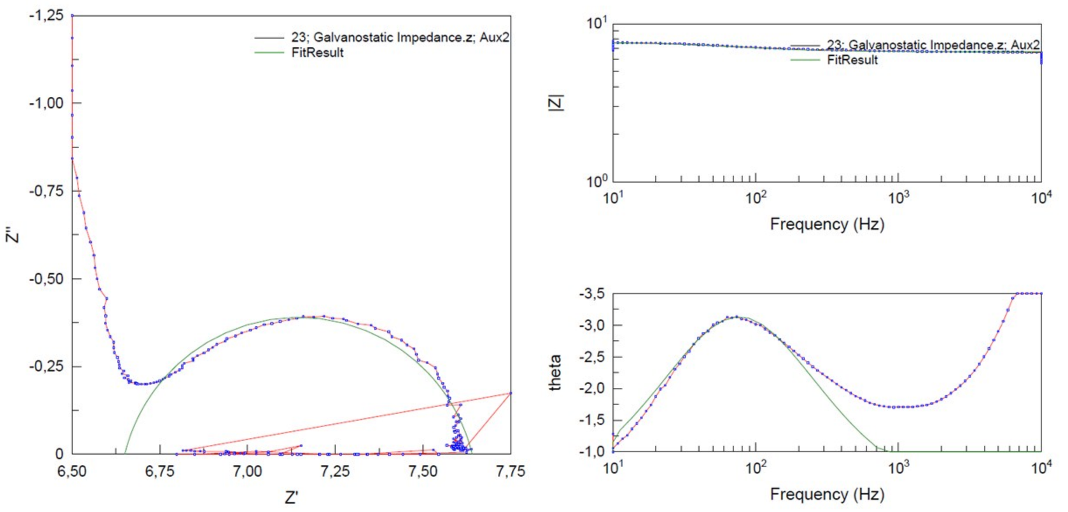

Figure SI4: Example of fitting curve of impedance measurement (1M H_2SO_4 vs. KOH at 38.5 mA/cm^2), which resulted in R_{WDR}=1.29 Ohm cm^2, Q_{DL}=7.41 mF cm^2 and n=0.85. Values of Nyquist plot (a) should be multiplied by membrane surface area (1.3 cm^2).

The fitting occurs according the equivalent circuit (see Figure 2 of the manuscript), where *n* is a fitting parameter, to compensate for non-idealities. The n-value can vary slightly (+-0.1) in order to optimize the R and Q values.

Additional example of co-ions case

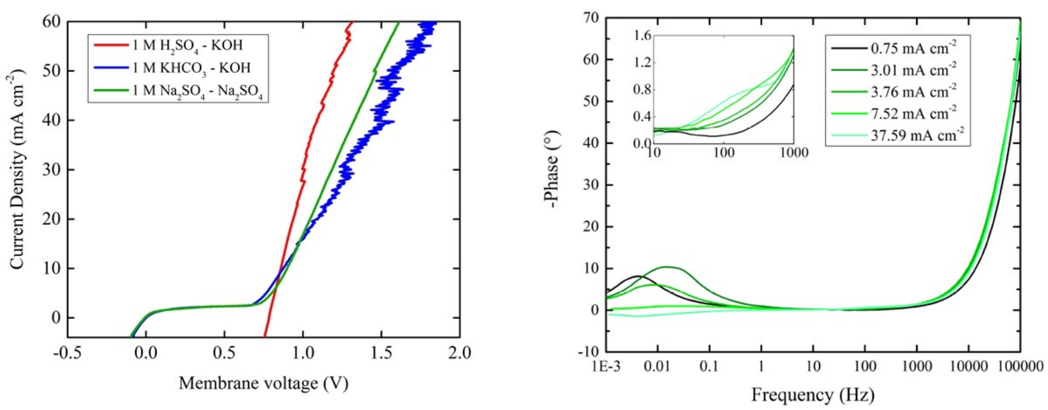

Figure SI5: i-V curve of 1M Na_2SO_4 vs. Na_2SO_4 compared to previous tested electrolytes and bode plot of 1M Na_2SO_4 vs. Na_2SO_4 under various current densities, showing similar behavior as the case of co-ions (1M $KHCO_3$ vs. KOH).