

Unlocking catalyst potentials in zero-gap membrane-electrode assemblies

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Part I: Methods

Chemicals and Materials

The 1 M KOH anolyte used in this study was prepared by diluting 10 M KOH (ACR chemical reagents). CeTech Carbon Cloth with a microporous layer (MPL – W1S1011) was purchased from FuelCell Store and used as the gas-diffusion layer (GDL). Nickel foam was purchased from GoodFellow. Ruthenium-Iridium coated Titanium plate was purchased from CHB Electronics Co. (China). Hydrobromic acid (48%), potassium bromide and potassium bicarbonate were purchased from Chem-Supply. Cesium bicarbonate, Polytetrafluoroethylene (PTFE) dispersion, silver nanopowder (< 150 nm), and copper nanopowder (40-60 nm) were purchased from Sigma-Aldrich. The Fumasep FBM – Bipolar membrane was purchased from FuelCell Store. Sustainion® X37-50 Grade RT membrane was obtained from Dioxide Materials; PiperION A20 membrane, Nafion™ NR212 membrane, Sustainion XA-9 ionomer and PiperION-A TP-85 Ionomer were purchased from SCI Material Hub. Graphene oxide (GO) powder was supplied by Huiheng Technology Co. (China).

MilliQ grade ultrapure deionized water was used to prepare all the solutions.

Electrode preparation

A direct current magnetron sputter deposition technique was used to sputter a thin Ag catalyst layer (CL) on top of CeTech W1S1011 Carbon Cloth GDLs in Melbourne Centre for Nanofabrication (MCN). A nominal Ag or Cu thickness of 300 nm was deposited. The deposition rate was determined by depth profiling a silicon substrate reference sample following 5 min of sputtering with 50 W applied energy power. The sputtering process was conducted under an argon atmosphere at a pressure below 1 μ bar. The resulting Ag CL corresponded to a mass loading of 0.315 mg cm⁻².

For catalyst-coated electrodes prepared via ink spray deposition, silver or copper nanoparticles were dispersed in a 1:1 isopropanol/water mixture at a concentration of 2.08 mg cm⁻³. The catalyst ink additionally contained 10%wt PiperION ionomer and 20%wt PTFE dispersion relative to the catalyst mass. The dispersion was spray-coated on Carbon Cloth GDLs preheated to 140 °C on a hotplate, using an ultrasonic spraying machine (UAC4000M from CHEERSONIC). The catalyst loading was controlled to 1.0 ± 0.1 mg cm⁻² for 10-hour stability test. For ECSA measurements, electrodes with varied catalyst loadings were prepared following the same procedure.

For the anode, nickel foam (0.9mm, 99.5% purity) was used as the oxygen evolution electrode. The Ni foam was compressed using a rolling machine (MSK-HR-01) to a thickness of 0.3 mm prior to cell assembly.

Commercially available ion-exchange membranes (IEMs) were used to separate the anode and cathode compartments. Prior to use, the membranes were pretreated and ion-exchanged by immersion in 1 M

KOH for 24 hours, with the electrolyte refreshed after the first 12 h. The IEMs were subsequently rinsed and stored in MilliQ water before being assembled into MEAs.

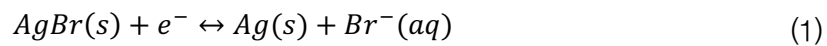
A customized bipolar membrane (BPM) was fabricated following previously reported procedures¹. The BPM was assembled via hot-pressing process and consisted of a NafionTM N212 cation-exchange layer (CEL), a 20 μm PiperION anion-exchange layer (AEL), and a graphene oxide (GO_x) layer serving as the water-dissociation catalyst.

Reference electrode preparation

An alkaline tolerant Ag|AgBr layer was fabricated on a 0.1 mm thick Ag foil via electrodeposition following a previous reported procedure with minor modifications.² The Ag sheet (0.1 mm thickness) was cut into rectangular foils with dimensions of 5 cm $\times$ 2 mm. Before electrodeposition, Ag foils were cleaned by sequential sonication in 1 M KOH and 1 M HNO_3 solutions for 5 minutes each in centrifuge vials. The foils were rinsed with deionized water for 1 minute between each cleaning step.

Then, electrodeposition was conducted in a batch cell under ambient temperature and pressure. One Ag foil functioned as the working electrode, the other worked as the counter electrode, and the saturated KCl Ag|AgCl served as the reference electrode (RE). The electrolyte consisted of a mixed solutions containing 100 mM KBr and 100 mM HBr, and a 2 cm length of each Ag foil was immersed in the electrolyte during deposition. The electrodeposition protocol consisted of four steps: (i) open circuit potential (OCV) measurement; (ii) a potentiodynamic sweep from -0.1 V vs. OCV to -0.3 V vs. OCV at a scan rate of 0.01 V/s for five cycles to reduce residual silver oxide; (iii) potentiostatic deposition at +0.88 mV vs. Ag|AgCl until 1.2 C/cm² had passed through the working electrode to form the Ag|AgBr layer; and (iv) a final OCV measurement.

After electrodeposition, 10 μl Sustainion ionomer solution was drop-cast onto each side of the Ag|AgBr foil surface to form a thin ionomer coating layer. The coated electrodes were subsequently immersed in 1 M KBr for at least 48 h prior to use to ensure complete exchange of residual Cl^- with Br^- . The equilibrium redox reaction for the Ag|AgBr RE and its corresponding Nernst potential expression are given below:



$$E = E^o - \frac{RT}{F} \ln a_{\text{Br}^-} \quad (2)$$

Reference electrode stability testing

The potential stability of developed Ag|AgBr REs was examined by applying controlled current cycles in electrolytes ranging from pH 0 to 14. A batch cell was used for the tests at ambient conditions. In this

configuration, a three-electrode setup was employed, where the developed RE served as the working electrode, the platinum plate worked as the counter electrode, and the saturated KCl Ag|AgCl was as the RE. The current cycling protocol consisted of sequential steps of 0 nA for 10 min, +200 nA for 5 mins, 0 nA for 5 mins, and -200 nA for 5 min. This sequence was repeated for five cycles. The applied current magnitude (200 nA) corresponds to the small measurement current passing through the RE when subjected to a simulated ± 4 V potential difference and connected to a data acquisition module with ≥ 20 M Ω resistance. The electrolytes consisted of 0.5 M K₂SO₄ as the supporting electrolyte, with the pH adjusted to 0, 1, 7 and 13 by adding H₂SO₄ or KOH. For the pH 14 condition, a 1 M KOH solution was used directly.

MEA electrolyser setup

All experiments presented in this work were conducted in a zero-gap membrane electrode assembly (MEA) electrolyser (Dioxide Materials). In the MEA configuration, anode and cathode end plates were made of 304 stainless-steel plates as current collectors with a serpentine flow pattern. To seal the cathode and anode compartments, we used two 0.3 mm thick polytetrafluoroethylene (PTFE) gaskets with a 1.5 x 1.5 cm² window in the middle, which were fabricated using a cutting machine of Cricut Maker 3. The Ag-based cathode and anode electrodes were placed on either side of an oversized 9 cm² (3 x 3 cm²) membrane and the cell was compressed by eight bolt screws with 4 Nm torque applied. The active electrode area is defined by the gasket opening and corresponds to a square region with a side length of 1.5 cm, resulting in a geometrical surface area of 2.25 cm². This value was used to normalize the applied current densities reported here.

Electrochemical measurements

During electrochemical measurements for CO₂R, the inlet CO₂ gas was humidified by passing through a MilliQ water gas bubbler at room temperature before entering the cathode chamber. The gas flow rate was maintained at 30 sccm using a mass-flow controller (Bronkhorst). The 100 ml anolyte was recirculated through the anode flow channel at a constant flow rate of 20 ml min⁻¹ using a peristaltic pump (ISMATEC). All experiments were performed using a potentiostat (Metrohm Autolab PGSTAT302), including chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS).

To monitor the potential of individual compartments with MEAs, an additional data acquisition module (ADAM-4019+) was connected to the electrodes, including the working electrode, counter electrode, two embedded Ag|AgBr REs, and an external Ag|AgCl RE. During CP operation, each potential was continuously recorded using LabVIEW-based programming software.

To evaluate ohmic losses within individual cell components, EIS measurements were performed at each constant current density over a frequency range from 1 MHz to 1 Hz, with 10 points per frequency decade. The ohmic resistance of the full cell was determined in a two-electrode configuration (between

the anode and cathode). Additional EIS measurements were conducted in a three-electrode setup (between the anode and RefA, or between the cathode and RefC) to estimate the ohmic resistances of the anode and cathode compartments separately.

Product analysis

The composition of product stream was analysed using an online gas chromatography (Compact GC), with periodic injections every 5 min. The GC is fitted with molecular sieve 5A columns and two thermal conductivity detectors (TCDs) for the detection of hydrogen and carbon monoxide.

The Faradaic efficiency (FE) of the gas products was calculated using the following equation:

$$FE_{product} = \frac{P \times V \times c_{product} \times F}{R \times T \times z \times J} \quad (3)$$

Where P is the pressure of 101.3 kPa, V is the volumetric flow rate of the outlet gas mixture measured by GC, $c_{product}$ is the volume fraction of the product determined from GC calibration using standard mixtures, F is the Faraday constant (96485 C mol^{-1}), R is the gas constant ($8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$), T is the temperature of 298 K, z is the number of electrons transferred per product molecule, and J is the total current.

The current density j can be calculated as:

$$j = \frac{J}{A} \quad (4)$$

Where A is the active electrode area (2.25 cm^2).

The partial current density of each product could be determined via:

$$PCD_{product} = j \times FE_i \quad (5)$$

Material Characterization

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) was performed using a Hitachi TM3030 microscope. We estimated the electrochemical surface area (ECSA) of cathodes in MEAs by measuring the double-layer capacitance. The capacitance can be determined by conducting cyclic voltammetry (CV) at scan rates ranging from 0.01 to 0.5 V s^{-1} within a 0.1 V potential window in the non-Faradaic region. From the slope of the capacitive current versus scan-rate plots, the double-layer capacitance was determined and normalized by the specific capacitance of smooth Ag foil (0.119 mF cm^{-2}) to calculate the ECSA values³. The zeta potential of the coating films and IEMs was determined using an electrokinetic analyzer - SurPASS (Anton Paar GmbH, Graz, Austria)

by measuring the streaming potential as a function of the applied channel pressure over a range of pH values.

Micro-CT Scanning and Analysis

Micro-CT scanning was performed with a Phoenix Nanotom M (Waygate Technologies) operated using xs control and phoenix datos|x acquisition software.

Electrode samples were mounted in a bundle for scanning simultaneously. A fifteen minute scan was conducted collecting 1799 projections through a full 360° rotation of the specimens. An x-ray tube voltage and current of 80 kV and 300 µA was used, respectively. Resolution was optimized to 10 µm to image the full sample on the detector in a single scan. Volume reconstruction of the micro-CT data was performed using the phoenix datos|x reconstruction software applying an inline median filter, ROI-CT filter and beam hardening correction filter during reconstruction and exported in a 32-bit format.

The reconstructed volume was imported to Avizo3D Pro (Thermo Fisher Scientific) for analysis. Data was converted to 16-bit and individual electrodes cropped out of the volume for independent analysis. The Ag deposits in the CL are readily apparent in the micro-CT data, with metal appearing much brighter in scans. The volume of dense deposits ($V_{deposit}$, cm³) was segmented using Avizo's interactive top-hat tool to threshold deposits consistently for each electrode (Figure S24). The remaining volume of the CL was then determined using an ambient occlusion algorithm to segment space around the metal deposits in the CL ($V_{occluded}$, cm³). The CL density (mg cm³) was determined using:

$$CL_{density} = (Ag_{loading_{rate}} * A_{geo}) / (V_{deposit} + V_{occluded}) \quad (6)$$

DRT analysis

In this work, DRT calculation was implemented through an open-source toolbox provided by the Ciucci group⁴. The key parameters used were the same as those reported in the previous work⁵.

Part II: Supporting Figures

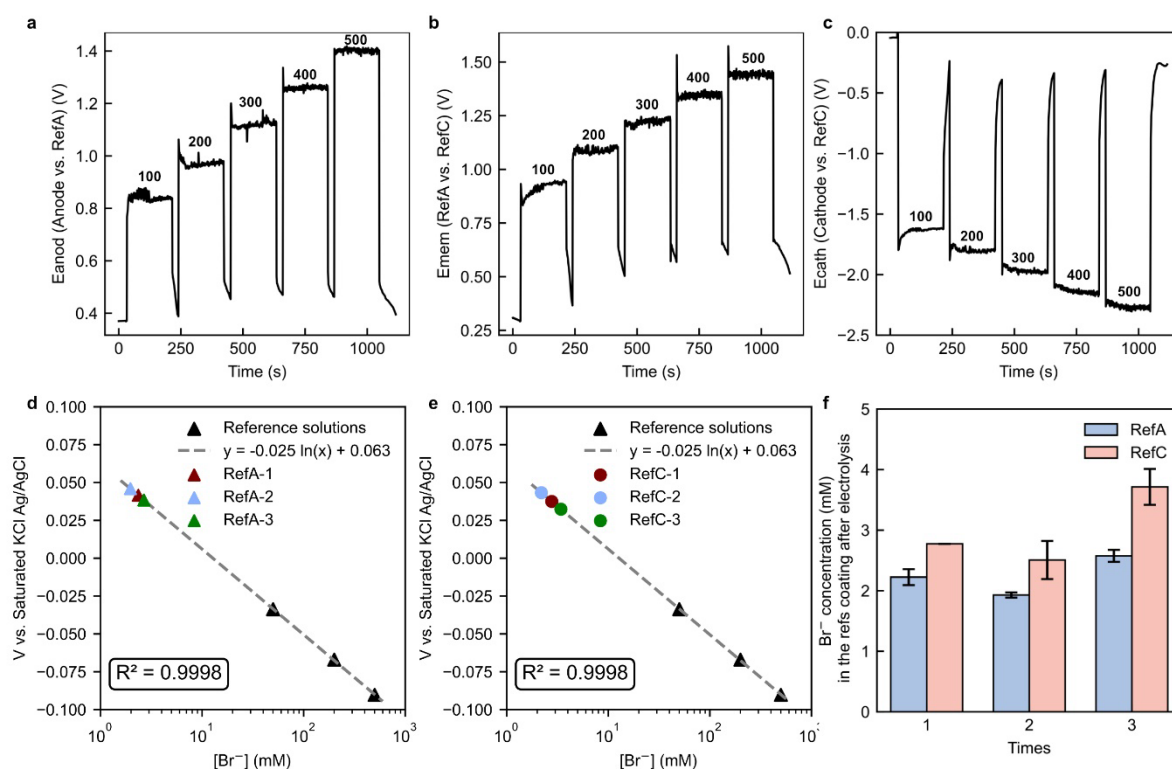


Figure S1 Measured potentials of (a) anode, (b) transmembrane, and (c) cathode by using coated Ag/AgBr electrodes, as a function of time at different current densities ranging from 100 to 500 mA cm⁻² in a customized BPM-based MEA system. The Nernstian slope was determined from OCV measurements where the ‘Reference solutions’ points are uncoated Ag/AgBr electrodes in reference electrolyte solutions containing varied Br⁻ concentrations with 0.5 M K₂SO₄. RE at anode side (RefA) is the fully coated reference placed at the anode side, while RE at cathode side (RefC) is positioned at the cathode side during CO₂ electrolysis. Similar OCV measurements were performed for the coated Ag/AgBr electrodes, including (d) RefA and (e) RefC in pure 0.5 M K₂SO₄ solution and were repeated three times after conducting each electrolysis test. (f) Measured Br⁻ concentration in Sustainion coating on Ag/AgBr after the 1st, 2nd and 3rd repetitive test in BPMEA for CO₂ electrolysis. (After each usage, the coated Ag/AgBr was re-soaked in 1M KBr for at least 48 h before reuse). The error bar indicates the standard deviation of measured values for 2 repetitive experiments.

Notes: OCV measurements were conducted for the uncoated Ag/AgBr in different electrolytes comprised of varied Br⁻ concentration and 0.5 M K₂SO₄, as well as for the coated Ag/AgBr in 0.5 M K₂SO₄.

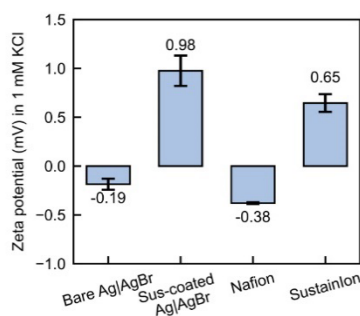


Figure S2 Measured zeta potentials of different surfaces in 1mM KCl electrolyte, including bare Ag/AgBr, Sustainion ionomer-coated Ag/AgBr, Nafion membrane, and Sustainion membrane. The error bar indicates the standard deviation of measured values for 2 repetitive tests.



Figure S3 Photo of delaminated PFSA (same functional group as Nafion) ionomer-based coating on Ag|AgBr RE.



Figure S4 Photo of a delaminated and carbonated coating layer on Ag|AgBr RE composed of a of fluorinated ethylene propylene (FEP) polymer and perfluorosulfonic acid (PFSA) ionomer after annealing up to 265 °C, based on the previous reported method².

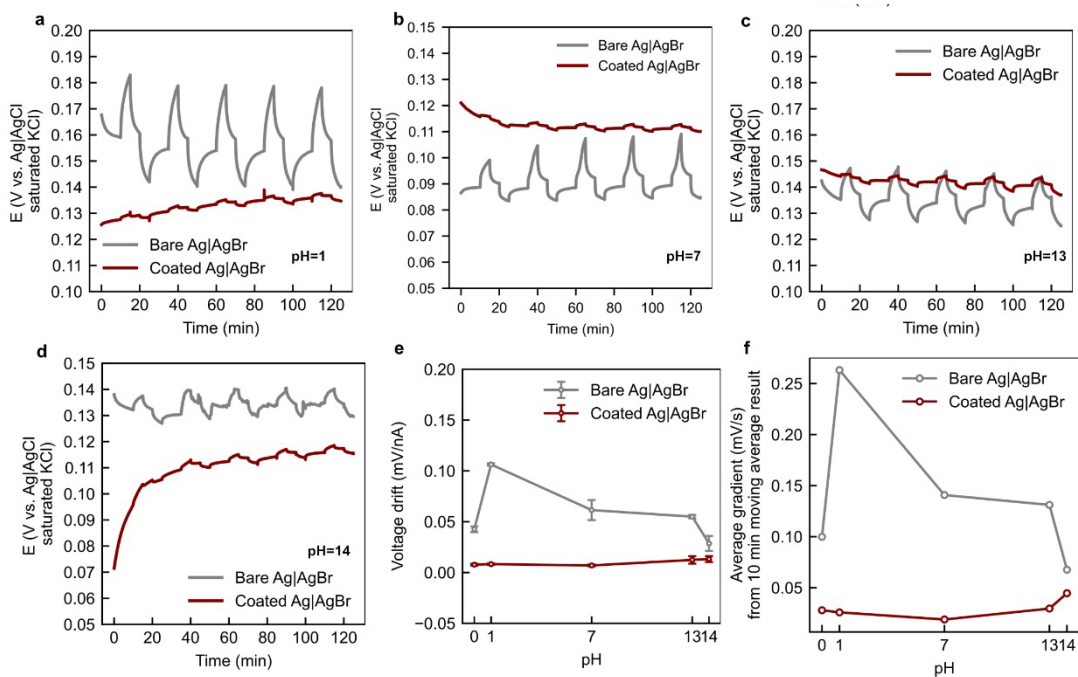


Figure S5 Polarization profiles of the Sustainion ionomer-coated and bare Ag|AgBr REs at (a) pH 0, (b) pH 1, (c) pH 13 and (d) pH 14 under simulated operating conditions. Based on polarization profiles, we obtain the comparison results of (e) the voltage drifts and (f) the average gradient from 10 mins moving average plots of the coated and bare Ag|AgBr in the electrolytes across a broad pH range from 0 to 14.

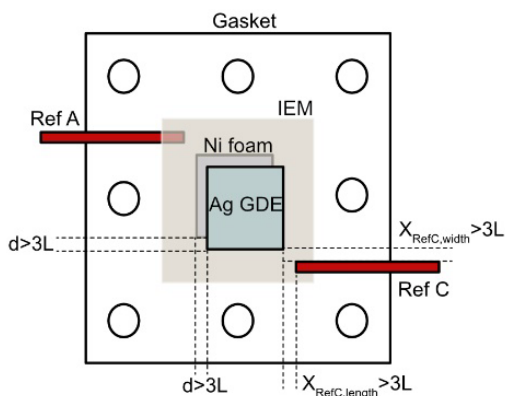


Figure S6 Illustration of the misaligned electrode configuration where d is the misaligned distance and L is the membrane thickness. For example, Fumasep FBM bipolar membranes is thicker than monopolar membranes with 130 -160 μm thick.

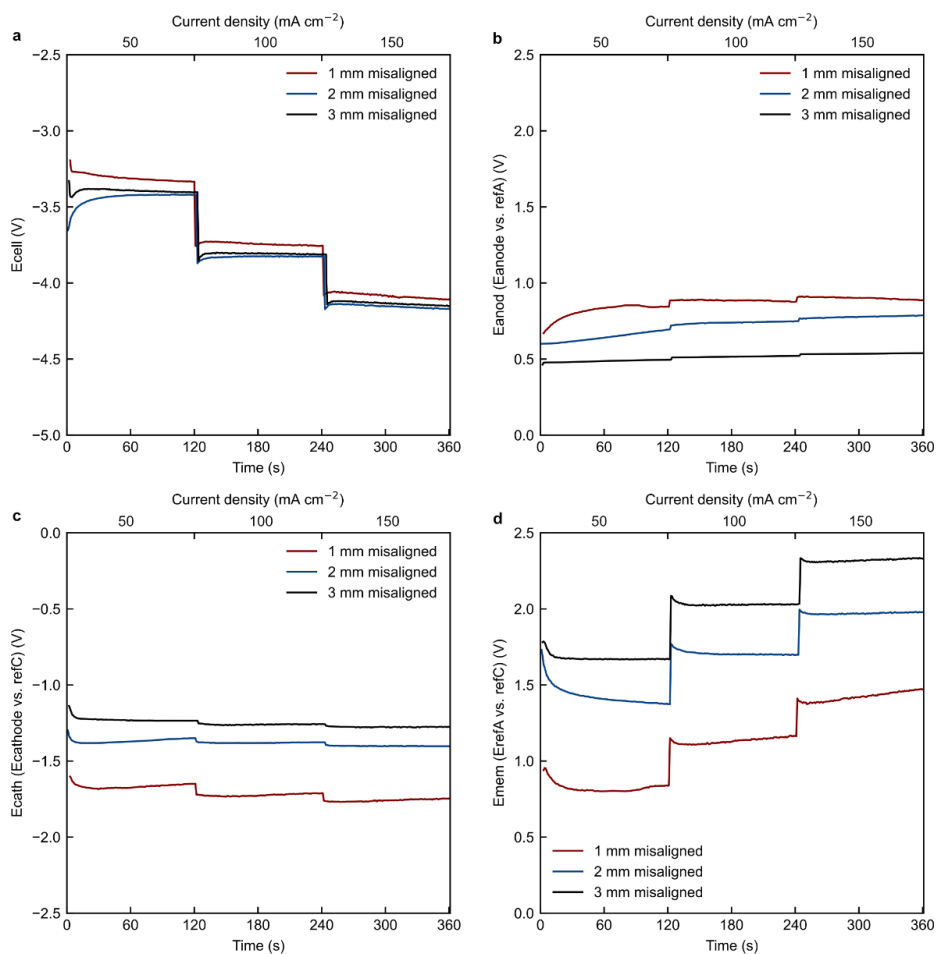


Figure S7 Measured potentials of (a) whole cell, (b) anode, (c) cathode, and (d) membrane as a function of time at different current densities ranging from 50 to 150 mA cm^{-2} under misaligned electrodes design by changing d but keeping same active area ($1.5 \times 1.5 \text{ cm}^2$).

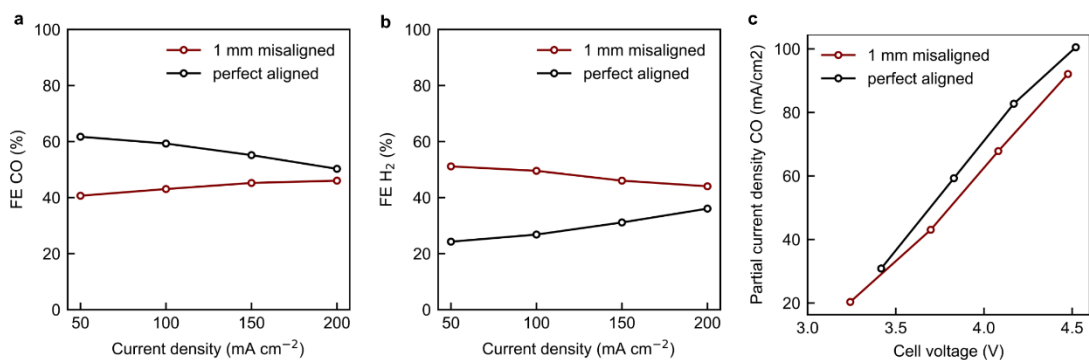


Figure S8 The FEs of (a) CO and (b) H₂ as a function of current density (50 to 200 mA cm^{-2}), and (c) the CO partial current density over cell voltage under the conditions of precise electrode alignment and intentionally electrode misalignment of 1 mm.

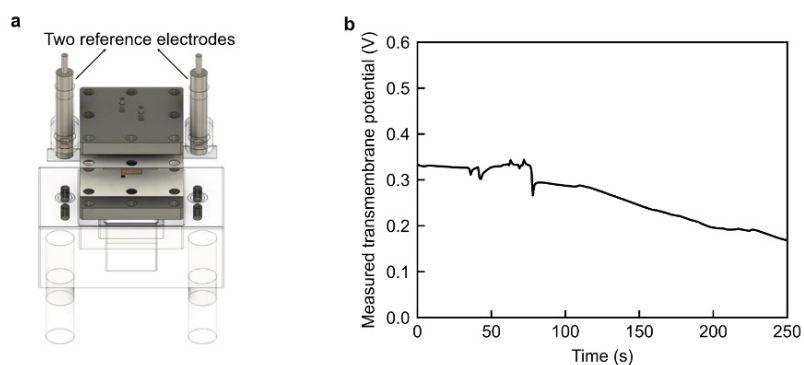


Figure S9 (a) Illustration of a typical transmembrane potential measurement configuration employing an extended membrane strip as a salt bridge with conventional REs. (b) Time-resolved transmembrane potential measured during water electrolysis under 10 mA cm^{-2} in an MEA configuration, using 1 M KOH as catholyte and $0.5 \text{ M H}_2\text{SO}_4$ as anolyte.

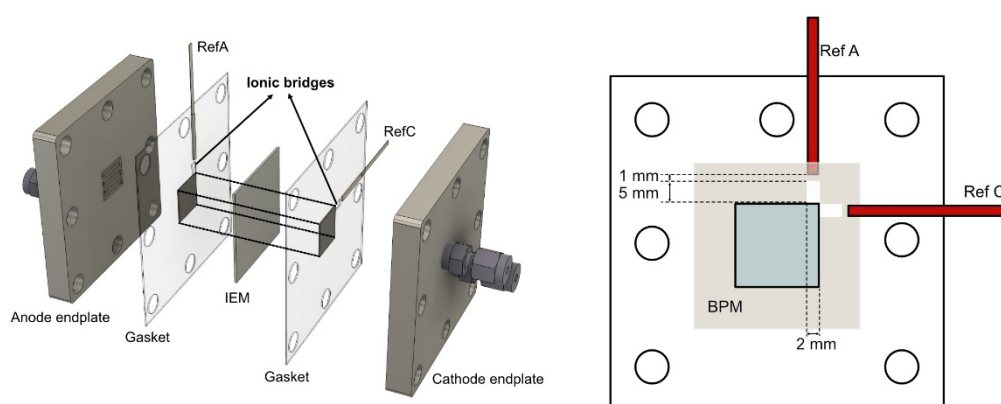


Figure S10 Schematic of voltage measurement setup and the corresponding REs placement and gasket cut design.

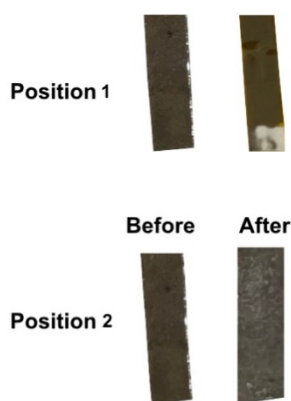


Figure S11 Photos of the REs placed on the anode side before and after 1 hour of electrolysis at Positions 1 and 2. In the case of Position 1, the intrusion of alkaline electrolyte (1 M KOH anolyte) led to corrosion of RefA.

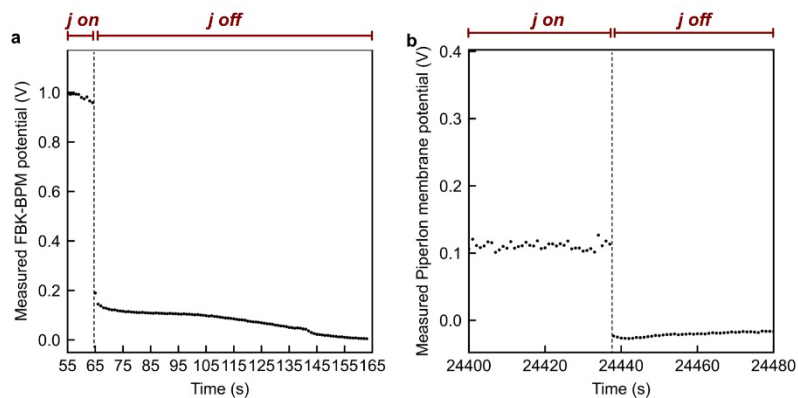


Figure S12 OCV decay process for measured transmembrane potential after electrolysis in (a) FBK-based BPMEA and (b) PiperION-based AEMEA. j_{on} indicates with applied current density while j_{off} means the open circuit condition without applied power.

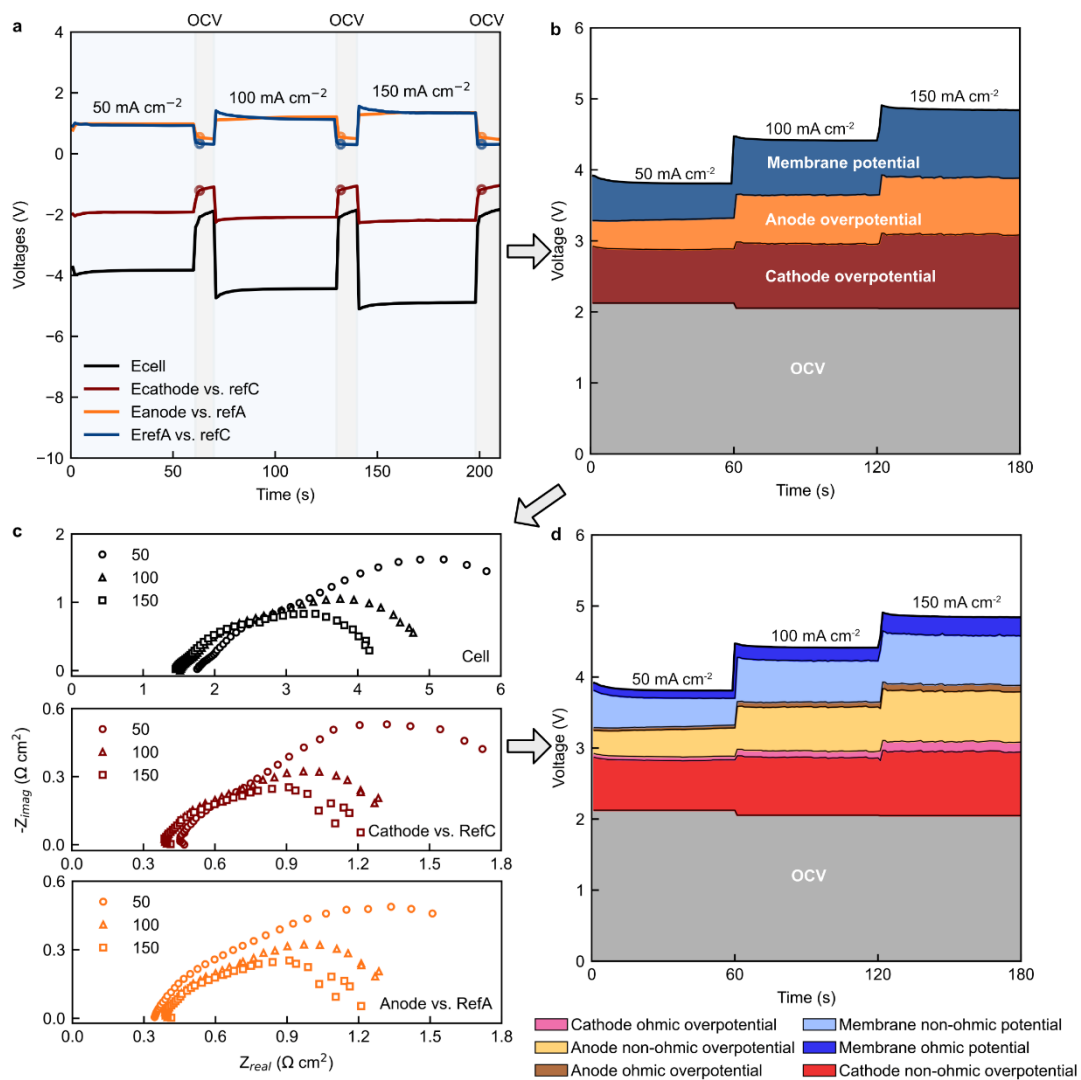


Figure S13 Workflow for overpotential determination in FBK-based BPMEA for CO₂RR.

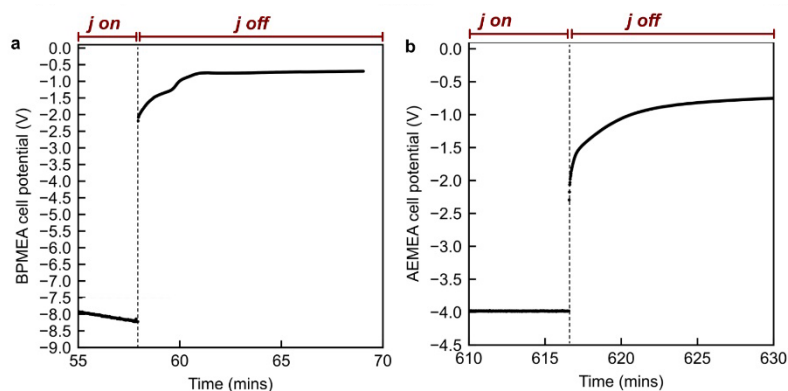


Figure S14 OCV decay process of whole cell potential after electrolysis in (a) FBK-based BPMEA and (b) PiperION-based AEMEA. j_{on} indicates with applied current density while j_{off} means the open circuit condition without applied power.

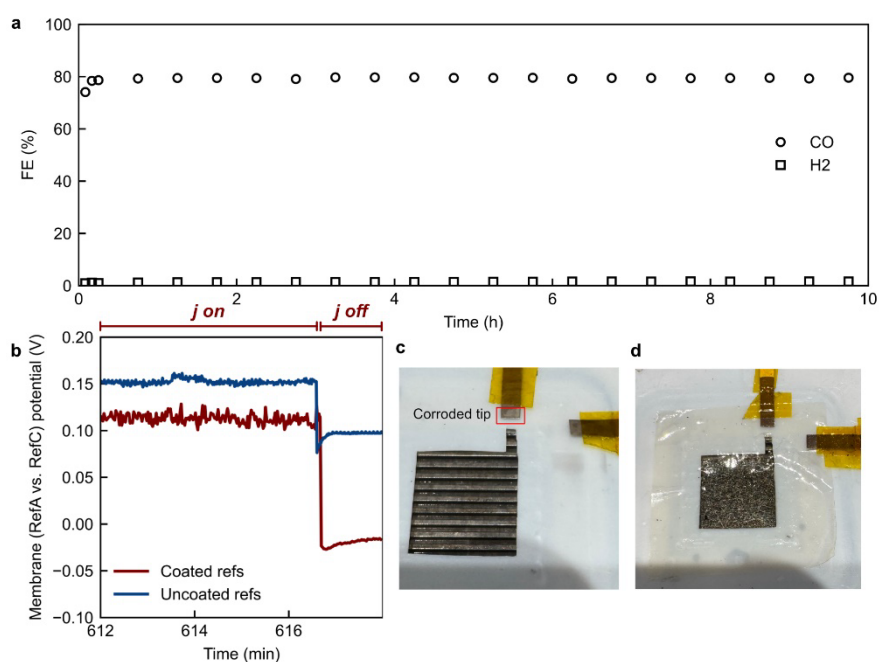


Figure S15 (a) FEs of CO and H₂ as a function of time during 10 h electrolysis at 100 mA cm⁻² in AEMEA using 0.1M CsHCO₃ as the anolyte. (b) The corresponding measured membrane potential during OCV decay process after electrolysis. Photos of (c) uncoated and (d) coated REs after electrolysis.

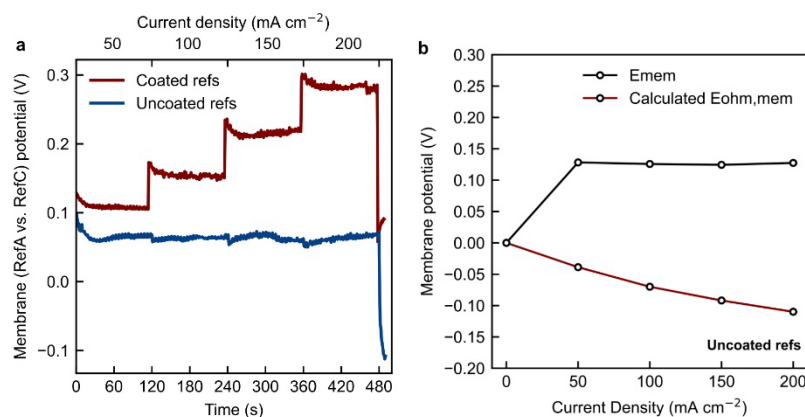


Figure S16 (a) Transmembrane potentials measured using coated and uncoated Ag|AgBr REs as a function of time at different current densities (50 to 200 mA cm^{-2}). (b) The comparison between the measured transmembrane potential and the membrane ohmic potential calculated from EIS measurements using the uncoated Ag|AgBr REs.

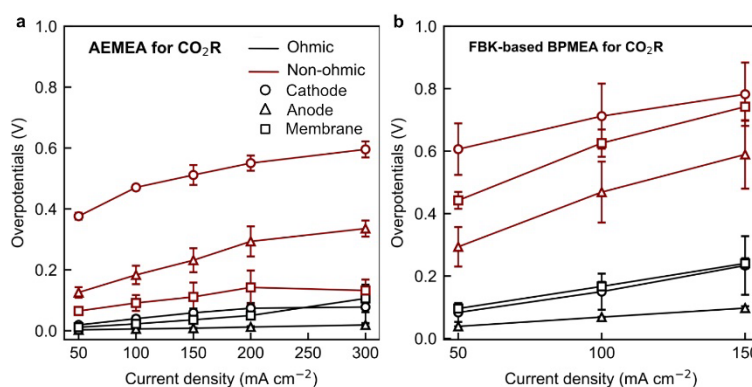


Figure S17 Deconvoluted contributions of anode, membrane, and cathode non-ohmic and ohmic overpotentials as a function of current density for (a) AEMEA and (b) BPMEA. The error bar indicates the standard deviation of measured values for at least 2 repetitive experiments.

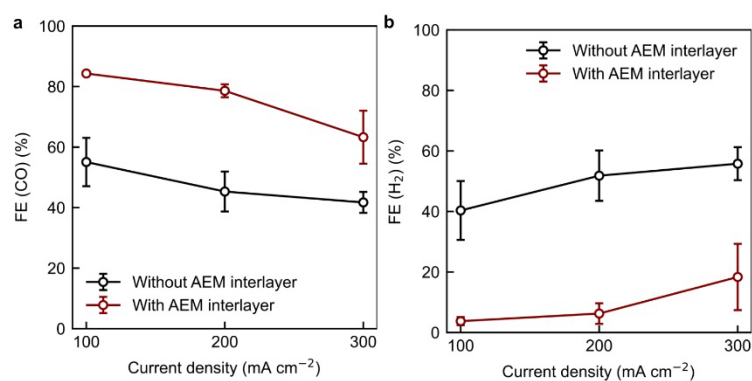


Figure S18 Comparison of (a) FE(CO) and (b) FE(H_2) as a function of current density for the customized BPM with and without an AEM interlayer between CL and the membrane. The error bar indicates the standard deviation of measured values for 2 repetitive experiments.

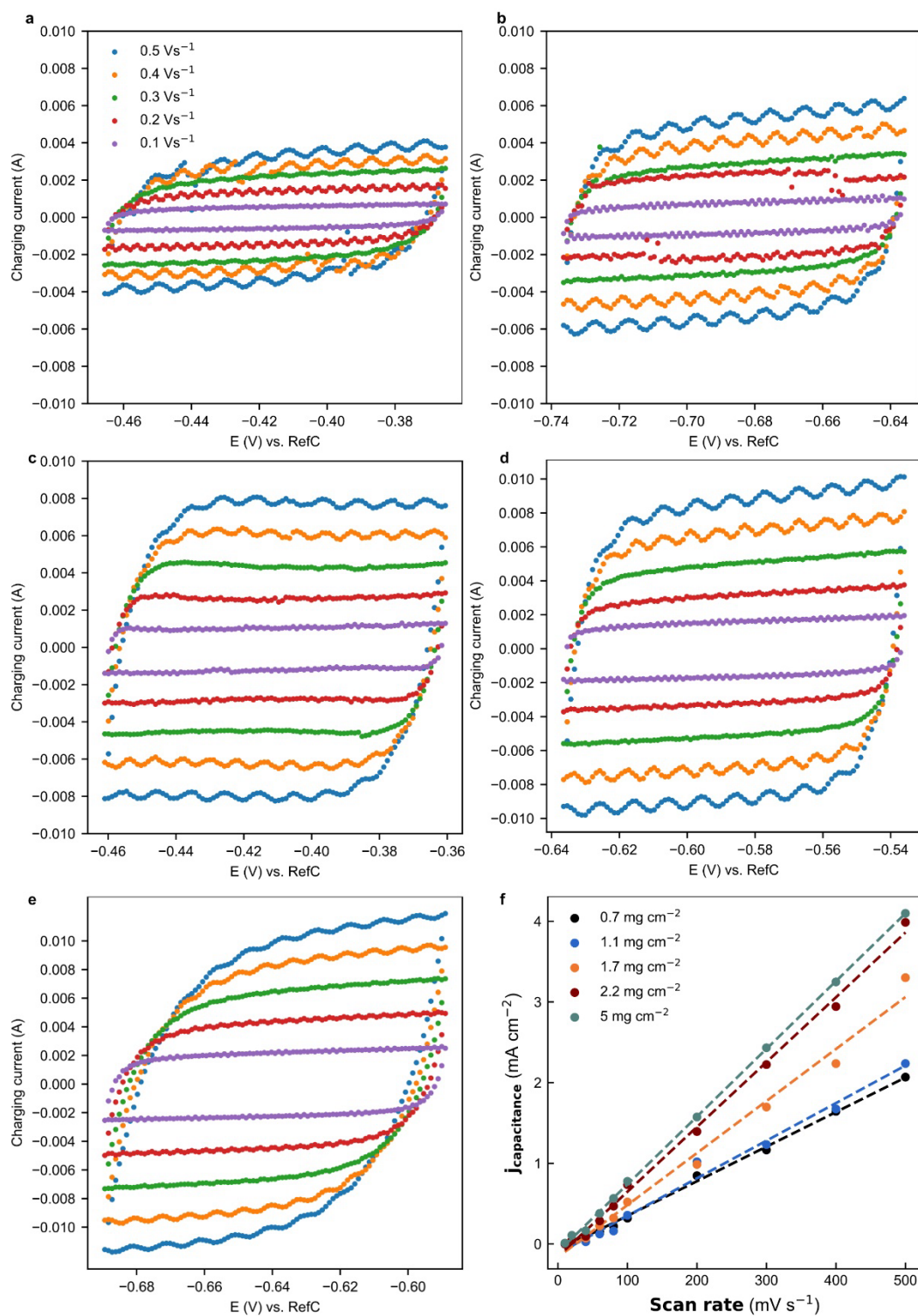


Figure S19 The cyclic voltammetry measured at different scan rates from 0.1 to 0.5 V s⁻¹ for Ag NP catalysts with loadings of (a) 0.7, (b) 1.1, (c) 1.7, (d) 2.2, and (e) 5.0 mg cm⁻² after CO₂ electrolysis. (f) Comparison of the capacitive current as a function of scan rate for Ag NP catalysts with loadings from 0.7 to 5 mg cm⁻².

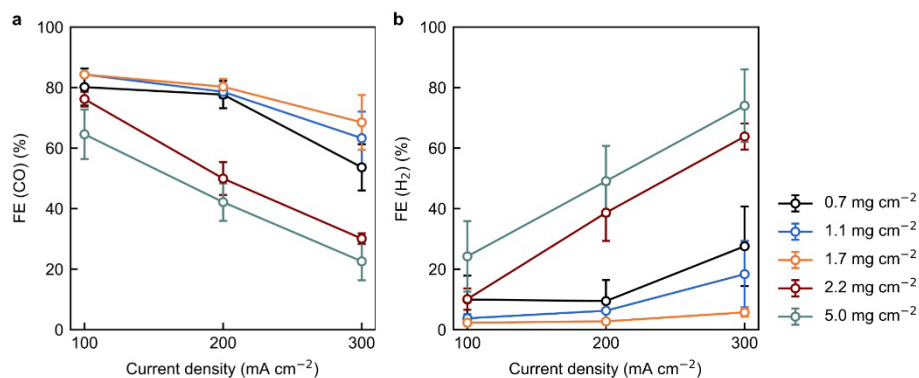


Figure S20 Comparison of (a) FEs(CO) and (b) FEs(H₂) as a function of current density for Ag NP catalysts with loadings of 0.7 to 5 mg cm⁻² using a customized BPM incorporating an AEM interlayer between CL and the membrane. The error bar indicates the standard deviation of measured values for at least 2 repetitive experiments.

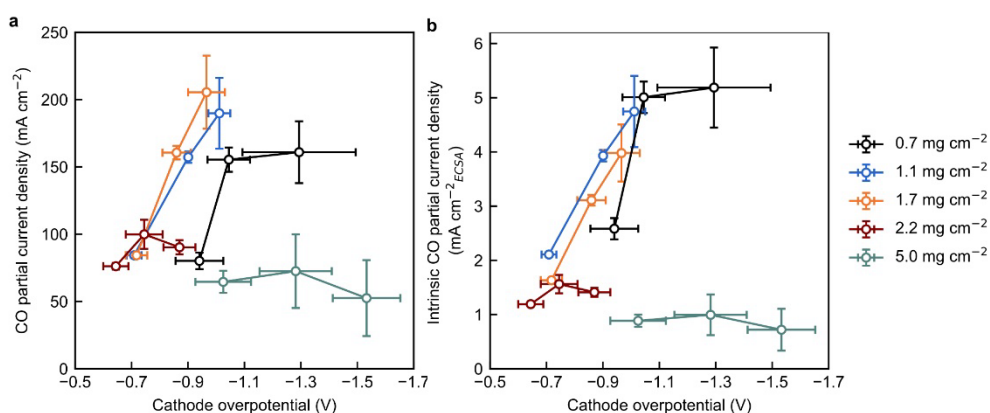


Figure S21 Comparison of (a) CO partial current density and (b) intrinsic CO₂R activity as a function of cathode overpotential for the Ag NP catalysts with loadings of 0.7 to 5 mg cm⁻². The error bar indicates the standard deviation of measured values for at least 2 repetitive experiments.

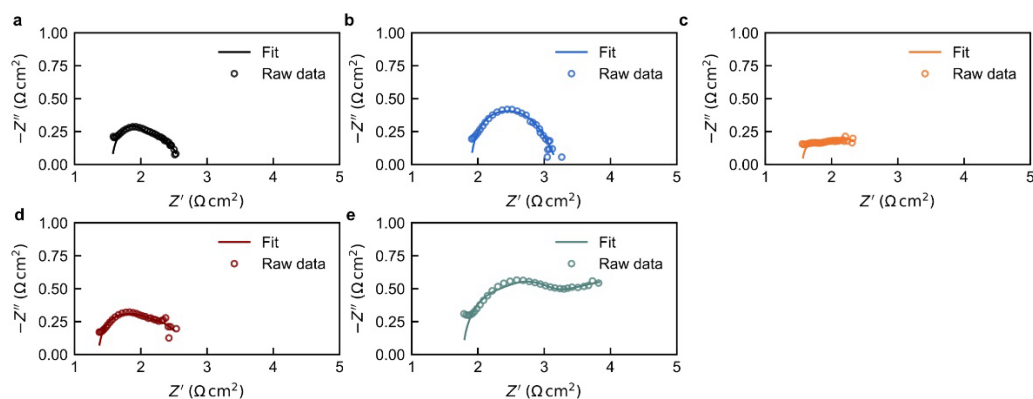


Figure S22 Full cell Nyquist plots of measured data and fitted values from EIS of catalysts with loadings of (a) 0.7, (b) 1.1, (c) 1.7, (d) 2.2, and (e) 5.0 mg cm⁻² under CO₂ electrolysis at 200 mA cm⁻².

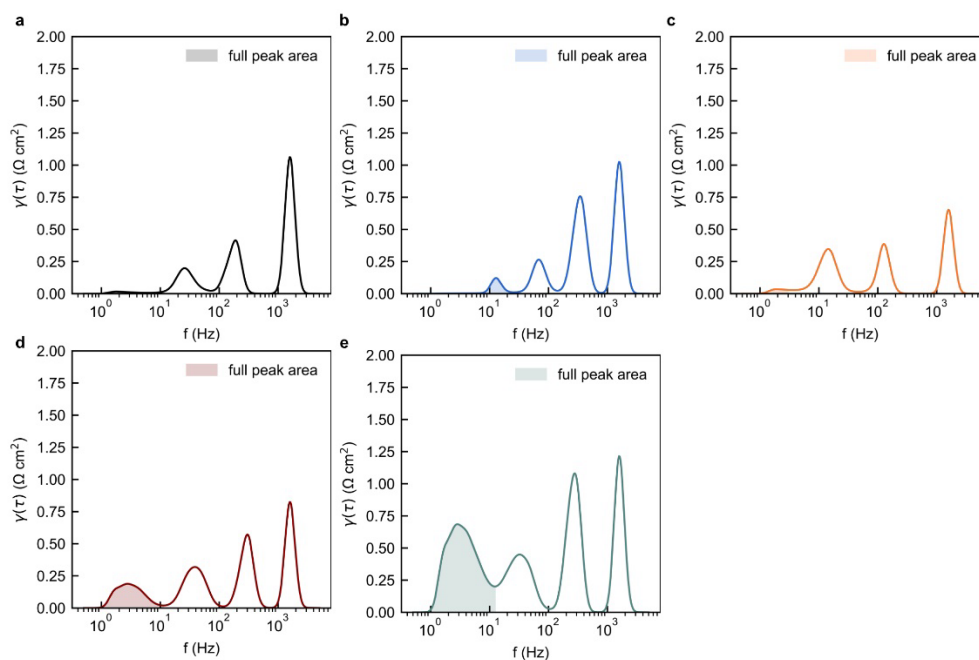


Figure S23 DRT analysis for catalysts with loadings of (a) 0.7, (b) 1.1, (c) 1.7, (d) 2.2, and (e) 5.0 mg cm⁻² under CO₂ electrolysis at 200 mA cm⁻². The shaded peak areas correspond to CO₂ mass transport resistance.

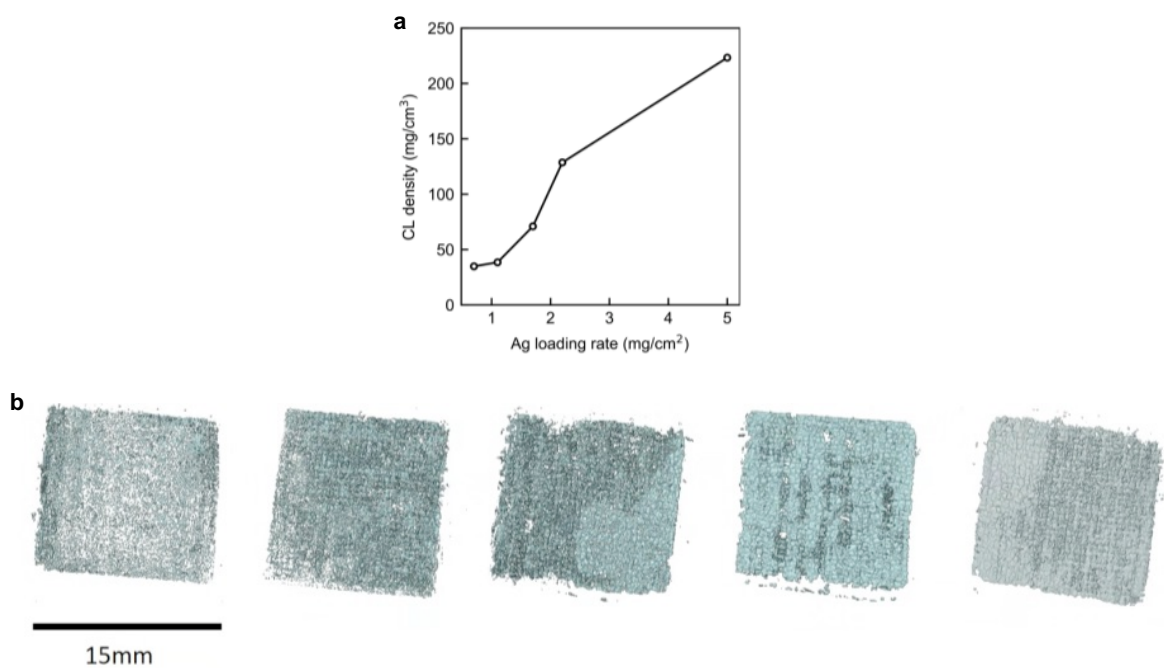


Figure S24 (a) The Micro-CT result of CL density over Ag catalyst loadings. (b) 3D render of segmented dense deposits on CL at cathode under increasing Ag loading rates of 0.7, 1.1, 1.7, 2.2 and 5 mg cm⁻² from left to right.

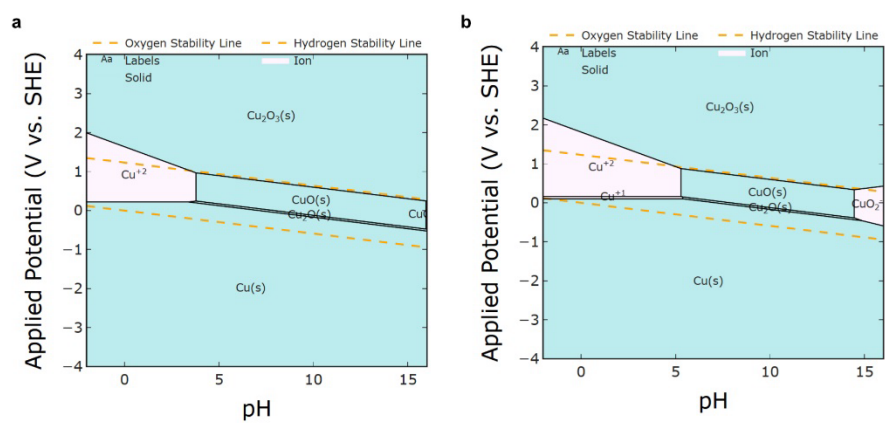


Figure S25 Pourbaix diagram for Cu. (a) $[Cu]=0.1$ M and (b) $[Cu]=0.0001$ M. Data accessed from the Materials Project Pourbaix (<https://materialsproject.org/pourbaix>) on 2026/04/08

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