

Cation-driven increases of CO₂ utilization in a bipolar membrane electrode assembly for CO₂ electrolysis

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Experimental section

All experiments were performed in a 5 cm² CO₂ MEA electrolyzer (Dioxide Materials). Ag GDE was used as cathode with an active surface area of 6.25 cm² (2.5 cm x 2.5 cm). The Ag GDEs were made by magnetron sputtering (AJA International Inc.) 100 nm Ag on Sigracet[®] 39BC gas diffusion layer (Ion Power GmbH) with 50 W DC power supply. Nickel foam (3 cm * 3 cm, Recemat BV) was used as anode. Between cathode and anode, a 4 cm x 4 cm bipolar membrane (Fumasep[®] FBM) or Sustainion[®] anion exchange membrane (X37-50 Grade RT, Dioxide Materials) was inserted to conduct ions. The cell was assembled and compressed using a torque wrench which was tightened to 4 Nm. Concentration of 0.2 M, 1 M and 3 M KOH (Sigma-Aldrich, 99.99%) solutions were used as anolyte. Humidified CO₂ was fed into the cell with 50 sccm flowrate through a mass controller (Bronkhorst High-Tech BV). The outlet flowrate was measured by a MFM (mass flow meter, Bronkhorst High-Tech BV). KOH anolyte was sent to the cell with a 20 mL/min flowrate via a peristaltic pump (MasterFlex[®]).

Chronopotentiometry at current density of 50, 100, 150, and 200 mA/cm² was applied using a potentiostat (PARSTAT). In BPM experiments, each current density was held for 20 minutes. While during AEM experiments, the time was shortened to 15 minutes due to serious salt formation problem, which could cause the cell to fail quickly. Gas products were analyzed by an online gas chromatography (compact GC 4.0, GAS). Injections were taken every 5 minutes and gas concentration already stabilized during the 2nd injection. Faradic efficiency was calculated based the average product concentration of 4 injections (BPM) or 3 injections (AEM). Anolyte samples were collected and analyzed by high-performance liquid chromatography (HPLC, Agilent Technologies).

In determining the CO₂ utilization efficiency towards CO, only two values must be determined. The amount of CO₂ converted to CO, and the total amount of the pure inputted CO₂ which is consumed on the cathode part. In our system the CO₂ conversion to CO was calculated using the outlet flow rate as measured by a mass flow metre and data from the GC which provided the CO concentration in the outlet stream:

$$\dot{V}_{(\text{CO}_2 \text{ to CO})} = C_{\text{CO}} \times \dot{V}_{(\text{outlet})} \text{ (mL/min)}$$

where C_{CO} denotes CO concentration measured by GC. $\dot{V}_{(\text{outlet})}$ was measured by MFM. Note that one mole of CO₂ gas can be converted to one mole of CO gas, meaning the CO₂ consumption rate to produce CO is the same to the CO production rate. Therefore, we could estimate the CO₂ loss by using the equation:

$$\dot{V}_{(\text{CO}_2 \text{ lost})} = \dot{V}_{(\text{inlet})} - (\dot{V}_{(\text{outlet})} - \dot{V}_{(\text{H}_2)}), \text{ where } \dot{V}_{(\text{H}_2)} = C_{\text{H}_2} \times \dot{V}_{(\text{outlet})} \text{ (mL/min)}.$$

$\dot{V}_{(\text{inlet})}$ was measured by MFC. Here we considered the impact of $\dot{V}_{(\text{H}_2)}$ when calculating the CO₂ consumption rates because in the BPMEA cell case there is a large amount of H₂ gas in the outlet stream. In the AEMEA case, in contrast, H₂ volumetric flow rate was not considered due to its negligible H₂ production.

The CO₂ loss should arise from : 1) the formation of (bi)carbonate then crossover to anode and release as CO₂; 2) salt precipitation, and 3) formate product cross-over to the anode. We counted CO₂ to HCOO⁻ as loss since the liquid product in the MEA cells cannot be easily collected. All the CO₂ consumed in the cell is:

$$\dot{V}_{(\text{CO}_2 \text{ consumed})} = \dot{V}_{(\text{CO}_2 \text{ to CO})} + \dot{V}_{(\text{CO}_2 \text{ lost})}$$

Equations discussed:

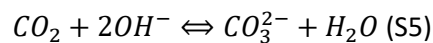
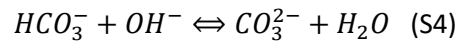
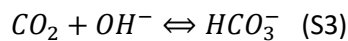
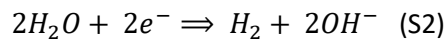
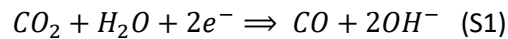


Table S1 pH of analyte before and after CO₂ reduction in both BPMEA and AEMEA cells

pH	BPM		AEM	
	before	after	before	after
0.2 M KOH	13.5	13.48	13.5	7.46
1 M KOH	14	14.08	14	13.55
3 M KOH	14.6	14.6	14.6	14.5
0.2 M KOH + 0.4 M K ₂ CO ₃	13.54	13.52	-	-

Table S2 Cell resistance of BPMEA and AEMEA cells in different solutions

Cell resistance (ohms)	BPM	AEM
0.2 M KOH	0.6	0.17
1 M KOH	0.75	0.18
3 M KOH	1.1	0.13
0.2 M KOH + 0.4 M K ₂ CO ₃	1	-

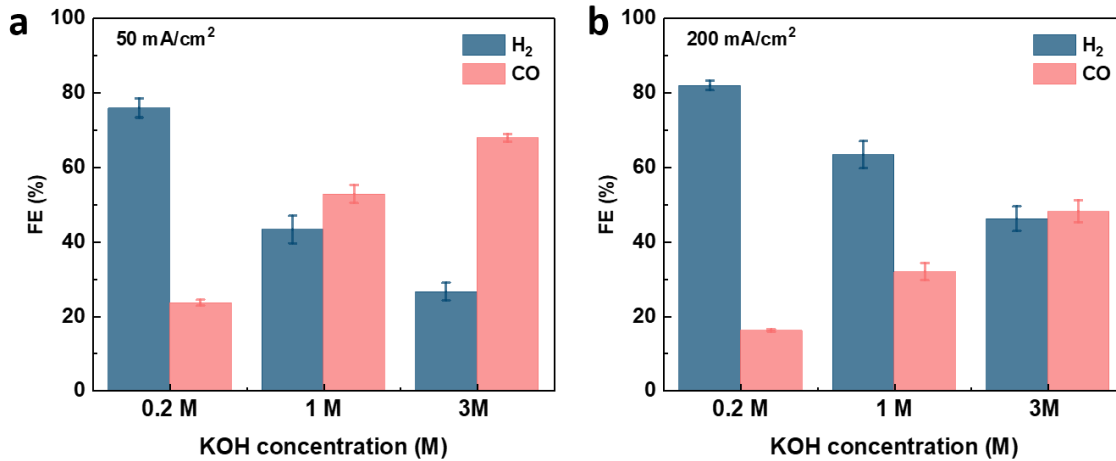


Figure S1 Faradaic efficiency of H₂ and CO as function of KOH analyte concentrations at 50 and 200 mA/cm² in BPMEA cell.

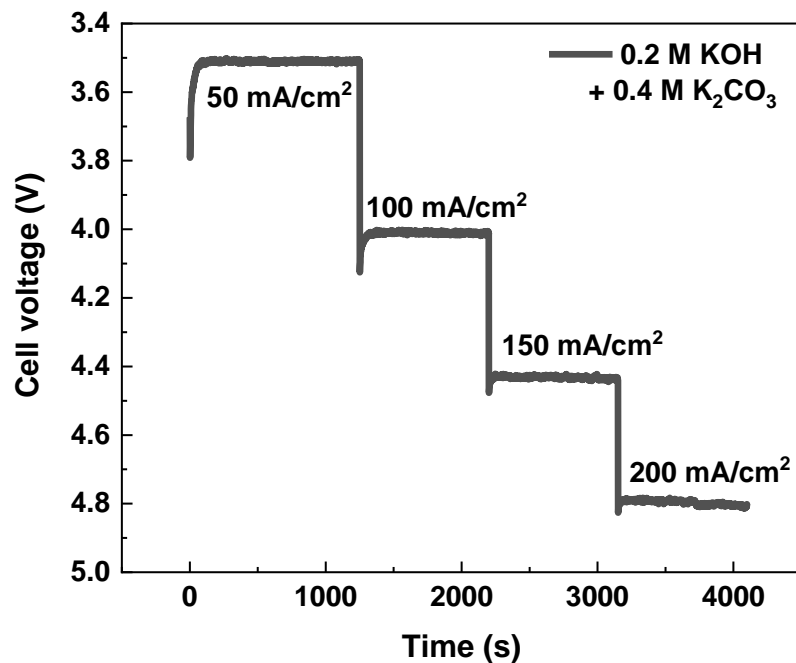


Figure S2 Cell voltage at different current densities in a BPMEA cell in 0.2 M KOH + 0.4 M K₂CO₃ electrolytes.

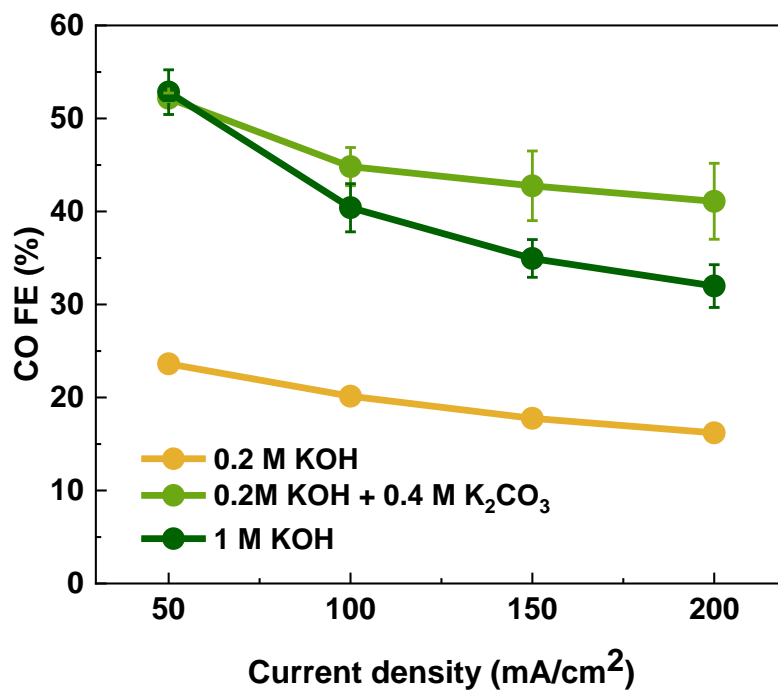


Figure S3 CO Faradaic efficiency in different concentrations of electrolyte.

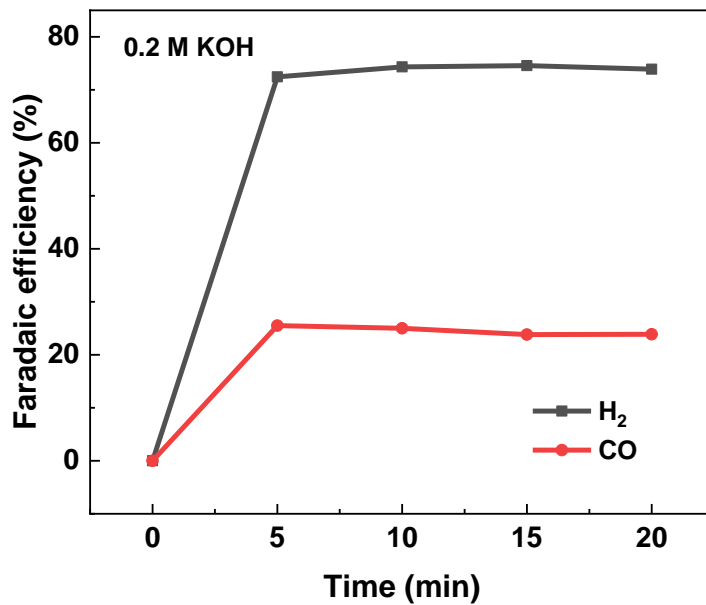


Figure S4 Faradaic efficiency as function of time in a BPMEA cell using 0.2 M KOH analyte.

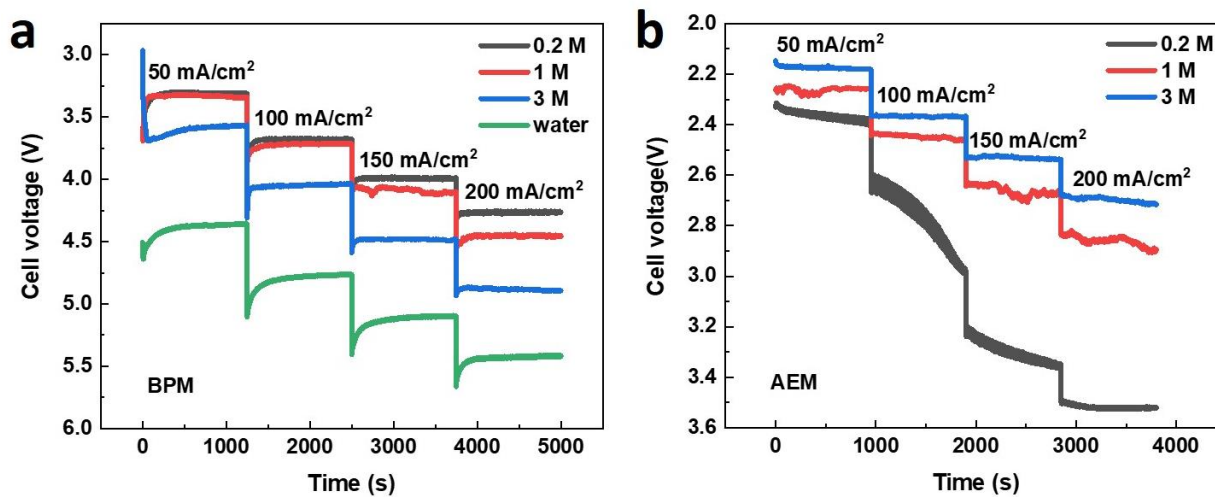


Figure S5 Cell voltage at different current densities in a BPMEA and a AEMEA cell in different electrolytes.

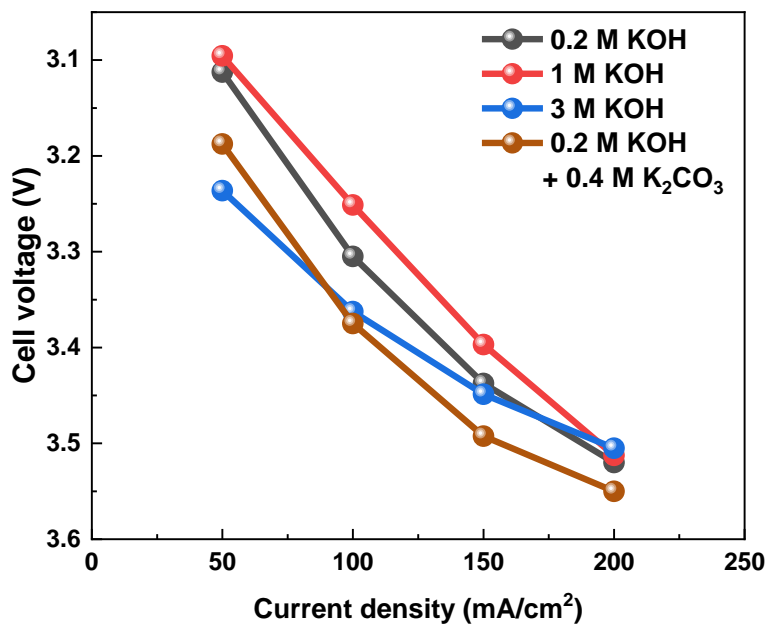


Figure S6 Ohmic resistance corrected cell voltage as function of current density in a BPMEA cell in different electrolytes.

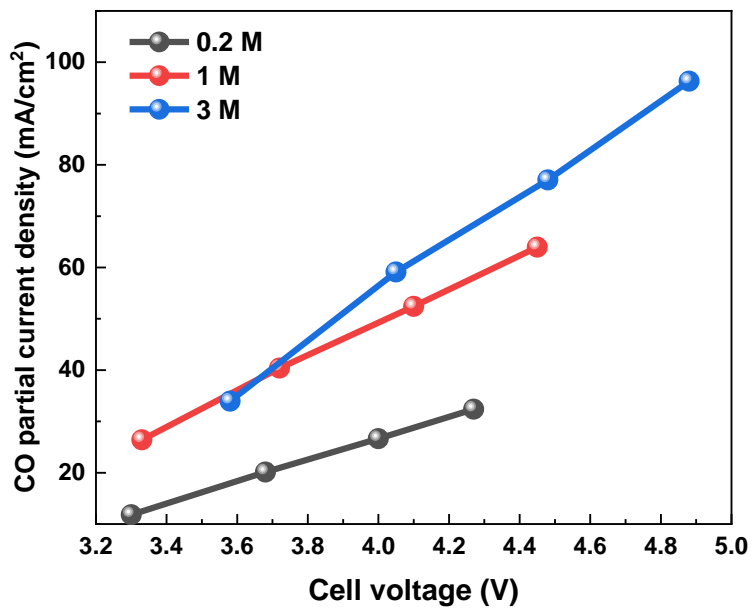


Figure S7 Partial current density of CO as function of cell voltage in different electrolytes.

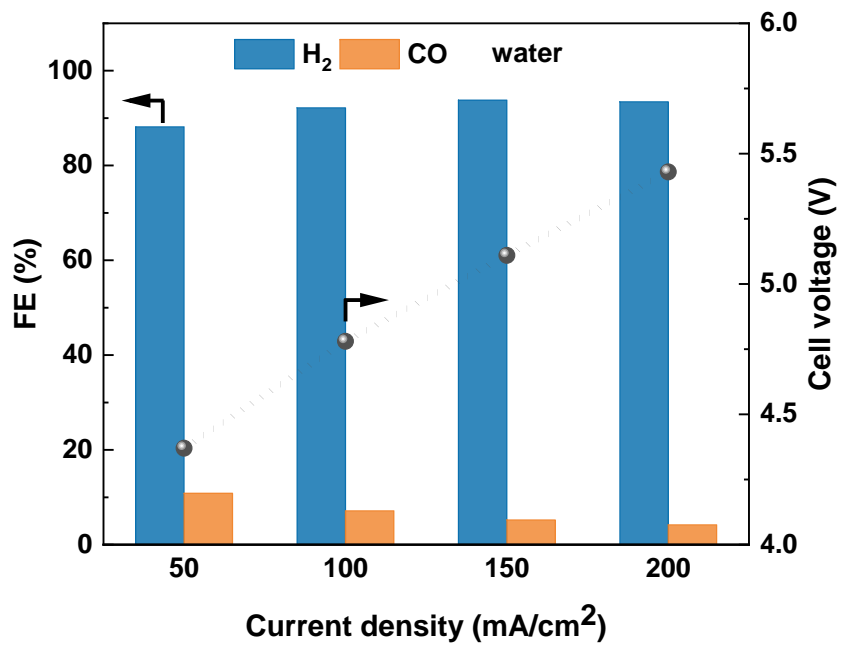


Figure S8 Faradaic efficiency and cell voltage as function of current density using water as analyte in a BPMEA.

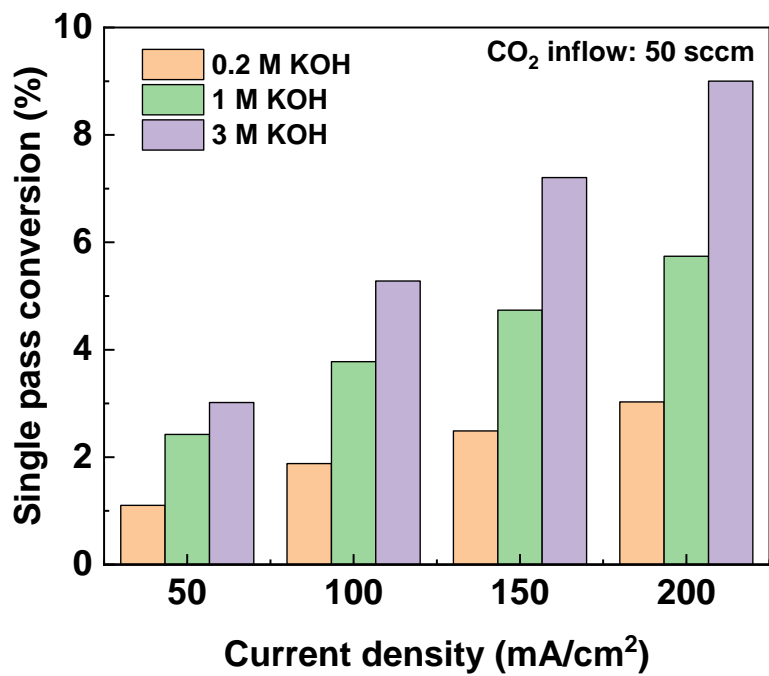


Figure S9 Single pass conversion of CO₂ reactant in a BPMEA cell.

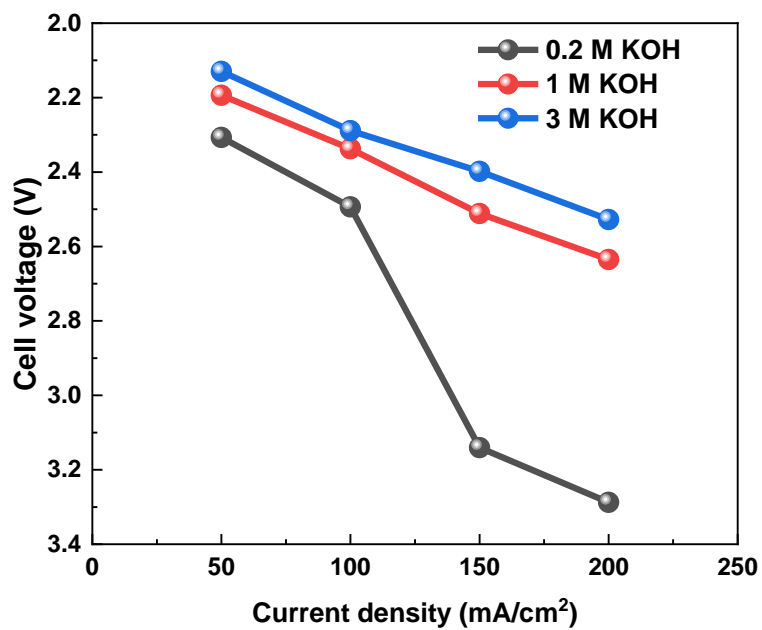


Figure S10 Ohmic resistance corrected cell voltage as function of current density in a AEMEA cell in different electrolytes.

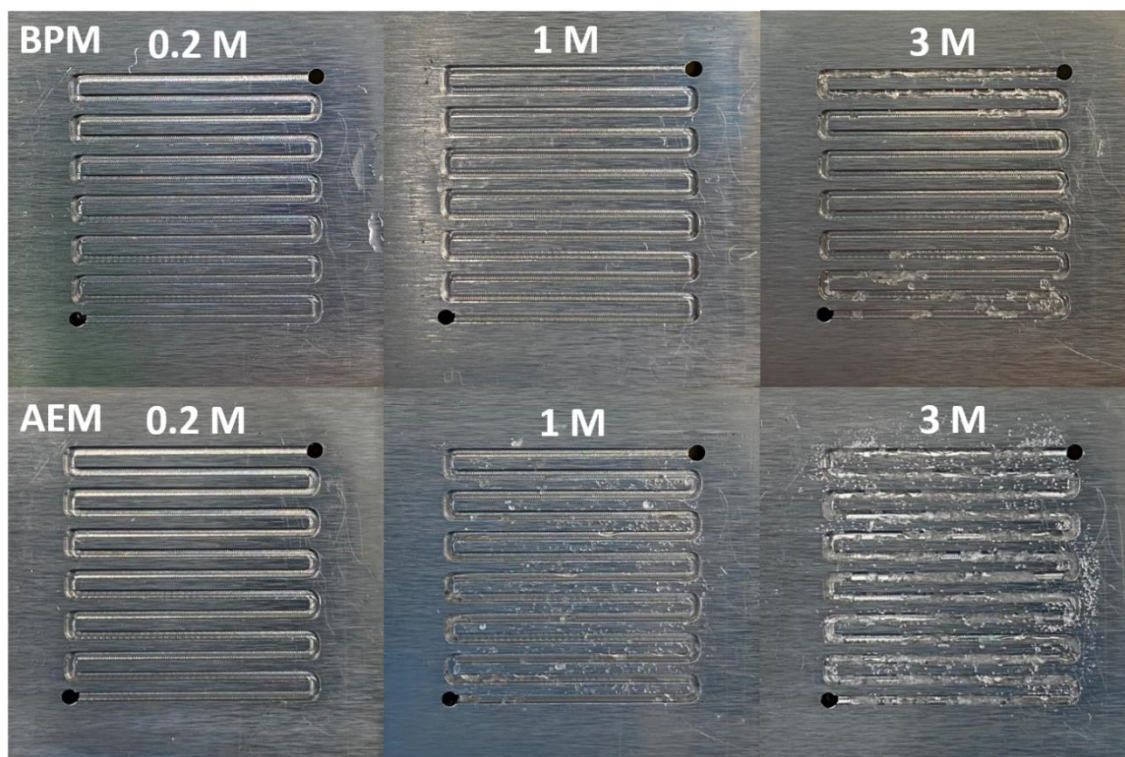


Figure S11 CO₂ flow field after ECO₂R in both BPMEA (80 min) and AEMEA cells (60 min) with varying current density from 50 mA/cm² to 200 mA/cm² in different KOH concentration electrolytes.

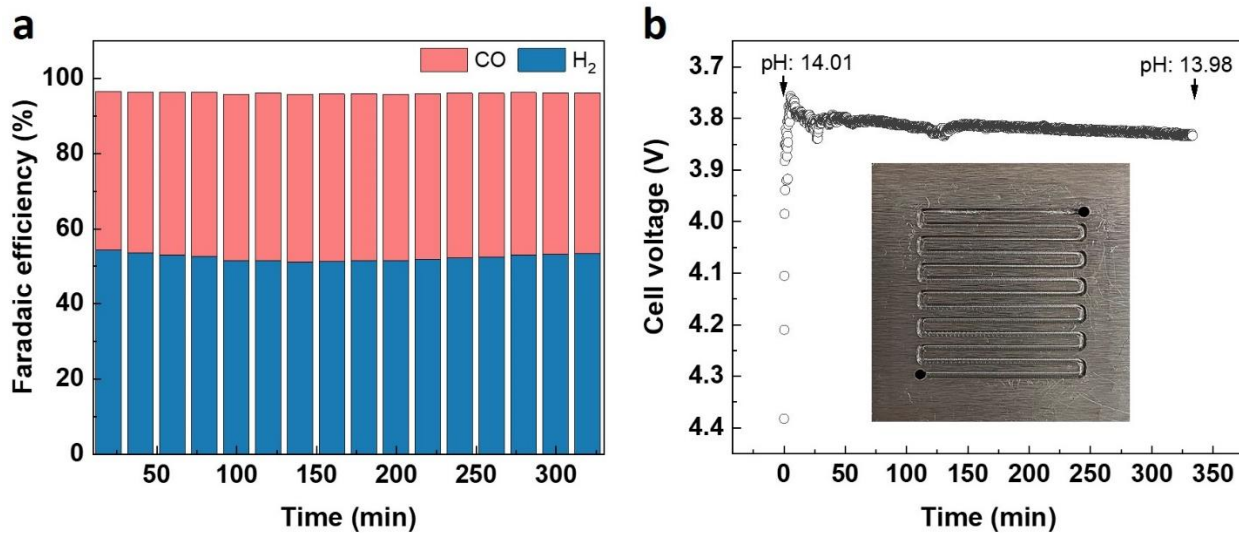


Figure S12 CO and H₂ Faradaic efficiency at 100 mA/cm² current density during 5.5 hours operation in a BPMEA. Inserted in figure b) shows the gas channel after CO₂ reduction test.

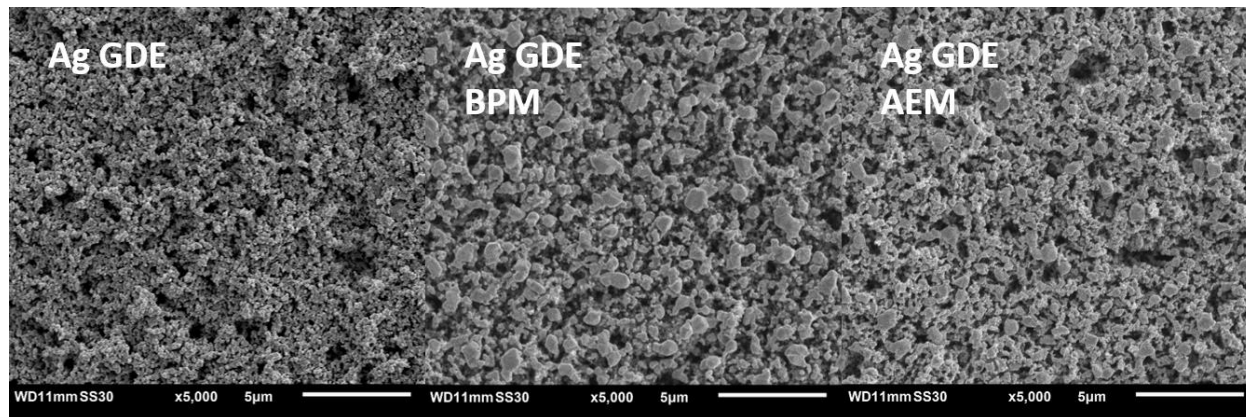


Figure S13 SEM image of Ag GDE before and after ECO₂R in both BPMEA and AEMEA cells with varying current density from 50 mA/cm² to 200 mA/cm² in 1M KOH electrolytes.