Porous dendritic copper: an electrocatalyst for highly selective CO_2 reduction to formate in water/ionic liquid electrolyte

Supplementary Material

Experimental Section

Chemicals

All chemicals including 1-ethyl-3-methylimidazolium tetrafluoroborate (98%), [EMIM](BF_4), tetrabutylammonium tetrafluoroborate, n-Bu_4BF_4, (99%), $CuSO_4.5H_2O$ (99.9%), H_2SO_4 99.8% and CH_3CN (99.9%) were purchased from Sigma-Aldrich.

Methods

For the construction of the 3D Cu nanodendritic porous network, a solution of 0.2 M $CuSO_4$, 1.5 M H_2SO_4 was initially prepared. Then, a Cu plate electrode (1 cm^2) was immersed into the solution and a current of 0.5 A was applied using a galvanostat. Under these conditions, intense H_2 bubbles were generated resulting in Cu deposition in the form of a porous structure.[1,2,3]

Electrochemical measurements were performed in a three-electrode two-compartment cell using a Bio-logic SP300 potentiostat. Ag/AgCl/3M KCl (hereafter abbreviated as Ag/AgCl) was used as the reference electrode and placed in the same compartment as the working electrode. A platinum counter electrode was placed in a separate compartment connected by a glass-frit and filled with the electrolytic solution. The surface of the working electrode was 1 cm^2. All potential values are given versus the potential of the Fc^+/Fc couple added as an internal standard to the solution after measurement. In MeCN (8% H_2O, 0.1M n-Bu_4BF_4): $E_{1/2}$ (Fc^+/Fc) = 0.42 V vs Ag/AgCl. In [EMIM](BF_4)/H_2O (92/8 v/v): $E_{1/2}$ (Fc^+/Fc) = 0.37V vs Ag/AgCl.

H_2 measurements were performed by gas chromatography on a Shimadzu GC-2014 equipped with a Quadrex column, a Thermal Conductivity Detector and using N2 as a carrier gas. Carbon monoxide, methane and other volatile hydrocarbons from the gas phase were analyzed using a gas chromatograph (Shimadzu GC-2010) equipped with a methanizer, a flame induction detector (FID) and a shincarbon ST (Restek) column. Methanol was assayed

by gas chromatography (Shimadzu GC 2010) using an Rtx-1 column (Restek) and a flame induction detector (FID). Formate, oxalate and glyoxylate concentrations were determined by ionic exchange chromatography (883 Basic IC, Metrohm).

^{13}C-formic acid analysis was carried out by ^{13}C-NMR spectroscopy. Electrolysis using a modified Cu electrode was carried out in [EMIM](BF_4)/H_2O (92/8% v/v) under $^{13}CO_2$ saturation. After 2 h, formic acid was analyzed by ^{13}C-NMR spectroscopy after addition of 0.2 ml of CD_3CN to 0.8 ml of the electrolysis solution. A blank experiment with $^{12}CO_2$ was also carried out. For analysis of ^{13}CO a mass spectrometer was directly connected to the electrochemical cell during standard bulk electrolysis under $^{13}CO_2$ saturation. The gas reference was Argon (MW = 40). Gaseous products were then analyzed by mass spectrometry every third minute. Control experiments were also run: (i) electrolysis with an Argon-saturated solution; (ii) electrolysis saturation of non-labelled CO_2.

SEM images were acquired using a Hitachi S-4800 scanning electron microscope. TEM and HRTEM images were obtained on a JEM-2100F transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV.

The X-ray powder diffraction (XRD) patterns were recorded using an X'Pert Pro P analytical diffractometer equipped with either a Cu−Kα radiation source ($\lambda_{K\alpha1}$ = 1.540598 Å, $\lambda_{K\alpha2}$ = 1.544426 Å) or a Co−Kα radiation source ($\lambda_{K\alpha1}$ = 1.78897 Å, $\lambda_{K\alpha2}$ = 1.79285 Å) with an X'Celerator detector. Rietveld refinements[23] were performed with the Full Prof suite of programs.

Electrochemical diffusion surface area (A_{diff})

The Randles-Sevcik equation served to calculate A_{diff}, the diffusion surface area:[1]

$$i_p = 2.69 \times 10^5\, n^{3/2} D^{1/2} A_{diff} C\, \nu^{1/2} \qquad (1)$$

Here, i_p is the peak current corresponding to the reduction of redox species (Fe^{3+}/Fe^{2+}), obtained by CV of a $K_3[Fe(CN)_6]$ solution, n is the number of exchanged electrons, D is the diffusion coefficient of the analyte (7.5×10^{-6} cm^2 s^{-1}),[1] A_{diff} is the diffusional surface area, C (mol.cm^{-3}) is the molar concentration of the analyte and ν is the scan rate (V s^{-1}).

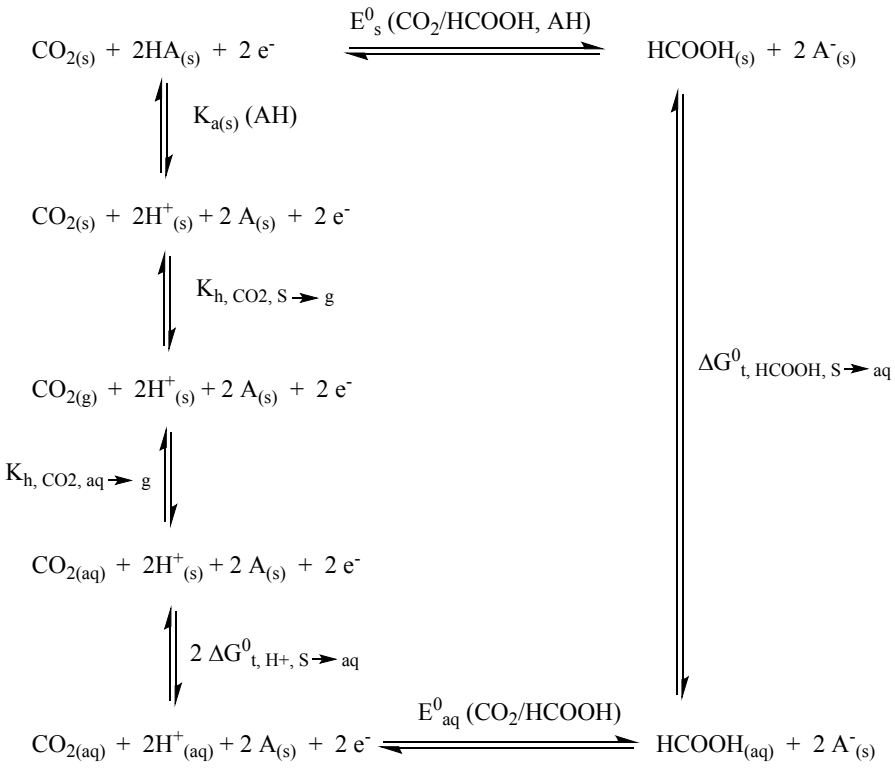
CV was recorded using either a Cu plate or a modified Cu electrode in 0.1M phosphate buffer pH 7.0 containing 5mM $K_3[Fe(CN)_6]$ (scan rate 50mV.s^{-1}). Using the experimental i_p value from the CV, application of the equation above allowed the determination of the A*diff* value.

Determination of the standard potential of the CO_2/HCOOH couple in CH_3CN

The method used below is directly taken from references [4] and [5] but we reproduce it in full for the sake of clarity. Of note however is the fact that we do not include the inter-liquid junction potential in the value of the standard potential of the CO_2/HCOOH couple versus NHE while we do it in a second stage when we refer it to the reference system used to measure electrochemical potentials.

We first determine the standard potential of the CO_2/HCOOH couple in a solvent S and in the presence of a weak acid AH referred to the aqueous normal hydrogen electrode (NHE). The redox half-reaction reads as follows:

$$CO_{2(s)} + 2\,HA_{(s)} + 2\,e^- = HCOOH_{(s)} + 2A^-_{(s)}$$



Scheme S1

We use the thermodynamic cycle shown in Scheme S1 and derive the following equation

$$E^0_S(CO_2/HCOOH,AH)=E^0_{aq}(CO_2/HCOOH)-\frac{RTln10}{F}pKa_{(s)}(AH)-\frac{RT}{2F}\ln\left(\frac{K_{h,\,CO_2,\,aq\to g}}{K_{h,\,CO_2,\,S\to g}}\right)-\frac{2\,\Delta G^0_{t,\ H^+,\ S\to aq}-\Delta G^0_{t,\ HCOOH,\ S\to aq}}{2F}$$

with

$E^0_{aq}(CO_2/HCOOH) = -0.11$ V vs NHE at pH 0 [6]

$\Delta G^0_{t,\ H^+,\ DMF\to aq} = -46\ kJ/mol$ [7]

$\Delta G^0_{t,\ HCOOH,\ DMF\to aq} = -24\ kJ/mol$ [5]

$$K_{h,\ CO_2,S\to g} = \frac{P_{CO_2}/P^0}{[CO_2]_{(S)}/C^0}$$

, with $[CO_2]_{(S)}$ the solubility if CO_2 in the solvent of interest under $P_{CO2} = 10^5$ Pa; $P^0 = 10^5$ Pa and $C^0 = 1$ mol.L^{-1}

$[CO_2]_{CH3CN} = 0.28$ mol.L^{-1} [8] and $[CO_2]_{aq} = 0.038$ mol.L^{-1} [9]

We obtain $E^0_{CH3CN}(CO_2/HCOOH, AH) = 0.216$ V vs NHE $- \frac{RTln10}{F} pKa_{(S)}(AH)$

Considering now that H_2CO_3 formed by hydration of CO_2 is the strongest acid in the CO_2-saturated CH_3CN and using the pKa value of 17.03 previously determined for this couple in CH_3CN,[4] we finally obtain $E^0_{CH3CN}(CO_2/HCOOH, H_2CO_3) = -0.79$ V vs NHE.

To refer this potential versus the Fc^+/Fc couple, we use the experimentally determined value of $E(Fc^+/Fc) = 0.42$ V vs Ag/AgCl/KCl 3 mol.L^{-1} ($E_{Ag/AgCl} = 0.210$ V vs NHE) and correct it with the inter-liquid potential (0.100 V)[1] between the aqueous electrolyte of the Ag/AgCl electrode and the CH_3CN solution containing n-Bu_4BF_4 (0.1 mol.L^{-1}). This yields $E_{CH3CN}(Fc^+/Fc) = 0.53$ V vs NHE.

Thus **$E^0_{CH3CN}(CO_2/HCOOH, H_2CO_3) = -1.32$ V vs Fc^+/Fc**

Supporting Figures

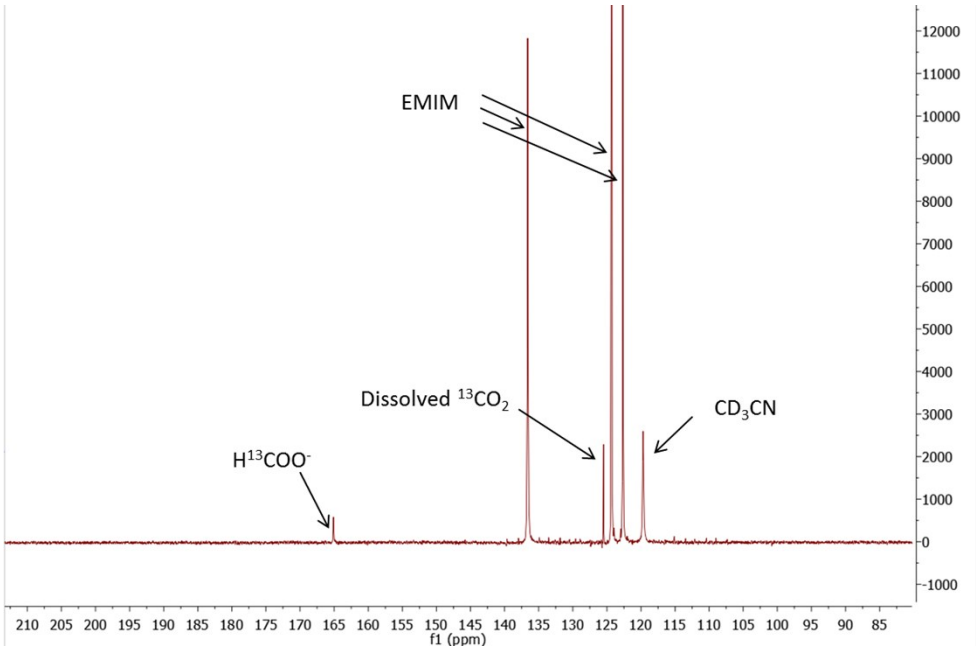


Figure S1: ^{13}C-NMR spectrum of an electrolytic solution using ^{13}CO2 reduction as the substrate in [EMIM](BF_4)/H_2O (92/8 v/v) (0.8ml solution + 0.2ml CD_3CN). ^{13}C-formate is observed at 165 ppm.

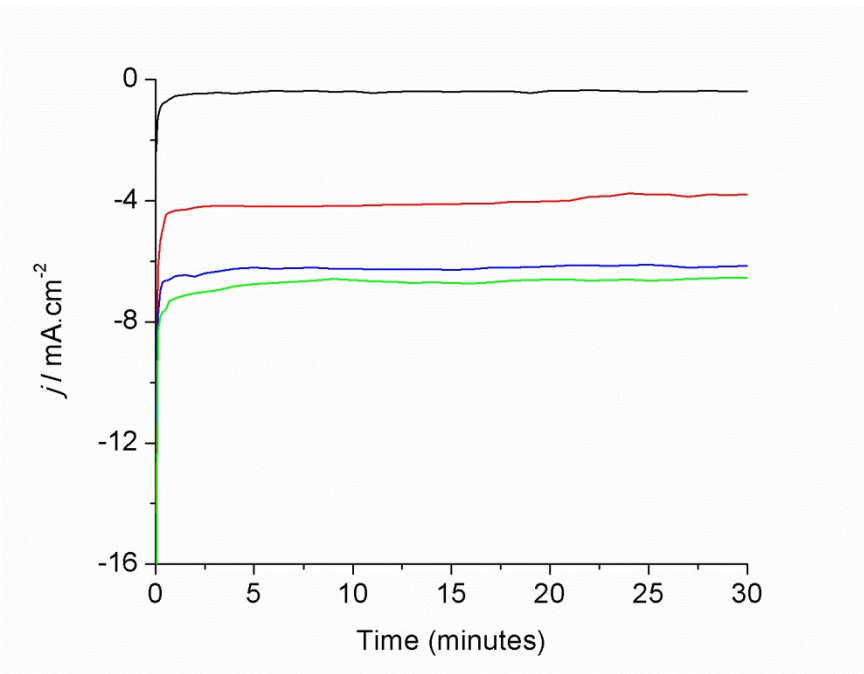


Figure S2: CPE at –1.55V vs Fc^+/Fc in [EMIM](BF_4)/H_2O (92/8 v/v) at CO_2 saturation using the modified Cu electrode obtained after different electrodeposition times: 40s (red), 80s (blue), 120s (green). The modified Cu electrode (80s electrodeposition) was also used under N_2 (black).

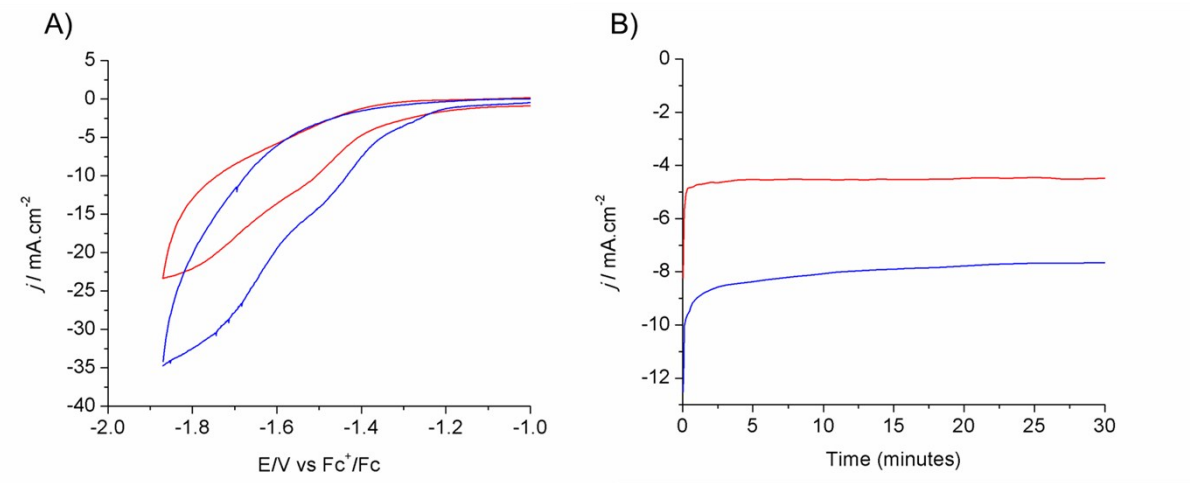


Figure S3: A) Cyclic voltamograms and B) current intensities during CPE using modified Cu electrodes obtained after different electrodeposition times (red: 40s; blue: 80s) in [EMIM](BF_4)/H_2O (85/15 v/v).

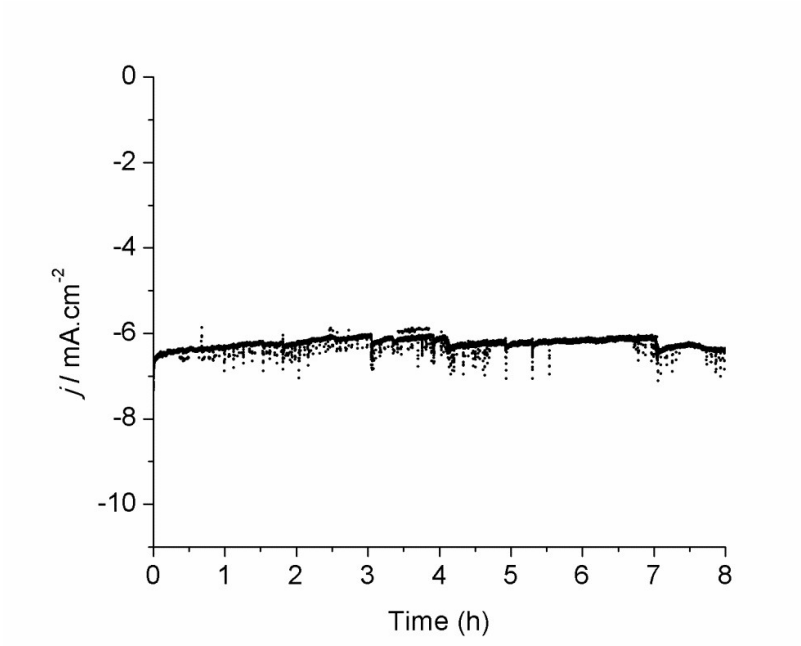


Figure S4: Catalytic current density during 8 h electro-reduction of CO_2 at –1.55 V vs Fc^+/Fc in [EMIM](BF_4)/H_2O (92/8% v/v) solution using a modified Cu electrode (80s electrodeposition).

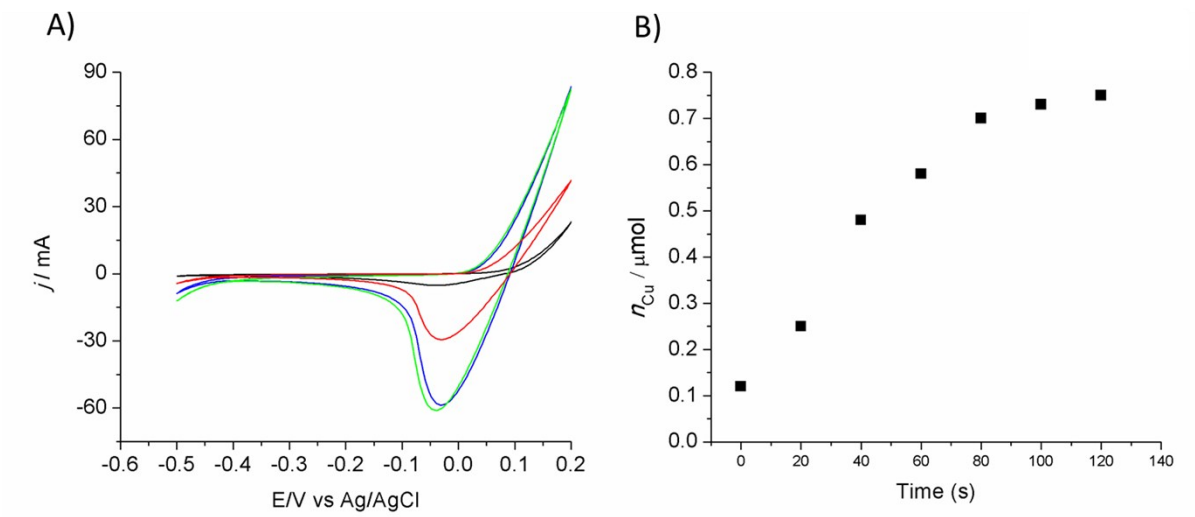


Figure S5: A) Cyclic voltammograms in H_2SO_4 0.5M using a Cu plate (black) or a modified Cu electrode (1 cm^2) obtained after 40s (red), 80s (blue) and 120s (green) electrodeposition. For sake of clarity the data for electrodes obtained after 20, 60 and 100 s are not shown. B) Surface concentration of active Cu calculated from the reduction peak in (A). From each CV total charge Q is calculated, and the amount of active Cu = $Q/(2x1.6x10^{-19}x6.02\ x10^{23})$.

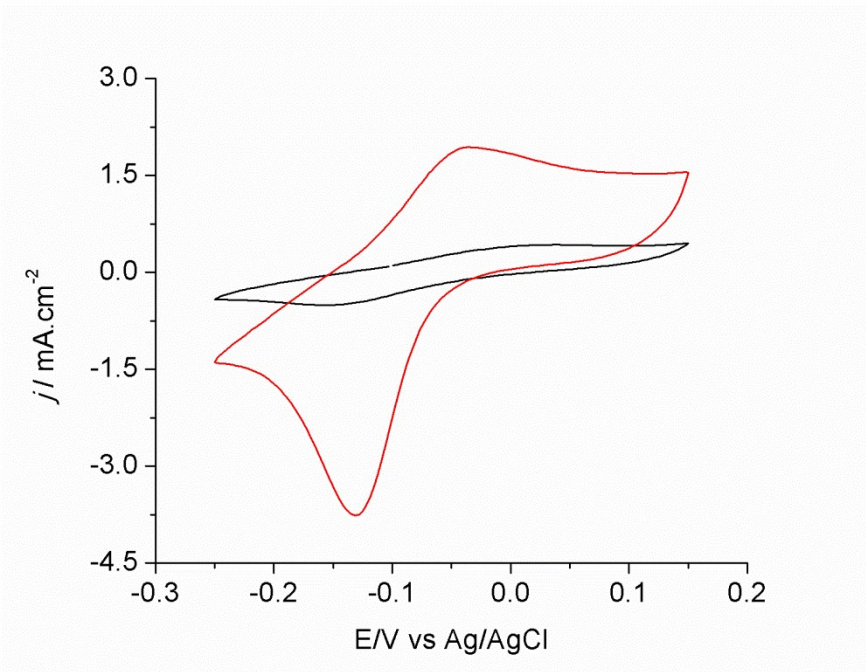


Figure S6: CVs of the Cu plate and the modified Cu electrode (80s deposition) in 0.1M phosphate buffer pH 7.0 containing 5mM $K_3[Fe(CN)_6]$ (scan rate 50mV.s^{-1}).

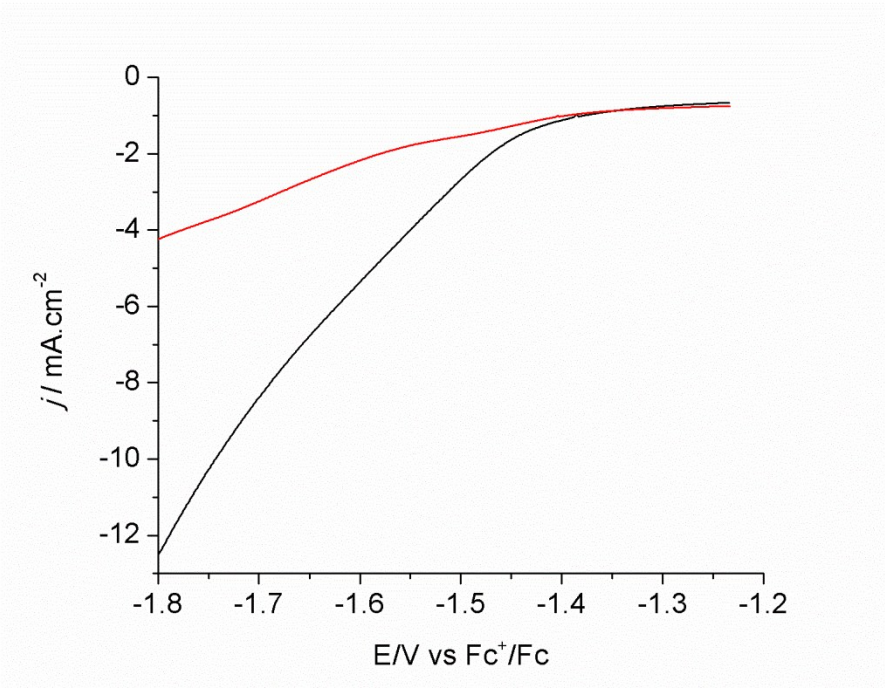


Figure S7: A) LSV of the modified Cu electrode (80s deposition) in MeCN/H_2O (92/8 v/v) + 0.1M n-Bu_4BF_4 under N_2- (red) and CO_2- (black) saturation conditions.

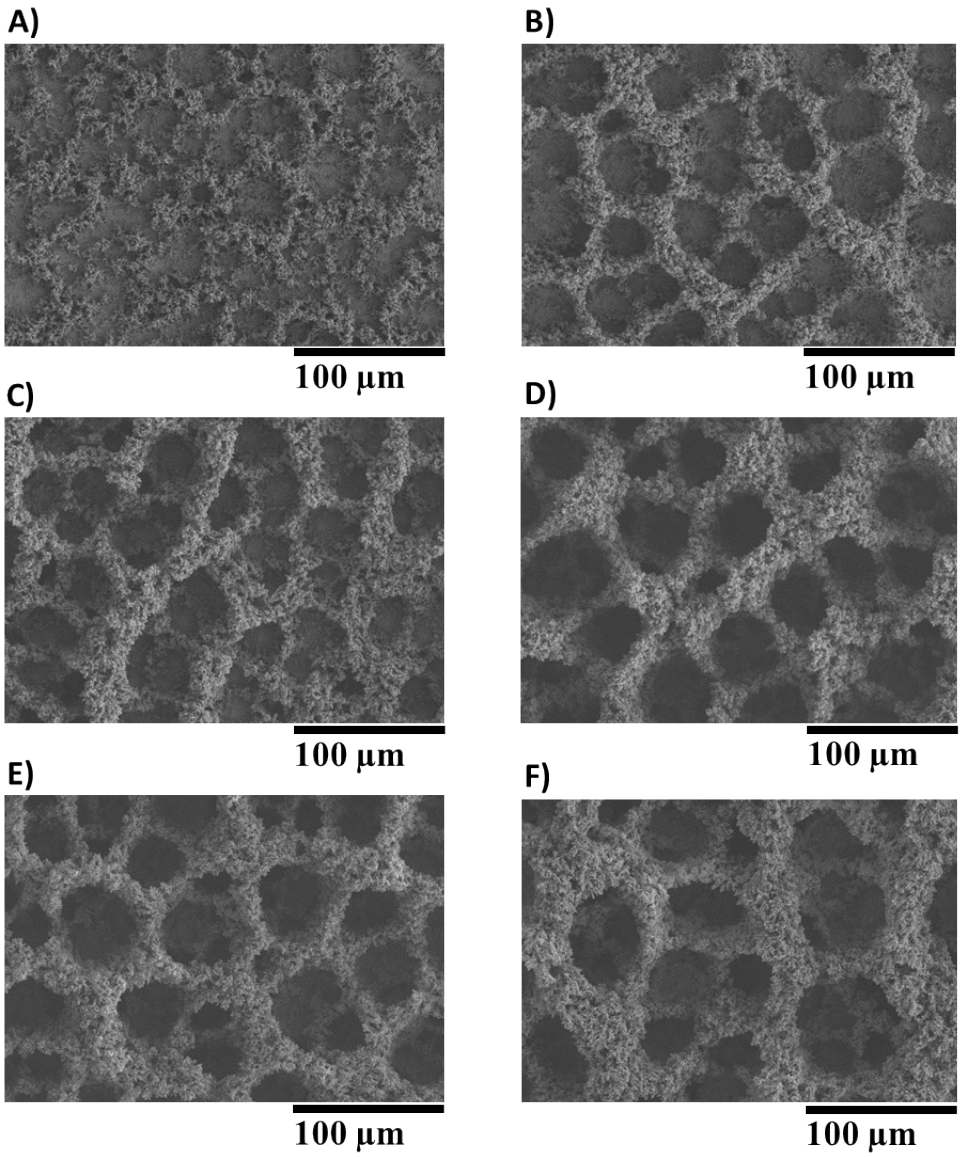


Figure S8: SEM images of the modified Cu electrodes obtained after 20s (A), 40s (B), 60s (C), 80s (D), 120s (E) and 160s (F) electrodeposition.

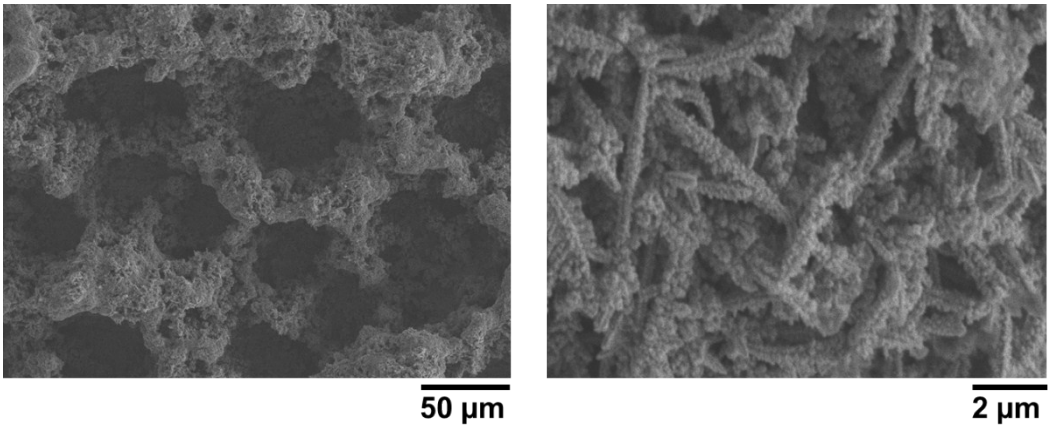


Figure S9: SEM image of the modified Cu electrode (80s electrodeposition) after long-term (8 h) electrolysis.

Table S1. Products and faradic yields during CPE at –1.55V vs Fc^+/Fc under CO_2 saturation in [EMIM](BF_4)/H_2O (92/8 v/v) using a modified Cu electrode obtained after different electrodeposition times

Electrodeposition time	Charge (C)	H_2 (%)	Formate (%)	CO (%)
40s	5.8	9	82	5
80s	8.6	8	83	5
120s	9.1	11	79	6

Table S2: Products and faradic yields during CPE at –1.55 V vs Fc^+/Fc under CO_2 saturation in [EMIM](BF_4)/H_2O (85/15 v/v) using modified Cu electrode obtained after different electrodeposition times.

Electrodeposition time	Charge (C)	H_2 (%)	Formate (%)	CO (%)
40s	10.2	35	50	8
80s	16.8	36	49	9

References:

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