

Supporting Information for:

Selective Conversion of CO₂ to CO with High Efficiency using an Inexpensive Bismuth Based Electrocatalyst

John L. DiMeglio and Joel Rosenthal*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716

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Experimental Methods

Materials and Methods. Reagents and solvents were purchased from Sigma Aldrich, Acros, Fisher, Strem, or Cambridge Isotopes Laboratories. Bismuth(III) nitrate pentahydrate (99.999%) was purchased from Alfa Aesar; ionic liquids including, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF₄), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄), and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) were purchased from either Alfa Aesar or Sigma-Aldrich. Electrochemistry grade tetrabutylammonium hexafluorophosphate (TBAPF₆), potassium bromide, sodium chloride and hydrochloric acid (36.5–38.0 % in water) were purchased from Sigma-Aldrich. Carbon dioxide was purchased from Keen Compressed Gas Company and was dried by passing through a Glass Indicating Moisture Trap (3.5 × 26 cm) containing 5Å molecular sieves (Restek). All other chemicals were used without further purification.

Electrochemical Measurements. Electrochemistry was performed using either a CHI-620D potentiostat/galvanostat or a CHI-720D bipotentiostat. Cyclic voltammetry was performed using a standard three-electrode configuration. The working electrode was either a bare glassy carbon disk electrode (GCE, 3.0 mm diameter CH Instruments), or a glassy carbon electrode onto which Bi-CMEC had been deposited. A piece of platinum gauze (Sigma 99.9%) was used as the counter electrode. All potentials were measured against a Ag/AgCl reference electrode (1.0 M KCl, CH Instruments) and converted to the SCE reference scale using $E_{\text{SCE}} = E_{\text{Ag/AgCl}} + 0.044 \text{ V}$. The supporting electrolyte employed for electrochemistry experiments in organic solution was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆). Cyclic voltammograms were recorded at 100 mV/s with iR drop compensation.

Electrodeposition of Bi-CMEC. A glassy carbon disk electrode (GCE, 3.0 mm diameter) or glassy carbon plate (1 cm × 3 cm) was polished with a slurry of 0.05 micron alumina powder in Millipore water. Residual alumina was rinsed from the GCE surface with Millipore water, and the electrode was then sonicated in Millipore water for five minutes. The polished GCE was placed in an electrodeposition bath containing 20 mM bismuth(III) nitrate, 1.0 M hydrochloric acid and 0.5 M KBr. The GCE was preconditioned by cycling the applied potential (10 cycles) from 0 to –0.55 V vs. SCE at a sweep rate of 100 mV/sec and was then briskly agitated in the deposition solution to remove any exfoliated material from the GCE surface. Controlled potential electrolysis (CPE) was initiated using this conditioned GCE in the quiescent Bi³⁺ solution at –0.21 V versus SCE until ~3 C/cm² of charge had been passed. The bismuth-modified GCE was sequentially rinsed with 1 M hydrochloric acid, Millipore water, and acetonitrile prior to being dried under a gentle stream of nitrogen.

Ex-situ Analysis of Bi-CMEC. Scanning electron microscopy images and energy dispersive X-ray (EDX) spectra were acquired with a JEOL JSM 7400F Scanning Electron Microscope (SEM). X-ray photoelectron spectroscopy was conducted using a VG ESCALAB 220I-XL spectrometer. The X-rays used were monochromatic Al K α X-rays (1486.7eV) with a power of 105W (15 kv, 7 mA). The operating pressure in the

main chamber was less than 1×10^{-8} torr. The X-ray spot size was elliptical in shape with a semi-major axis of roughly 400 μm .

Initial XPS survey scans were collected at a pass energy of 100 eV using a step size of 1.0 eV. High-resolution XPS spectra were collected at a pass energy of 20 eV using a step size of 0.1 eV. All atomic ratios (χ_i) were calculated from the high-resolution spectra and were determined using the equation:

$$\chi_i = \frac{A_i/S_i}{\sum_i A_i/S_i}$$

where A_i is the area calculated with a Shirley-type baseline, and S_i is the relative sensitivity factor. Atomic ratios do not include hydrogen in XPS.

Determination of Electrochemical Surface Area for Bi-CMEC. The electrochemically active surface area of a Bi-modified GCE ($A = 0.07 \text{ cm}^2$) was determined by Randles-Sevcik analysis of CV data recorded using a 0.91 mM solution of ferricyanide in Millipore water (0.1 M KCl). Variation in peak current (I_p) for the oxidation of ferrocyanide was plotted against the square root of scan rate ($\nu^{1/2}$)¹ as shown in Figure S6. The scan rate was varied from 10 – 500 mV/sec and a value of $D = 6.67 \times 10^{-6} \text{ cm}^2/\text{s}$ was used for the diffusion coefficient of ferrocyanide.² These experiments gave a calculated electrochemically active surface area of $0.09 \pm 0.008 \text{ cm}^2$ (average of four different Bi-modified GCEs), which corresponds to a roughness factor of 1.3.

Determination of Double-Layer Capacitance for Bi-CMEC. The capacitance of a Bi-modified GCE ($A = 0.07 \text{ cm}^2$) was determined by plotting the change in double-layer charging as a function of scan rate. Cyclic voltammograms (CVs) were obtained in MeCN containing 0.1M TBAPF₆ over a potential range in which no faradaic processes occurred. The resulting geometric current density was plotted as a function of scan rate (ν) as shown in Figure S7. A representative set of CVs for a Bi-modified GCE is also shown in Figure S7. A capacitance of $61 \pm 5 \text{ mF}$ was determined by taking the average values obtained for three Bi-modified GCEs.

CO₂ Reduction Electrolysis and Headspace Analysis. Current densities were determined by performing electrolyses in a gas-tight two-compartment cell, in which a Nafion 212 membrane served to separate the anode and cathode compartments. Each compartment contained 20 mL of MeCN with 0.1 M TBAPF₆, which was sparged with MeCN saturated CO₂ for at least 30 min. During electrolysis, a steady supply of MeCN saturated CO₂ gas was delivered to the headspace of both the cathodic and anodic compartments at a rate of approximately 60 sccm.

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1. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*; John Wiley & Sons: Hoboken, NJ, 2001; p 231.
 2. Konopka, S. J., McDuffie, B. *Anal. Chem.* **1970**, *42*, 1741–1746.

Faradaic efficiencies for CO production were determined using a single-compartment electrolysis cell. The electrolysis cell was sparged with MeCN saturated CO₂ for approximately 45 minutes, following which time the system was sealed and electrolysis initiated. The headspace of the electrolysis cell was sampled periodically by manually removing 1.0 mL aliquots using a gas-tight syringe. These aliquots were analyzed by manual injection into a gas-sampling loop of a Shimadzu GC-2014 gas chromatograph (GC). This GC was equipped with two 10 port injection valves in line with 2m HaySepT 80/100 columns. Quantification of CO was accomplished using a flame ionization detector (FID) with methanizer after passage through a 3m HaySepD 80/100 column using helium (99.999%) as the carrier gas. Quantification of H₂ was accomplished using a thermal conductivity detector (TCD) after passage through a packed MolSieve 5A 60/80 column, using argon as the carrier gas (99.999%).

¹H and ¹⁹F NMR was performed on aliquots of the electrolyte solution at the completion of each electrolysis experiment to check for the formation of nonvolatile CO₂ reduction products and/or the decomposition of the electrolyte solution.

Schematics illustrations of single- and two-compartment electrolysis cells are shown in Figure S8.

Tafel Analysis. The current density (*j*) versus overpotential (*η*) data was obtained via stepped-potential electrolysis experiments using a two-compartment cell with a Nafion membrane separating the anode and cathode compartments. Measurements were conducted under a steady flow of CO₂ (~1 cm³/s).

Determination of $E^{\circ}_{\text{CO}_2/\text{CO}}$ under Electrolysis Conditions. In order to determine the standard potential for CO production under a given set of conditions, the strongest acid present must be considered. For conversion of CO₂ to CO in acetonitrile, the value of $E^{\circ}_{\text{CO}_2/\text{CO}}$ can be approximated by the expression below.³

$$E^{\circ}_{\text{CO}_2/\text{CO}} = 0.105 - \frac{RT \cdot \ln(10)}{F} pK_a(\text{HA, MeCN}) \text{ V} \quad (\text{versus SCE})$$

Under the electrolysis conditions we employ, the imidazolium ionic liquids (ILs) are the strongest acids present in solution, and have pK_a values of 32 in MeCN.⁴

Thus, for the present system:

$$pK_a(\text{IL, MeCN}) = 32, \text{ which leads to } E^{\circ}_{\text{CO}_2/\text{CO}} = -1.78 \text{ V versus SCE}$$

3. Costentin, C., Drouet, S., Robert, M., Saveant, J. M. *Science* **2012**, 338, 90–94.

4. Magill, A. M., Cavell, K. J., Yates, B. F. *J. Am. Chem. Soc.* **2004**, 126, 8717 – 8724.

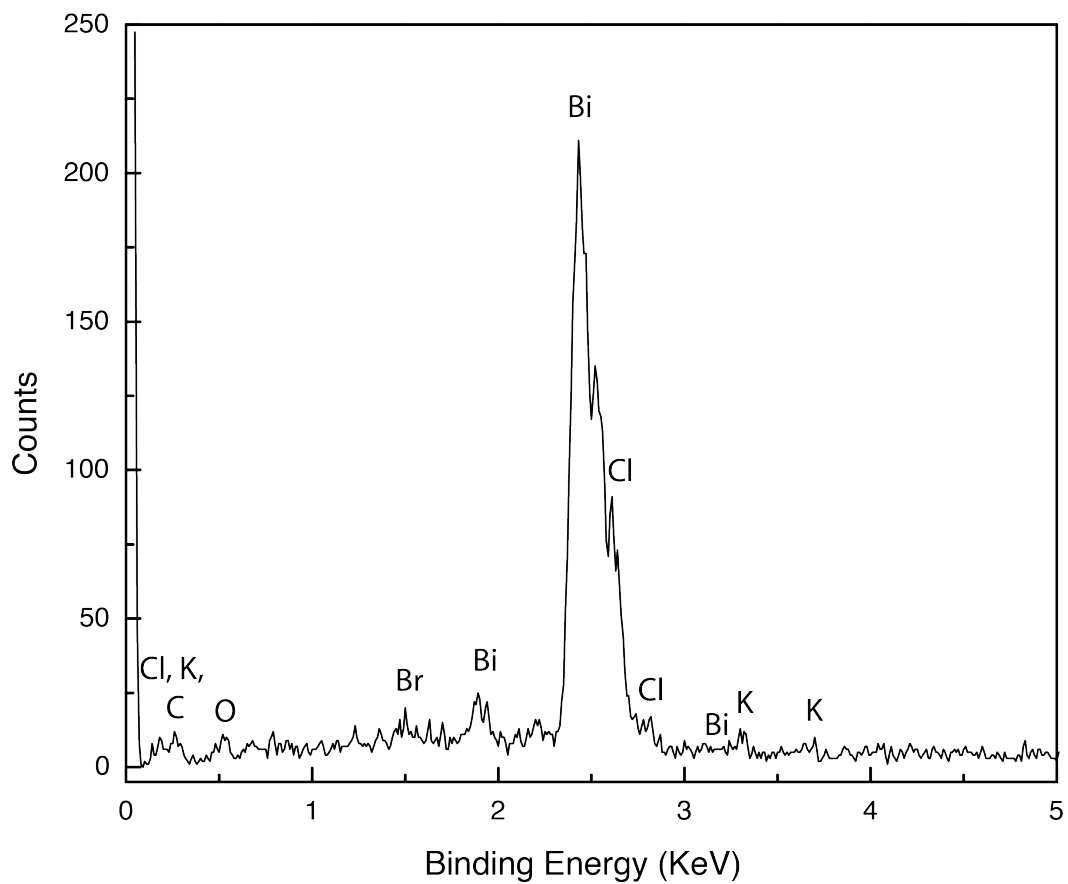


Figure S1. EDX spectrum recorded for Bi-CMEC on glassy carbon.

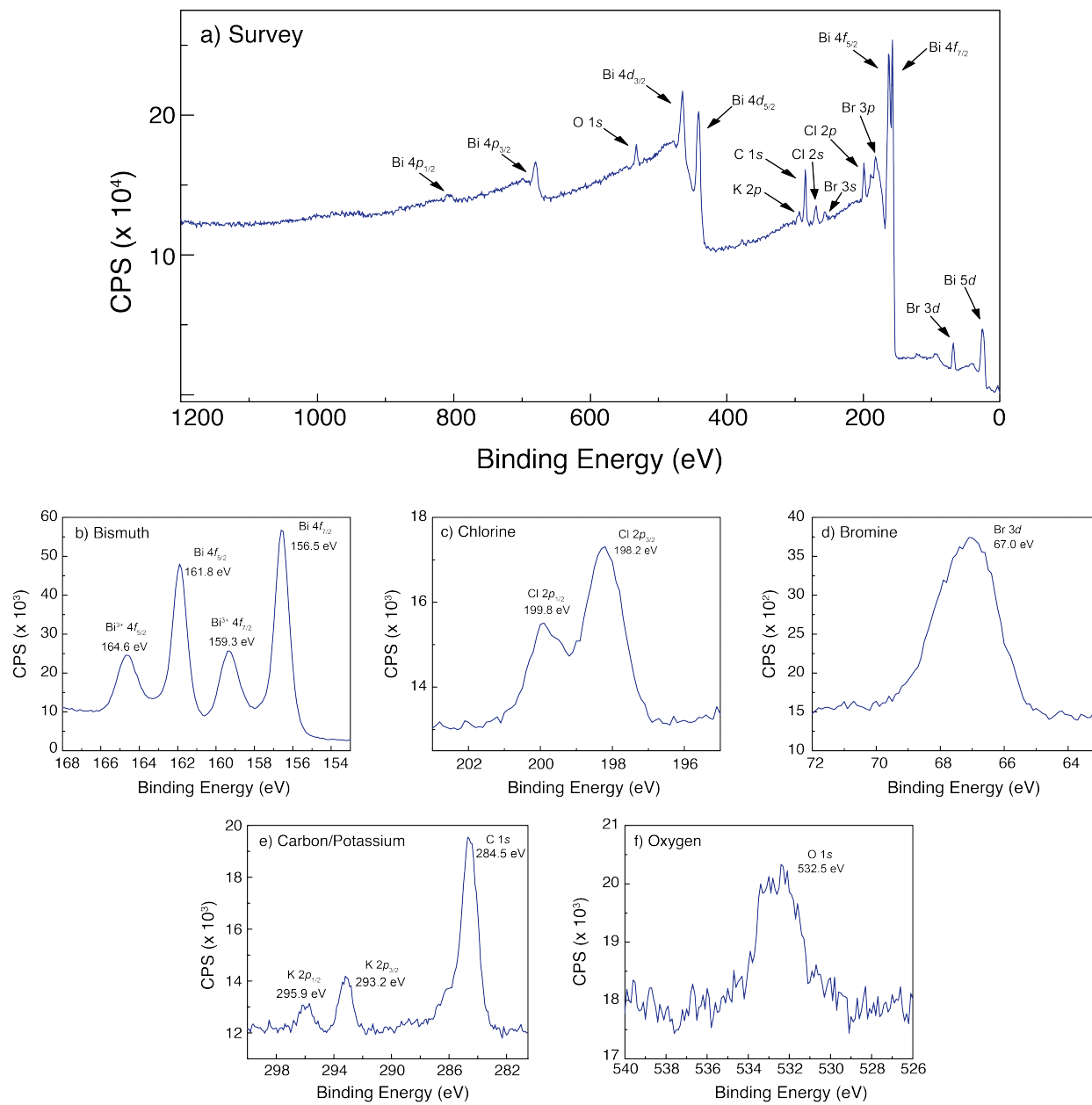


Figure S2. XPS spectra recorded for Bi-CMEC on a GCE (a) survey scan, (b) high-resolution bismuth region, (c) high-resolution chlorine region, (d) high-resolution bromine region, (e) high-resolution carbon/potassium region, and (f) high-resolution oxygen region.

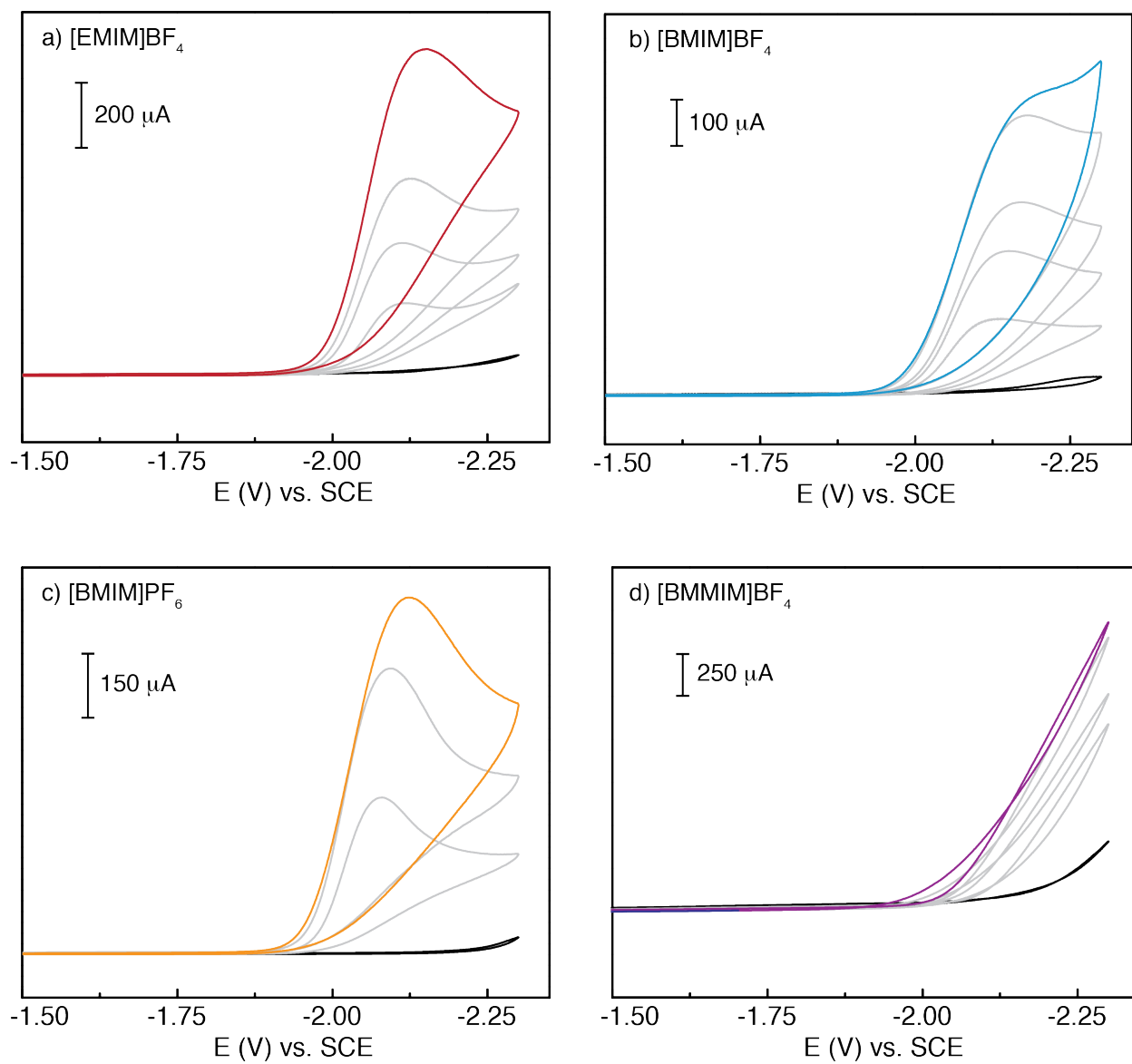


Figure S3. CVs of Bi-CMEC in CO₂ saturated acetonitrile (0.1 M TBAPF₆) containing up to 20 mM (a) [EMIM]BF₄, (b) [BMIM]BF₄, (c) [BMIM]PF₆ and (d) [BMMIM]BF₄.

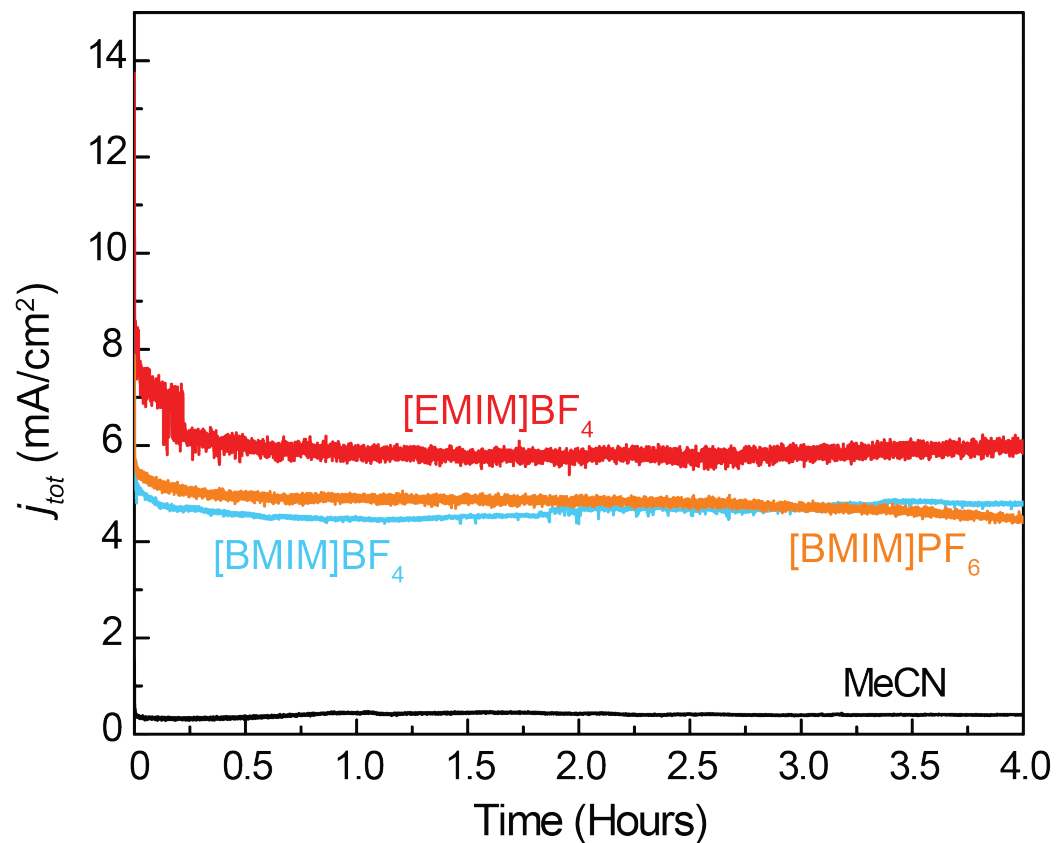


Figure S4. Extended total current density (j_{tot}) traces for Bi-CMEC in CO₂ saturated MeCN containing 0.1 M TBAPF₆ and 20 mM of either [EMIM]BF₄, [BMIM]BF₄ or [BMIM]PF₆.

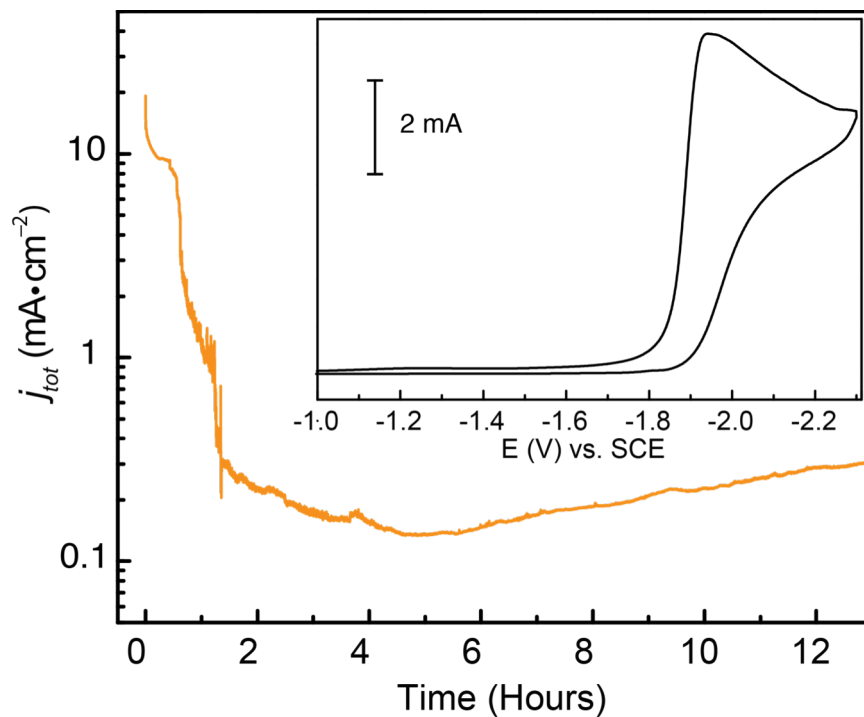


Figure S5. Total current density (j_{tot}) profiles for Bi-CMEC on GCE at -1.95 V in CO_2 saturated MeCN containing 20 mM [BMIM]PF₆ using a split solvent arrangement in which the anode compartment contained aqueous electrolyte (pH ~ 7.4). Inset: CV traces recorded for Bi-CMEC on GCE under the same conditions.

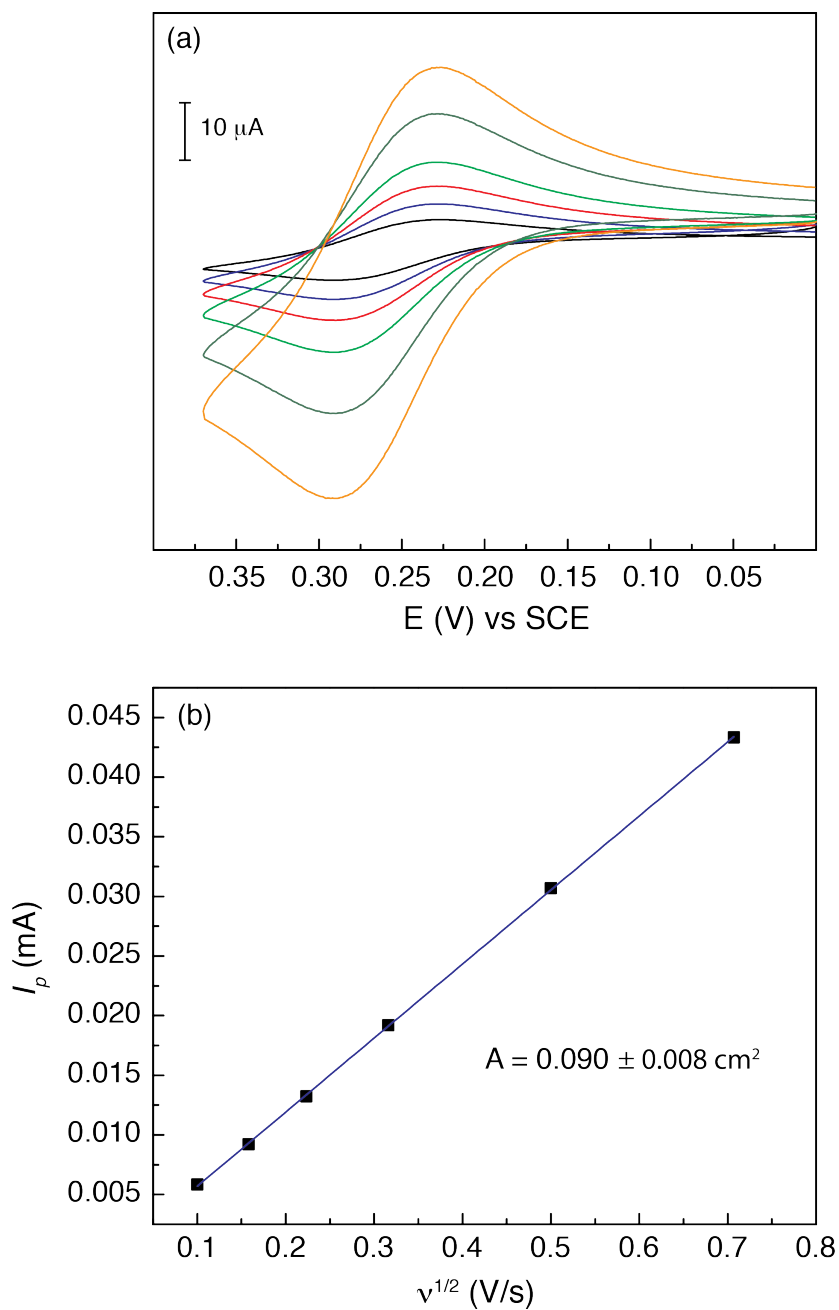


Figure S6. (a) CVs of a Bi-modified GCE in a 0.91 mM ferricyanide solution at various scan rates. (b) Plot of the peak cathodic current of the ferro/ferricyanide couple versus $v^{1/2}$.

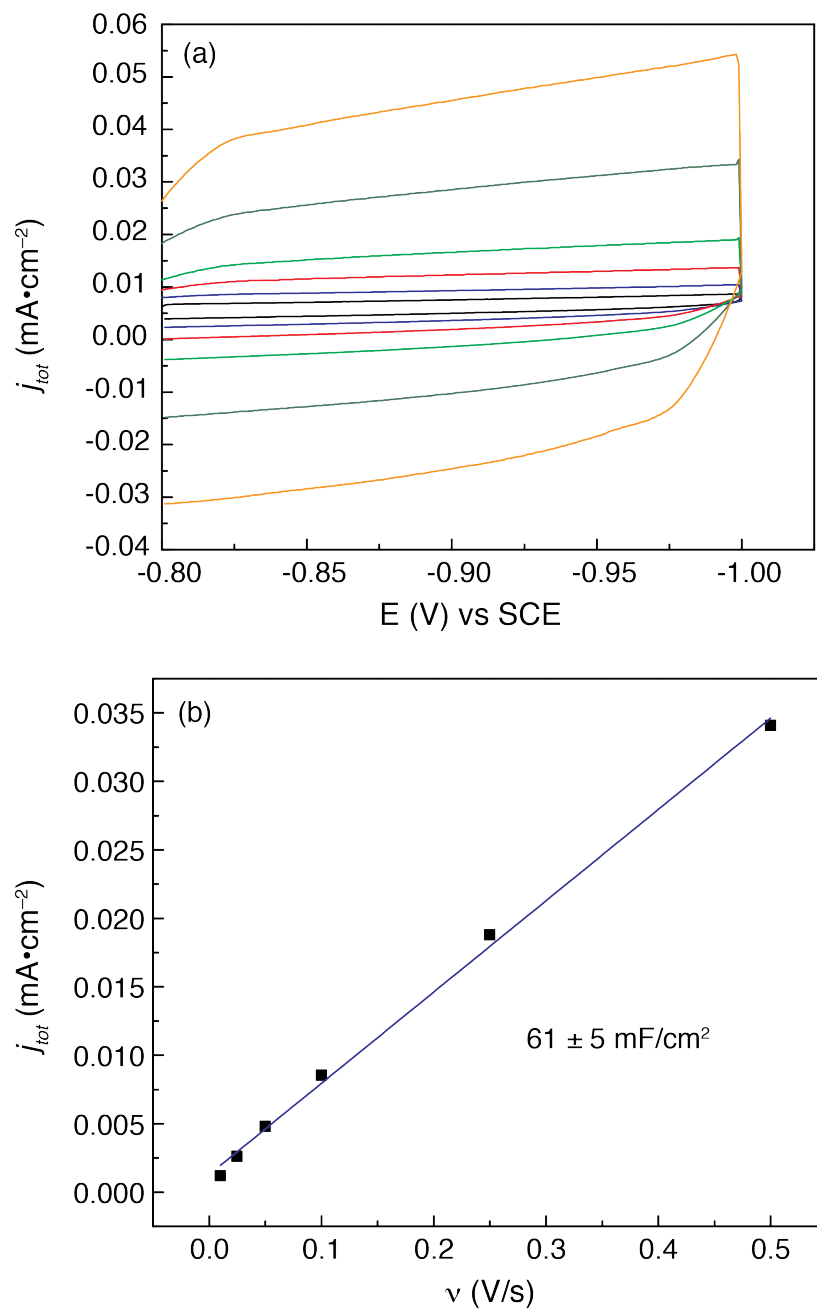


Figure S7. (a) CVs taken using a Bi-modified GCE electrode in a region where no faradic current is observed. Scan rates include 10, 25, 50, 100, 250, and 500 mV s^{-1} . (b) Plot of current density (j) due to double-layer charge/discharge against CV scan rate.

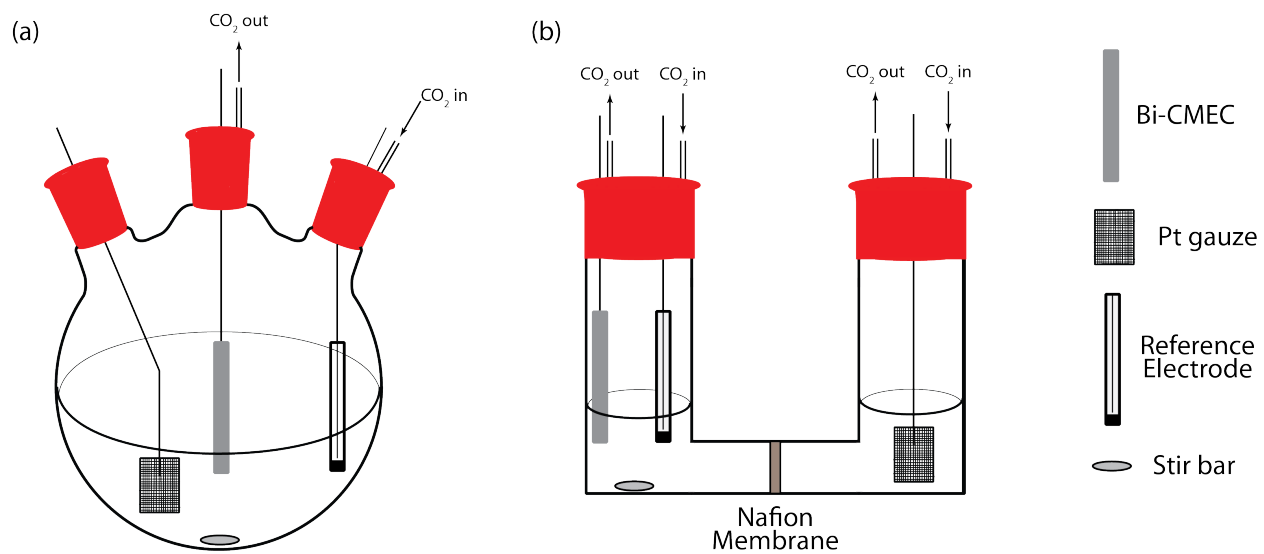


Figure S8. Schematic illustration of (a) single-compartment electrochemistry cell and (b) two-compartment electrochemistry cell employed for CO₂ electrolysis experiments.