

SUPPORTING INFORMATION (6 PP.)

Electrolysis of CO₂ to Syngas in Bipolar Membrane-based Electrochemical Cells

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1. Experimental details

Materials: NiSO₄·6H₂O (ACS reagent, >99%), FeSO₄·7H₂O (ACS reagent, >99%), Bi(NO₃)₃·5H₂O (trace metals basis, >99.99%), (NH₄)₂SO₄ (ACS reagent, >99%), KBr (ACS reagent, >99%), 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM⁺OTf⁻, >98%), Nafion 5% solution, and Ag nanopowder (trace metal basis, >99%) were purchased from Sigma Aldrich. The ionic liquid BMIM⁺OTf⁻ was heated to 80 °C in a vacuum oven overnight before use. All chemicals were stored in a desiccator with drierite in order to minimize adsorption of moisture from the air. Carbon paper (Toray 120) was purchased from the Fuel Cell Store and cut into desired dimensions with a paper trimmer. Bipolar membranes (Fumasep FBM) were purchased from FuMA-tech and stored in 1 M NaCl solution. Nafion 117 membrane was purchased from the Fuel Cell Store and pretreated before use. Anion exchange membranes (Neosepta AHA) were purchased from Astom Corp. and stored in 0.5 M NaCl. CO₂ gas (99.99%) was purchased from Praxair.

Electrode preparation: NiFeO_x and BiO_x catalysts were electrochemically deposited onto porous carbon paper according by slight modifications of literature methods.^{1,2} All potentials reported in this study were measured against a KCl-saturated Ag/AgCl reference electrode. NiFeO_x catalyst was deposited from a solution of 9 mM NiSO₄·6H₂O, 9 mM FeSO₄·7H₂O and 25 mM (NH₄)₂SO₄. The pH of the deposition solution was adjusted to 2.5 by addition of 0.5 M H₂SO₄. Cathodic deposition of NiFeO_x was performed at -50 mA/cm² for 100 s. The deposition current density was normalized to the geometrical area of the carbon paper. The NiFeO_x

catalyst was then washed with DI water and dried under a gentle air stream. The BiO_x catalyst was deposited cathodically from a solution of 20 mM Bi(NO₃)₃·5H₂O, 0.5 M KBr and 1 M HCl at -0.2 V for 200 s. The BiO_x catalyst was washed with 1 M HCl, DI water and acetonitrile, and then dried under a gentle air stream. Ag nanoparticles were drop-cast onto the carbon paper. First, a catalyst ink was prepared by mixing 8 mg of Ag, 200 μL of DI water (18.2 MΩ), 200 μL of isopropyl alcohol and 15 μL Nafion solution (5 wt%, Sigma-Aldrich). The catalyst ink was then painted on a 1 cm² area of the carbon paper and dried under a gentle air stream.

Materials characterization: Electron microscope images of the NiFeO_x, BiO_x and Ag nanoparticle catalysts on carbon paper were taken with FEI NanoSEM 630. Electrochemical Faradaic efficiencies was analyzed by using a Varian (model 90-P) gas chromatograph equipped with a molecular sieve packed column and a thermal conductivity detector. Ultra-high purity argon (Praxair) was used as the carrier gas.

Electrochemical characterization of electrodes: NiFeO_x, Ag, and BiO_x electrodes were first tested separately in a three-electrode configuration to confirm their respective catalytic activities. Catalysts (NiFeO_x, Ag NP or BiO_x) on carbon paper were used as working electrodes, Ag/AgCl was used as the reference electrode and a Pt mesh was used as the counter electrode. The reference electrode was always placed within a few mm away from the working electrode to minimize the solution iR drop, and the electrochemical data were not corrected for series resistance. For the NiFeO_x catalyst, 1 M NaOH was used as the electrolyte. Cyclic voltammetry was done between scan limits of 0.00 to 0.80 V at 20 mV/s scan rate. For the Ag catalyst, 0.5 M KHCO₃ was used as the electrolyte. Cyclic voltammetric scans were carried out from -0.40 to -1.50 V at 20 mV/s. For the BiO_x catalyst, 300 mM of BMIM⁺OTf in anhydrous acetonitrile saturated with CO₂ was used as the electrolyte. Cyclic voltammetry was performed between -1.10 and -2.10 V at 20 mV/s. All CO₂RR electrolytes were purged with CO₂ gas for one hour prior to the electrochemical experiments.

Full electrolysis cell experiments: Full cell measurements were made with NiFeO_x as the anode and Ag or BiO_x as the cathode in a cell with two gold-coated graphite flow fields. Different ion conducting membranes (BPM, AEM, Nafion) were used to separate the anode and the cathode chambers. The geometrical area of both the anode and cathode catalysts was 1 cm² on the carbon paper. The anode electrolyte was 0.1 M aqueous KOH solution delivered by a peristaltic pump. The cathode electrolyte was 0.5 M KHCO₃ in the liquid-phase configuration. In the gas-fed configuration, the cathode chamber was purged with CO₂ gas bubbled through DI water for at least an hour. During these experiments, the CO₂ gas flow rate was controlled at about 20 mL/min. Prior to the cathode assembly, the BiO_x catalyst was evenly coated with neat BMIM⁺OTf as the co-catalyst. j-V curves were measured by holding the electrolyzer at different constant currents or voltages for 10 minutes and then recording the responses of the cell. In experiments performed above room temperature, heating tape was used and the temperature was recorded inside the cathode flow field by means of a small hole drilled in the graphite block for insertion of a thermocouple. Long-term stability tests were performed at a constant current density. 100 ml of 0.1 M KOH was circulated by a peristaltic pump during the long term stability tests without changing the electrolyte.

2. Characterization of the BiO_x catalyst

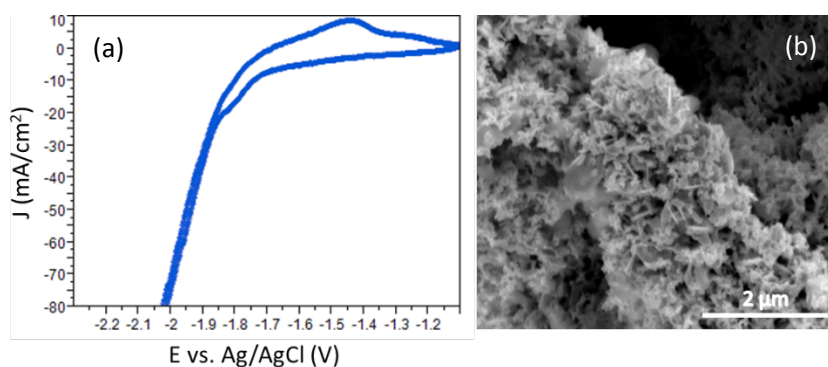


Figure S1. CO₂ reduction at the BiO_x catalyst on carbon paper in 300 mM BMIM⁺OTf in MeCN in a three-electrode configuration. d) SEM image of the electrodeposited BiO_x on carbon paper.

3. j-V comparison of gas phase vs. liquid phase cathode-based BPM cells

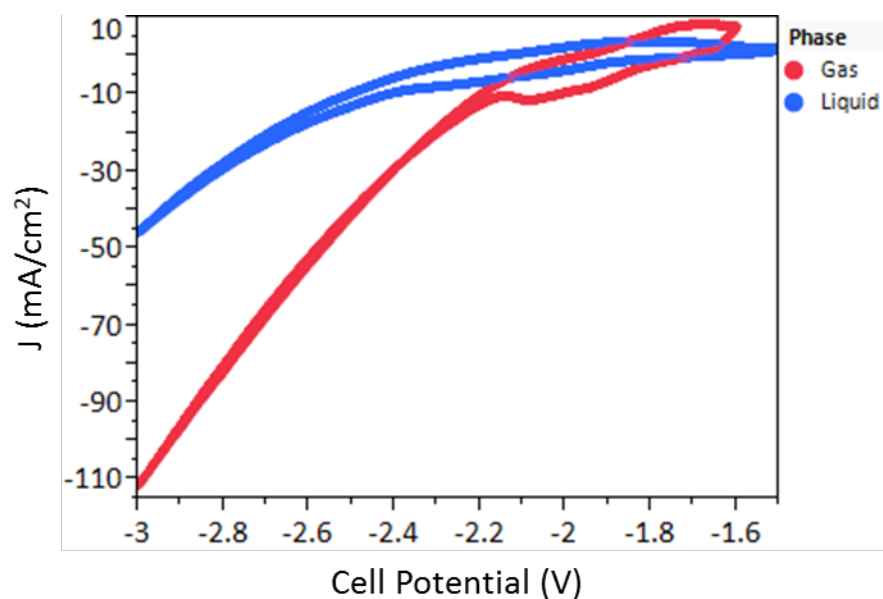


Figure S2. Comparison between gas-fed CO₂ and bicarbonate electrolyte in the cathode compartment of bipolar membrane based cells. Ag nanoparticles were used as cathode catalyst in both cases. In the liquid phase cell, 0.5 M NaHCO₃ saturated with CO₂ was used as electrolyte; in the gas phase cell, humidified CO₂ gas was flowed directly into the cathode through the porous carbon paper contact. 0.1 M NaOH solution and Ni foam were used as anode electrolyte and catalyst, respectively. Cyclic voltammetry was performed between -1.6 to -3 V at 100 mV/s. In both cases, the shape of the j-V curve at high driving voltages indicates that the current is kinetically limited. The lower current density and higher overpotential onset of current in the liquid-phase cathode cell reflect the free energy loss associated with acid-base neutralization at the BPM/catholyte interface.

4. Long term stability of BPM- and Nafion-based cells in the liquid-phase electrolyzer

The stability of the Nafion and BPM cells were compared at a constant current density of 50 mA/cm² (Figure S2), under the conditions used to acquire the data in Figure 3b, where the Faradaic efficiency for CO production was in the range of 45-60%. The voltage needed to drive the electrolysis reaction increased rapidly (within the first minute) in the Nafion cell, and then increased more gradually as the pH of the anode decreased over a period of hours. In contrast, the voltage in the BPM cell was stable during 12 hours of electrolysis.

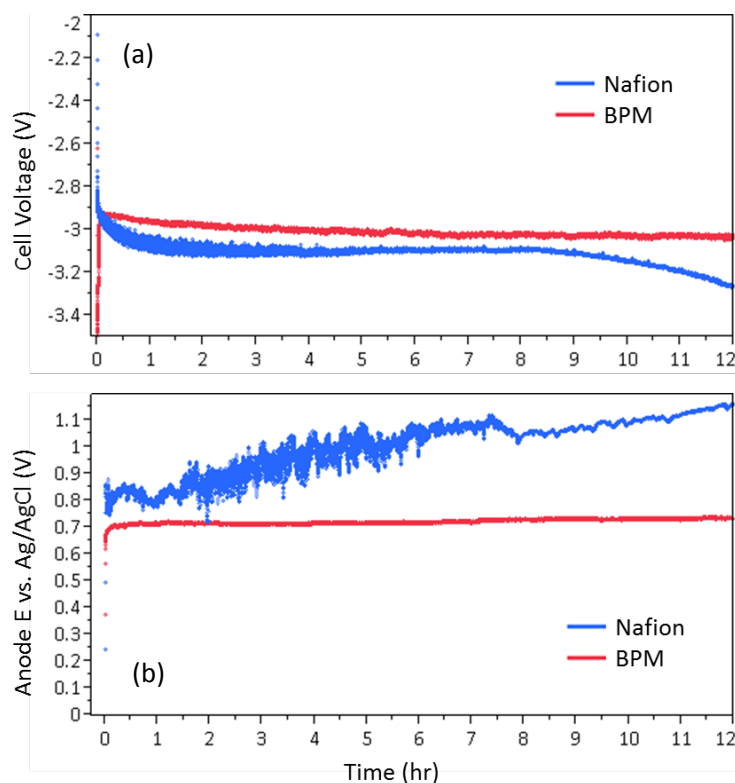


Figure S3. Constant current comparison in the liquid phase cell between BPM and Nafion membrane. 0.1 M KOH was used as the anolyte and 0.5 M of KHCO₃ bubbled with CO₂ gas was used as the catholyte, with carbon-supported Ag and NiFeO_x as cathode and anode catalysts, respectively; a) Full cell voltage over 12 hours. b) Anode potential measured vs. a Ag/AgCl reference electrode. The anode potential increased over 12 h due to the acidification of the anolyte.

5. j-V curve fitting

Fits to the current-voltage data (lines in Figure 2 and 4b,d) were calculated according to Equation S-1, which models the Tafel behavior of the electrode and the series resistance, R_s , of the electrolyzer. Here j is the current density, E is the applied cell potential, j_0 is the exchange

$$j = j_0 \exp \frac{\alpha F}{RT} (E - E_0 - jAR_s) \quad (\text{S-1})$$

current density, α is the transfer coefficient, F is Faraday's constant, A is the electrode area, R is the gas constant, T is the absolute temperature, and E_0 is the formal potential for the CO_2RR .

The current-potential data were fitted to Eqn. S-1 using Mathematica software. $0.1 < \alpha < 0.7$ and $R_s > 0$ constraints were imposed in the fitting process to maintain realistic values. All other parameters were determined without constraints to reach the best fit. The α low values obtained are consistent with a multi-electron reaction in which the first electron transfer is the rate-determining step.³

For Figure 2a – Liquid phase electrolyzer with different membranes

	AEM	Std error	BPM	Std error	Nafion	Std error
j_0 (mA/cm ²)	0.82	0.02	1.69	0.004	2.25	0.003
α	0.12	0.02	0.10	0.01	0.14	0.03
R_s (Ω)	16.2	3.8	1.7	2.3	18.1	2.8
E_0 (V)	1.37	0.07	1.99	0.03	1.57	0.04

For Figure 4b – Gas phase electrolyzer with different membranes

	AEM	Std error	BPM	Std error	Nafion	Std error
j_0 (mA/cm ²)	0.33	0.07	0.25	0.02	0.18	0.03
α	0.11	0.08	0.13	0.02	0.1	0.01
R_s (Ω)	290	165	0	4	6.9	6
E_0 (V)	1.52	0.10	1.94	0.03	1.33	0.02

For Figure 4d – Gas phase electrolyzer with BPM at different temperatures

	Room	Std error	30 °C	Std error	40 °C	Std error	50 °C	Std error
j_0 (mA/cm ²)	0.86	0.01	0.98	0.01	0.85	0.01	0.91	0.02
α	0.13	0.02	0.13	0.02	0.13	0.02	0.12	0.02
R_s (Ω)	0	4	0	4	0	5	0	7
E_0 (V)	2.18	0.05	2.13	0.05	2	0.05	1.93	0.07

	60 °C	Std error	N ₂	Std error
j_0 (mA/cm ²)	1.12	0.02	1.19	0.05
α	0.11	0.01	0.15	0.13
R_s (Ω)	0	7	33.4	11
E_0 (V)	1.81	0.08	2.4	0.5

Numerical fitting of j - V data to eqn. S-1 was good in cases where the series resistance was large, i.e., with AEM and Nafion membranes in Figs. 2a and 4b. The fits were poor when the series resistance was low, especially in Fig. 4d, because the impedance of the bipolar membrane, operating in reverse bias, cannot be modeled as a simple series resistance.⁴

6. j - V data for the gas-fed bipolar membrane cell at high bias

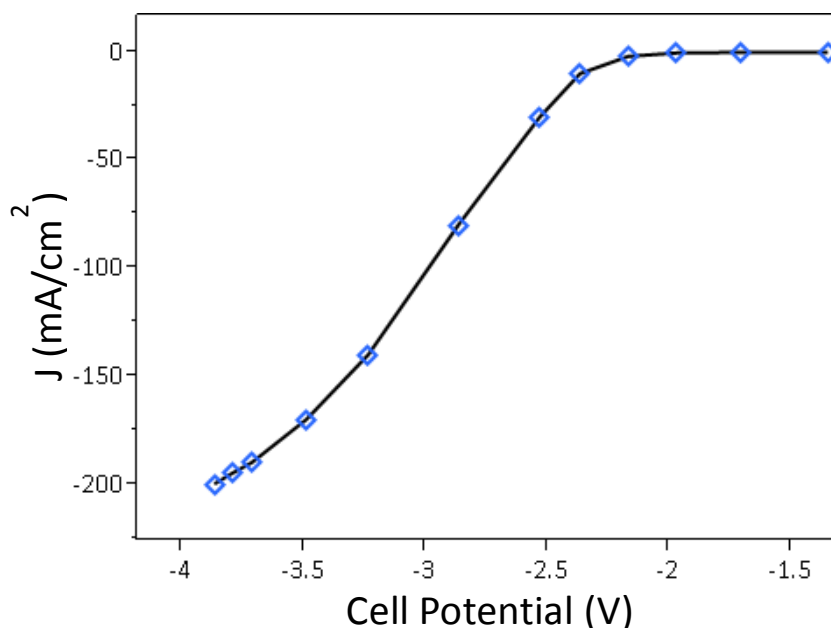


Figure S4. j - V curve for the gas-fed BPM-based electrolyzer at 60 °C. NiFeO_x catalyst with 0.1 M aqueous KOH was used in the anode; $\text{BiO}_x/\text{BMIM}^+\text{OTf}^-$ catalyst with gas-fed humidified CO_2 was used in the cathode. The line through the data points is a simple interpolation and does not represent a fit to equation S-1.

7. References

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