

Supporting Information

Bronze Alloys with Tin Surface Sites for Selective Electrochemical Reduction of CO₂

Anthony Vasileff¹, Chaochen Xu¹, Lei Ge², Yao Zheng^{1}, Shi-Zhang Qiao^{1*}*

¹School of Chemical Engineering, The University of Adelaide, Adelaide SA 5005, Australia

²School of Chemical Engineering, The University of Queensland, Brisbane QLD 4072, Australia

Corresponding Authors

[*s.qiao@adelaide.edu.au](mailto:s.qiao@adelaide.edu.au); yao.zheng01@adelaide.edu.au

1. Experimental Section

Materials

All chemicals (analytical reagent grade) used in this work, including copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), sodium borohydride (NaBH_4), polyvinylpyrrolidone (PVP; 40000 m.w), and potassium bicarbonate (KHCO_3) were purchased from Sigma-Aldrich and used without further purification. Carbon paper (CP, AvCarb MGL 190, Product Code: 1594008) was bought from FuelCellStore. Ultra-pure water ($18.2 \text{ M}\Omega \cdot \text{cm}$, PURELAB Option-Q) was used in all experiments. Scientific grade (HiQ) 5 % H_2/Ar was purchased from BOC. Ultra high purity N_2 (99.999 %) and laser grade CO_2 (99.995 %) were purchased from BOC and used in all electrochemical experiments.

Synthesis of Electrocatalysts

Preparation of Bronze Alloy Nanoparticles: 30 ml of 1 mM PVP in water was added to a three neck flask which was then purged with nitrogen for 30 min under stirring. Specific ratios of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were added to 5 ml of water and the mixture was sonicated for 10 min to form a homogenous solution. Excess NaBH_4 was dissolved in 5 ml of water and then added to the flask via syringe. Following this, the salt solution was added dropwise to the flask via syringe. The nanoparticles were then washed in water three times and then in ethanol three times by centrifugation (8500 rpm). The washed nanoparticles were dried under vacuum at 60°C for 12 h. The dried powder was then transferred to a silica boat and annealed at 500°C (heating rate of 5°C min^{-1}) for 5 h under a flow of 5 % H_2/Ar (30 ml min^{-1}) and cooled at a rate of 1°C min^{-1} . The alloy nanoparticles were then collected and used for electrode fabrication.

Preparation of Cu Nanoparticles: The method used to prepare the Cu nanoparticles was the same as that outlined for the alloy nanoparticles. However, no $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was used in the synthesis process.

Preparation of Sn Nanoparticles: The method used to prepare the Sn nanoparticles was the same as that outlined for the alloy nanoparticles. However, no $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was used in the synthesis process and the nanoparticles were annealed at 200 °C instead of 500 °C.

Electrode Preparation: CP (1 x 1 cm) was pre-treated by plasma cleaning and acid washing to remove metallic contaminants. The treated carbon paper was washed with water and dried in a vacuum oven at 60 °C. To prepare the catalyst suspensions, each alloy/metal nanoparticle powder was dispersed in ethanol at 20 mg ml⁻¹. The resultant mixtures were then sonicated for 1 h to form homogenous suspensions. 50 µl of catalyst suspension (loading of 1 mg cm⁻²) was then dropped on each side of a dried piece of carbon paper and dried in a vacuum oven for 12 h at 60°C.

Material Characterizations

The chemical composition of the nanoparticles was measured using EDS (SuperX) under STEM mode (FEI Titan Themis, 200 kV). SAED patterns were collected under TEM mode (Philips CM200, 200 kV). Crystal structure and chemical structure of the samples were characterized by XRD (Rigaku MiniFlex, Cu K α), and by XPS (Kratos Axis Ultra, mono Al K α (1486.6eV)).

Electrochemical Measurements

Electrochemical measurements were performed on a 760E bipotentiostat (CH Instruments, Inc., USA) using a gas tight three-electrode H-cell with anode and cathode compartments separated by a proton exchange membrane (Nafion 117). The alloy NP/CP samples were directly applied as the working electrodes. Ag/AgCl (4.0 M KCl) and a RuO₂ coated titanium mesh electrode (25 x 50 mm) were used as the reference and counter electrodes, respectively. All electrochemical measurements were conducted under stirring in KHCO₃ electrolyte which had been saturated with either N₂ or CO₂. CV scans at 100 mV s⁻¹ between -1.0 and -1.4 V vs. Ag/AgCl were first recorded until a stable current response was obtained and LSV scans were

obtained at a scan rate of 5 mV s⁻¹. For chronoamperometric responses, the cell was first purged with CO₂ (10 min, 100 ml/min) and sealed. After applying a reduction potential, 100 µl of the head space was drawn using a gas tight syringe. The gas sample was manually injected into the inlet of a gas chromatograph (GC, 7890B, Agilent, USA) in splitless mode. The GC was fitted with a Plot-Q and a 5Å sieve column in series, TCD and methanizer/FID detectors, and Ar as the carrier gas. The catholyte was collected and analyzed using H¹ nuclear magnetic resonance spectroscopy (NMR, A500a DD2 500 MHz, Agilent, USA). H¹ chemical shifts were referenced to phenol and DMSO internal reference peaks in 10 vol% D₂O solvent. For the electrolyte concentration study, salinity of 1 M was maintained between the different bicarbonate solutions by adding KCl.

All electrochemical measurements were iR compensated and all potentials discussed in the results were given against the reversible hydrogen electrode (RHE). The conversion of reference potentials from Ag/AgCl to RHE was calculated using the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.224 + 0.059pH$$

Overpotentials for CO and HCOO⁻ production were calculated using the following equation:

$$\eta = E_{RHE} - E^0$$

Where E⁰ is the equilibrium potential which is -0.11 V for CO production and -0.02 V for formate production.

2. Supplementary Figures

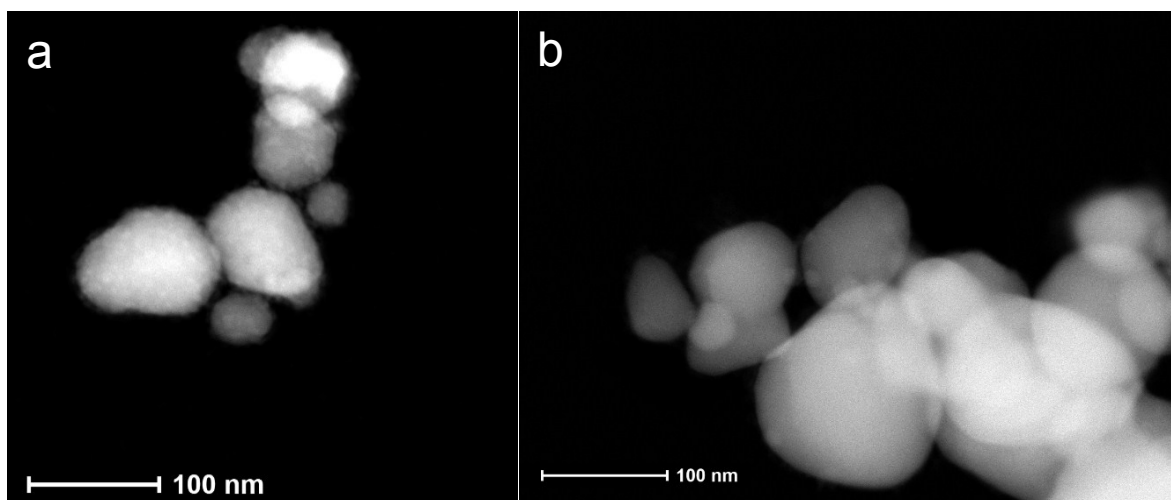


Figure S1. STEM images of a) α bronze and b) η' bronze nanoparticles.

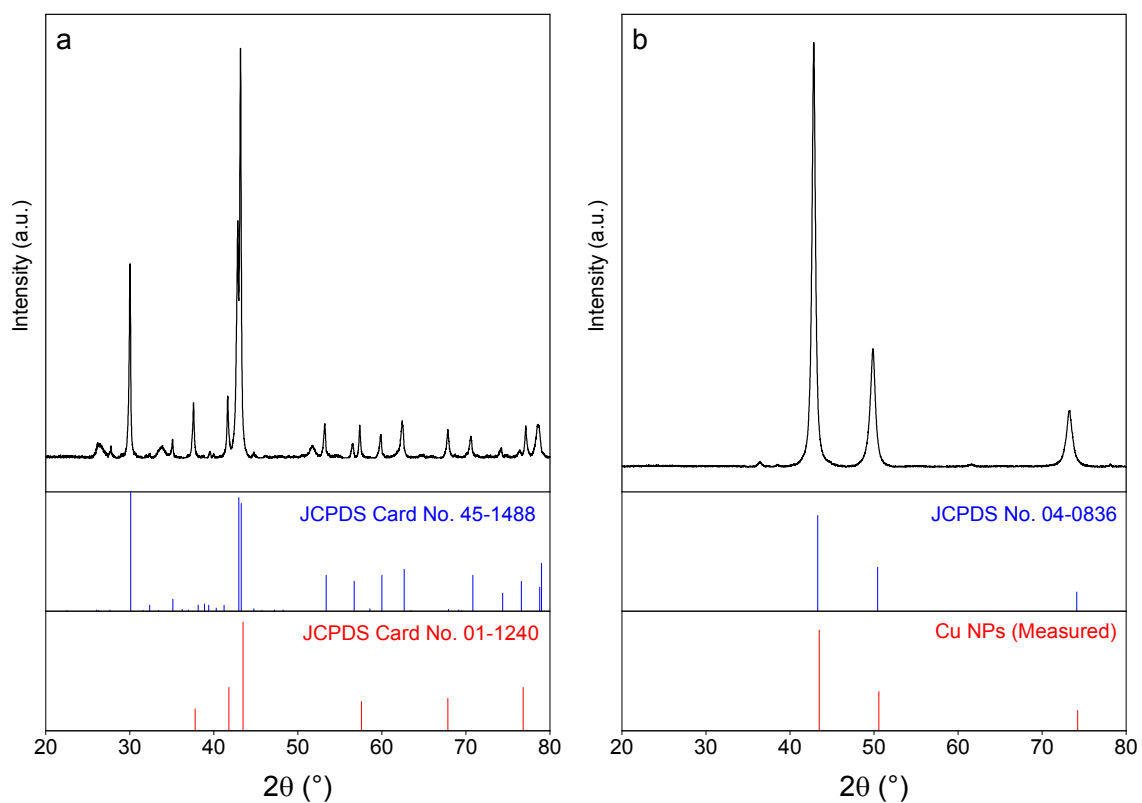


Figure S2. XRD spectra of a) η' bronze and b) α bronze nanoparticles.

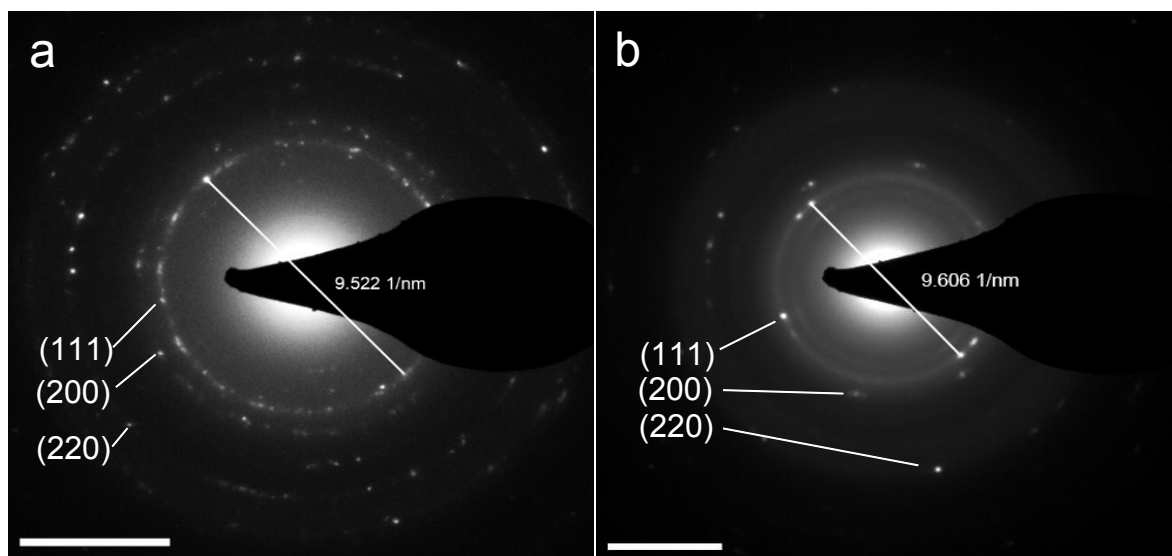


Figure S3. SAED image of a) α bronze NPs and b) Cu NPs. Scale bar is 5 nm⁻¹ in each panel.

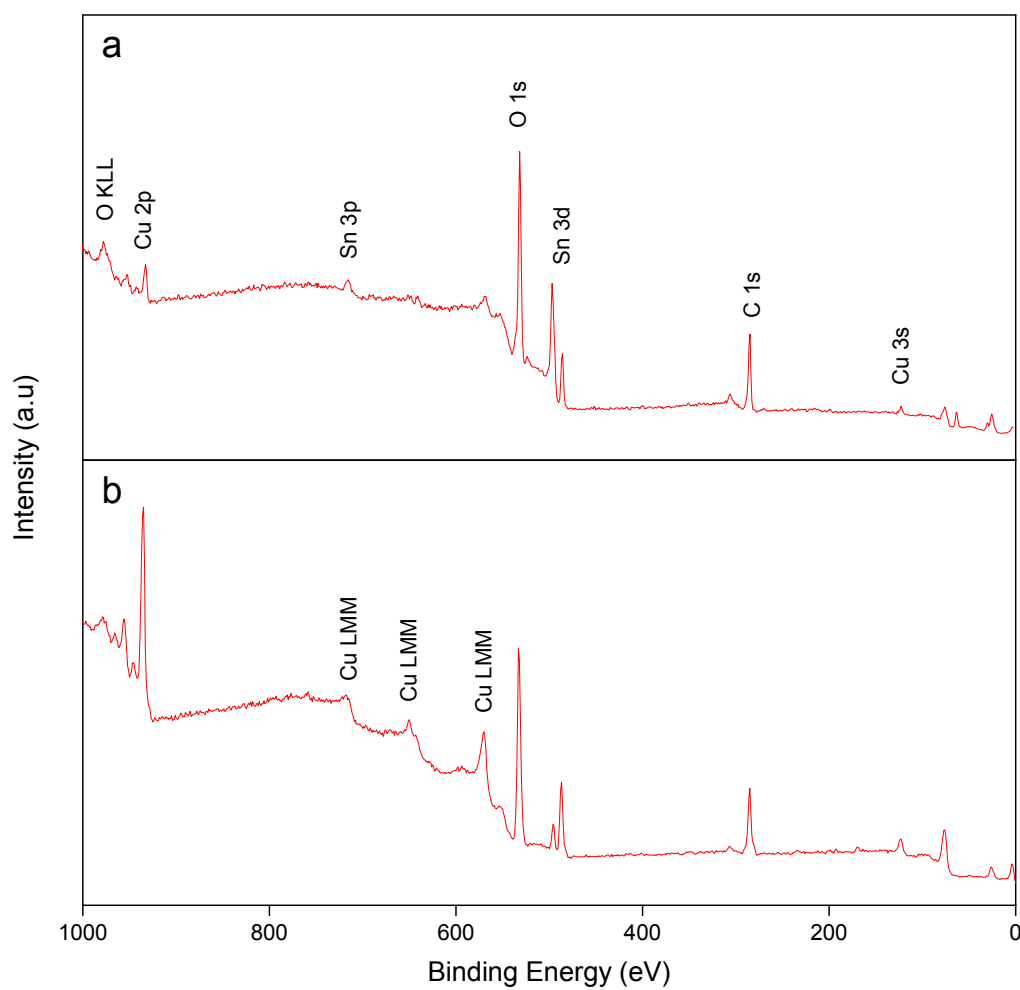


Figure S4. XPS Survey spectra for a) α bronze and b) η' bronze.

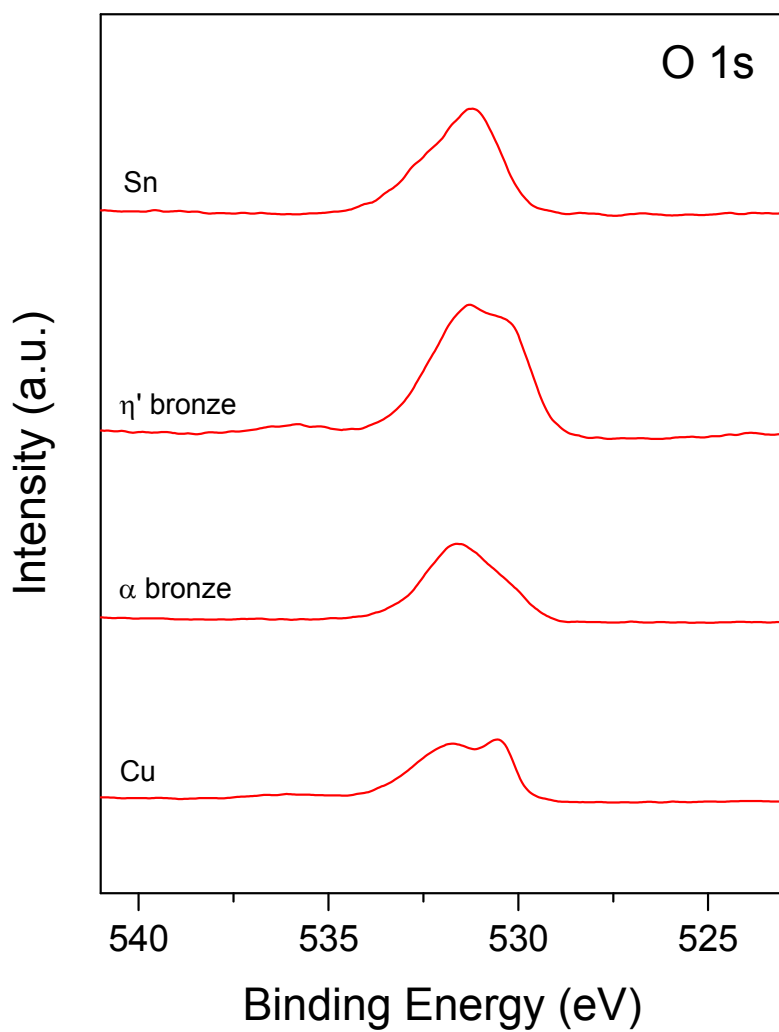


Figure S5. XPS O 1s spectra for the bronze NPs, Cu NPs, and Sn NPs.

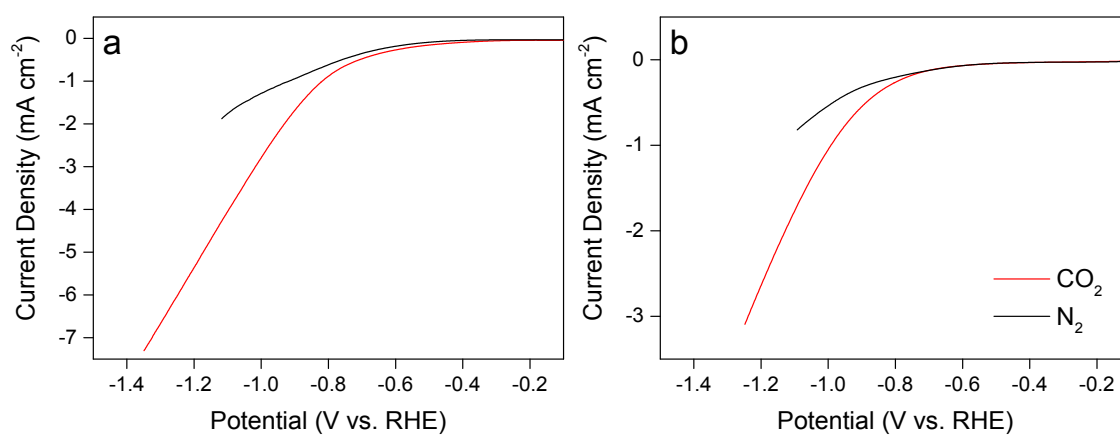


Figure S6. LSV plots in CO_2 (red line) and N_2 (black line) saturated 0.1 M KHCO_3 for a) α bronze and b) η' bronze.

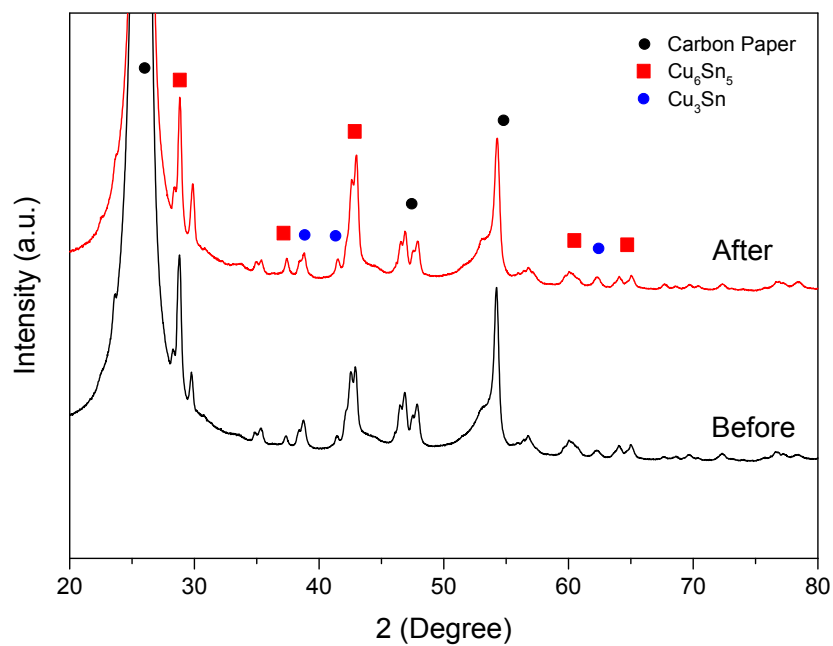


Figure S7. XRD spectra of η' bronze on carbon paper before and after the 6 h stability test.

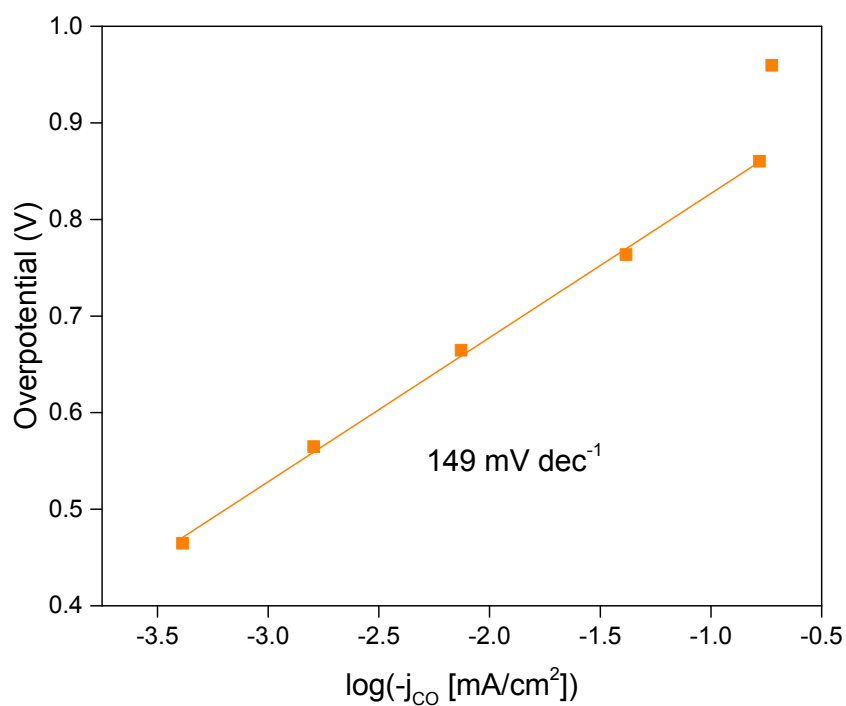


Figure S8. Tafel plot for CO formation on Cu NPs.

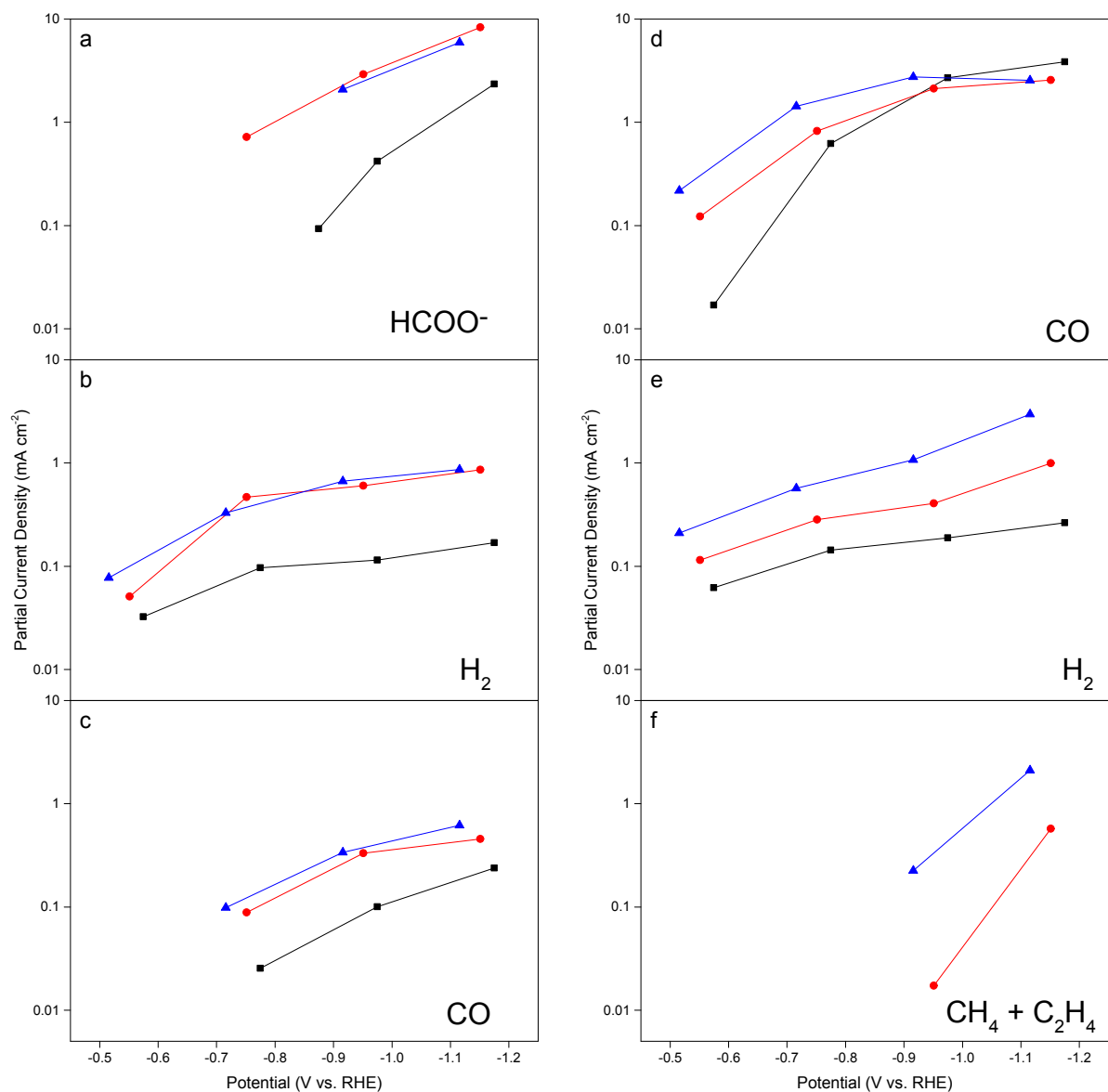


Figure S9. Figure S5. Plots of partial current in 0.1 M (black squares), 0.5 M (red circles), and 1.0 M (blue triangles) KHCO₃ electrolyte for various reduction products on a-c) η' bronze and d-f) α bronze. The ionic strength of the electrolyte was kept constant by the addition of KCl.

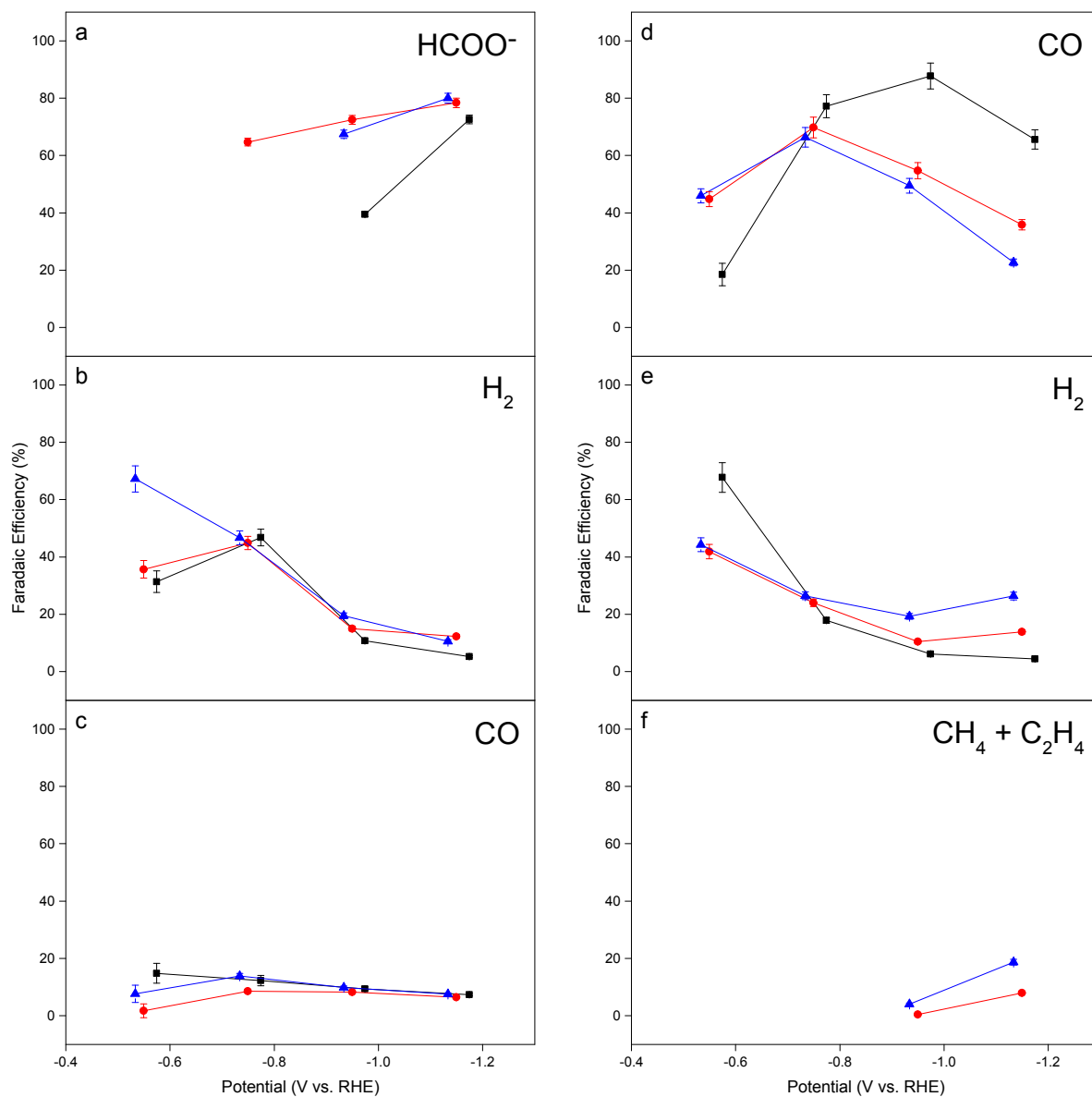


Figure S10. Plots of Faradaic efficiency in 0.1 M (black squares), 0.5 M (red circles), and 1.0 M (blue triangles) KHCO₃ electrolyte for various reduction products on a-c) η' bronze and d-f) α bronze. The ionic strength of the electrolyte was kept constant by the addition of KCl.

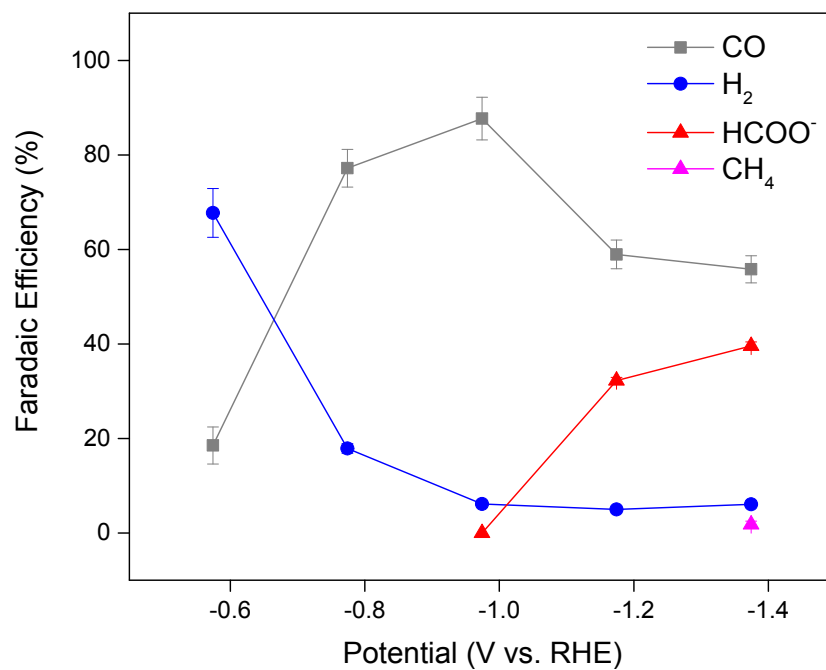


Figure S11. Faradaic efficiency profile for α bronze at higher overpotentials in 0.1 M KHCO₃ electrolyte for various reduction products.