Supporting Information


Electrocatalytic Reduction of Gaseous CO\(_2\) to CO on Sn/Cu-
Nanofiber-Based Gas Diffusion Electrodes

*Wenbo Ju,* Fuze Jiang, Huan Ma, Zhengyuan Pan, Yi-Bo
Zhao, Francesco Pagani, Daniel Rentsch, Jing Wang, * and
Corsin Battaglia*
Supporting Information

**Electrocatalytic Reduction of Gaseous CO$_2$ to CO on Sn/Cu-Nanofiber-Based Gas Diffusion Electrodes**

**Wenbo Ju†,* Fuze Jiang‡, Huan Ma, Zhengyuan Pan, Yi-Bo Zhao, Francesco Pagani, Daniel Rentsch, Jing Wang*, Corsin Battaglia**

1. **Chemicals and Materials**

Polyvinylidene fluoride (PVDF, average M$_w$ $\sim$ 150000), polycaprolactam (nylon-6, pellets), N,N-dimethylformamide (DMF, ACS reagent, $\geq$ 99.8 %), dopamine hydrochloride (DA-HCl, 98 %), boric acid (H$_3$BO$_3$, puriss p.a.), ethylenediaminetetraacetic acid (EDTA, 99 %), borane dimethylamine complex (DMAB, 97 %), tin(II) sulfate (SnSO$_4$, $\geq$ 95 %), phosphoric acid (H$_3$PO$_4$, 85 %), and sulfuric acid (H$_2$SO$_4$, 98 %) were purchased from Sigma-Aldrich. Acetone (AnalaR Normapur, 99 − 100 %), formic acid (AnalaR Normapur, 99 − 100 %), and potassium hydroxide (KOH, AnalaR Normapur, 85.0 − 100.5 %) were from VWR. 10 mM tris(hydroxymethyl)-aminomethane hydrochloride solution (10 mM Tris-HCl, pH 8.5) was obtained from Teknova. Copper(II) chloride dihydrate (CuCl$_2$·2H$_2$O, $\geq$ 99 %) was from Merck. Copper rod ($\varnothing = 5$ mm, 99.99+ %) was from Goodfellow. Pt gauze (1024 mesh·cm$^{-2}$, 99.9 %) and Pt wire ($\varnothing = 0.5$ mm, 99.9 %) were purchased from MaTecK. Unless otherwise specified, all the materials were used as received. Deionized water from a Milli-Q water purification system (Millipore, 18.2 MΩ·cm) was used to prepare solutions. Argon (Ar, 5.0) and carbon dioxide (CO$_2$, 4.8) were from Messer. Epoxy resin (EpoxiCure™ 2) was purchased from Buehler.

2. **Electrospinning of nanofiber membranes**
PVDF dissolves in a mixture of DMF/acetone (1:1 wt.) for a PVDF solution at 14 wt. %. Nylon-6 dissolves in formic acid for a nylon solution at 15 wt. %. PVDF and nylon nanofiber membranes were prepared by electrospinning with the 14 wt. % PVDF solution and the 15 wt. % nylon solution, respectively. A multi-jet electrospinning system (NaBond Technologies Co., Ltd.), consisting of three spinnerets and a rotating drum collector, was used for the fabrication of nanofiber membranes. The distance between the spinneret array and the drum collector was 10 cm. A 20 kV voltage was applied between the spinnerets and the grounded collector. The extrusion rate was 1 ml·h⁻¹ for PVDF, and 0.5 ml·h⁻¹ for nylon. Electrospinning for both kinds of membranes lasted 2 hours. After electrospinning, all membranes were treated by hot pressing at 125 °C for 10 s to eliminate fluffiness, and to improve intra-membrane lamination and mechanical strength.

3. Electroless Cu plating on nanofibers

A 2 g·l⁻¹ DA-HCl solution was prepared by dissolving DA-HCl powder in a 10 mM Tris-HCl solution. Electrospun nanofiber membranes were immersed in the DA-HCl solution for 12 hours with strong stirring. A polydopamine (pDA) layer formed on nanofibers through a DA polymerization process [¹]. Subsequently, the pDA-coated nanofiber membranes were sonicated in deionized water for 10 min to remove non-uniformly aggregated pDA particles and dried under vacuum overnight. A Cu precursor for electroless plating consists of 50 mM CuCl₂, 50 mM EDTA, and 100 mM H₃BO₃. Its pH was meticulously neutralized to 7 with a 3 M KOH solution. EDTA sequestered Cu²⁺ ions to form Cu-EDTA. The prepared Cu precursor was stored in a fridge set to 4 °C. For Cu plating, DMAB was used as the reducing agent. The addition of 0.1 mole DMAB in 1 liter Cu precursor was shortly before the immersion of pDA-coated nanofiber membranes. The reaction took place at 35 °C (in water bath) for 2 hours. After the Cu plating, all samples were sonicated for 3 – 5 min to remove non-uniformly aggregated Cu particles.
Figure S1. SEM images of (a) electrospun PVDF nanofibers, (b) polydopamine-coated PVDF nanofibers, and (c) Cu-coated PVDF nanofibers. SEM images of (d) electrospun nylon nanofibers, (e) polydopamine-coated nylon nanofibers, and (f) Cu-coated nylon nanofibers. (g) Scheme of electroless Cu coating on electrospun polymer nanofibers.

4. Characterization of Sn underpotential deposition on a Cu rotating disk electrode

A polycrystalline Cu rotating disk electrode (RDE, Ø = 5 mm) was employed to investigate the underpotential / overpotential deposition (UPD / OPD) of Sn on Cu surfaces. The Cu RDE was mechanically polished with sandpaper (Buehler, silicon carbide) to the grit of P2500, and with alumina slurry (eDAQ, 0.3 µm and 0.05 µm) on polishing cloths, followed by thorough rinsing with ethanol and deionized water. Then the Cu RDE surface was electrochemically polished in 50% H₃PO₄ at 2.1 V vs. a Pt wire for 60 s. The electrode surface was rinsed with deionized water, and then assembled into a RDE shroud (Pine research, Ø = 12 mm PEEK shroud). The electrochemical measurements on the Cu RDE were performed in a glass cell.
(Gamry instruments, EuroCell™) with a three-electrode configuration. A Pt wire was used as the counter electrode (separated with a glass frit from the cell body), and a leakless Ag/AgCl electrode (SI Analytics, 3 M KCl) was used as the reference. The electrochemical measurements were performed with a VersaSTAT 4 electrochemical workstation (Princeton Applied Research).

The double-layer capacitance ($C_{dl}$) of the Cu RDE was evaluated by cyclic voltammograms (CVs) at various scan rates in an Ar saturated 0.1 M H$_2$SO$_4$ (Figure S2a). The linear fitting of the double layer currents plotted against the scan rates determined a slope of 19.2 µF (see Figure S2b), which quantified the $C_{dl}$ of the Cu RDE. The $C_{dl}$ was divided by a value of 28 µF cm$^{-2}$ for a flat Cu electrode [2], leading to the electrochemical surface area (ECSA) of 0.686 cm$^2$. The CV of the Cu RDE in 0.1 M H$_2$SO$_4$ is shown as the dotted blue curve in Figure S2c.

In a 1 mM SnSO$_4$ + 0.1 M H$_2$SO$_4$ solution, multiple peaks can be observed in the CV (see solid red curve in Figure S2c). The correlations of different oxidation and reduction peaks were investigated by CVs acquired in different potential ranges (see Figure S2d). The reduction peaks I, II, and III couple to the oxidation peaks VII, VI, and V, respectively. Peak IV is relevant to the hydrogen evolution reaction (HER). Peak VII is comparable to the Cu oxidation peak in the CV of Cu RDE in 0.1 M H$_2$SO$_4$. Thus it is assigned to the Cu oxidation, and its coupled reduction peak I is assigned to the Cu oxide reduction.

The redox couples of II/VI and III/V were further investigated with CVs measured at different rotation speeds (see Figure S2e). The reduction peak II, which is insensitive to the rotation speed, is assigned to the UPD of Sn [3]. The transferred charge in peak II ($Q_{peak II}$) approaches to a constant value (see Figure S2f upper part), and the average of $Q_{peak II}$ for all investigated rotation speeds is 23.4 µC. Assuming a two-electron reduction from Sn(II) to Sn(0) and the electrosorption valency of 1 for the deposited Sn, the charge flux associated with the formation of a monolayer (ML) of Sn on Cu is $\sim$ 178 µC cm$^{-2}$ [3]. The average value
corresponds to a surface area of Sn (SA_{Sn}) of 0.131 cm$^2$. Sn UPD results in the deposition of a single atomic layer of Sn on the Cu surface, while OPD results in three-dimensional Sn island growth. With the single atomic layer growth mechanism by UPD, the coverage of Sn on Cu ($\theta_{Sn}$) is determined to be $\sim 0.2$ ML ($\theta_{Sn} = \frac{SA_{Sn}}{ECSA} = 0.131 / 0.686 \approx 0.2$), which agrees well with the work by Yan et al. [3]. Since peak VI couples to peak II, it is relevant to the stripping of Sn formed by UPD. The equilibrium potential of Sn UPD / stripping is at -0.11 V vs. RHE. Both peaks III and V are highly sensitive to the rotation speed. The limiting current density ($j_{l,c}$) at peak III, which has been normalized to the geometric surface area of the Cu RDE (0.196 cm$^2$), is proportional to square root of the rotation speed ($\omega^{1/2}$) (see Figure S2f lower part), following the Levich equation [4] shown as below:

$$j_{l,c} \propto zFD_{Sn}^{2/3} \omega^{1/2}v^{-1/6}C_{Sn}^*$$  \hspace{1cm} (S1)

where $z$ is the number of transferred electrons in the reaction, $F$ is the Faraday constant (96485.3 A·s·mol$^{-1}$), $D_{Sn}$ is the diffusion coefficient of Sn$^{2+}$ in the solution, $v$ is the scan rate of the potential sweep, and $C_{Sn}^*$ is the concentration of Sn$^{2+}$ in the bulk solution.

Peak III is relevant to the OPD of Sn. Peak V corresponds to the stripping of overpotentially deposited Sn. The equilibrium potential of Sn OPD / stripping is at -0.24 V vs. RHE.
Figure S2. (a) CVs of a Cu RDE acquired in a double layer potential range at different scan rates in Ar-saturated 0.1 M H₂SO₄; (b) double layer current as a function of scan rate, and the
quantification of $C_{dl}$ by the slope of the linear fitting; (c) CVs of a Cu RDE in 0.1 M $H_2SO_4$ and in 1 mM $SnSO_4 + 0.1$ M $H_2SO_4$, scan rate: 50 mV·s$^{-1}$; (d) CVs of a Cu RDE acquired in different potential ranges in 1 mM $SnSO_4 + 0.1$ M $H_2SO_4$, scan rate: 50 mV·s$^{-1}$; (e) CVs of a Cu RDE acquired at different rotation speeds, scan rate: 50 mV·s$^{-1}$; (f) quantitative analysis of $Q_{peak \ II}$ (upper), $Q_{peak \ III}$ (lower, with y-axis on the left) and $j_{i,c}$ (lower, with y-axis on the right) at different rotation speeds.

5. Electrochemical Sn underpotential deposition on Cu nanofibers

Electrochemical Sn UPD on Cu-coated nanofiber electrodes was carried out in an electrochemical cell with a three-electrode configuration. A Pt gauze (2 cm$^2$) was used as the counter electrode, and a leakless Ag/AgCl electrode (SI Analytics, 3 M KCl) was used as the reference. The electrolyte was Ar-saturated 1 mM $SnSO_4 + 0.1$ M $H_2SO_4$. According to the study of Sn UPD on a Cu RDE (see Figure S2), we selected the chronoamperometry technique for Sn UPD on Cu-coated nanofiber electrodes that a deposition potential of -0.2 V (vs. RHE) was applied. Figure S3a shows the applied potential including a linear potential sweep from 0.11 to -0.2 V at a scan rate of 10 mV·s$^{-1}$ and then a constant potential at -0.2 V for 200 s. Figure S3b shows the corresponding chronoamperogram. After Sn UPD, the Sn-decorated Cu (Sn/Cu) nanofiber electrodes were rinsed with deionized water, and dried in a desiccator under vacuum.
Figure S3. (a) Applied potential for Sn UPD on a Cu-coated PVDF electrode with a geometric area of 2.88 cm$^2$, and (b) the corresponding chronoamperogram.

6. Materials characterization

Environmental scanning electron microscopy (ESEM, Thermo Fisher Quanta 650) was used to visualize the electrode morphology, to analyze elements in nanofibers (energy dispersive X-ray spectroscopy, EDS), and to image the spatial distribution of elements (EDS elemental mapping). EDS and EDS element mapping were operated at an acceleration voltage of 10 kV. Cross sections were prepared and imaged by a combined focused ion beam-scanning electron microscope (FIB-SEM, Helios NanoLab DualBeam). Element mapping was done by using an EDS system (X-MaxN, Oxford Instruments) attached to the same FIB-SEM system. For SEM, an acceleration voltage of 5 kV was used at a current of 50 pA. X-ray diffraction (XRD) patterns were collected on a Bruker D8 diffractometer equipped with a Goebel mirror selecting Cu Kα radiation ($\lambda=1.5406$ Å).

A four-point probe setup (PRO4, Microworld, Inc.) was used to measure the resistance of Cu-coated nanofiber electrodes. For an individual sample, 30 random positions were selected for measurements. The sheet resistivity $R_s$ was calculated according to Equation S2:

$$R_s = \frac{\pi}{\ln 2} \cdot \frac{V}{I}$$

(S2)

where $V$ and $I$ are the measured potential and current, respectively.

7. Analysis of gas permeability and gas flow simulations

A single-channel test section, which is formed by a gasket sandwiched between two back plates, was used for measuring the pressure drop across a porous material. The projected area for testing was 0.5 cm$^2$. The pressure drop between entrance and exit of the test section as a function of CO$_2$ flow was measured directly with a pressure transducer (Omega Engineering). A mass flow controller (Aalborg TIO totalizer) adjusted CO$_2$ flow rates from 5 to 50 ml·min$^{-1}$,
corresponding to face velocities from 10 to 100 cm·min\(^{-1}\), for which we observed a linear pressure drop response vs. CO\(_2\) flow rate.

The intrinsic permeability of a material \((k)\) can be calculated based on the measured pressure drop \((\Delta P)\) by using the Darcy’s law expressed as below \([5]\):

\[
k = \frac{v \cdot \mu \cdot L}{\Delta P}
\]

(S3)

where \(v\) is the face velocity, \(L\) is the thickness of the sample, and \(\mu\) is the fluid viscosity, which is \(1.48 \times 10^{-5}\) Pa·s for CO\(_2\) at 20 °C \([6]\).

The PaperGeo module of GeoDict (Math2Market GmbH) was employed to generate virtual fibrous three-dimensional models to represent actual materials. Geometric parameters of nanofiber membranes, including membrane thickness and distribution of fiber diameters, were acquired from top-view and cross-sectional SEM images. The model was based on the assumption of straight fibers isotropically distributing in the X-Y plane. According to the actual distribution of fiber diameters, the program generated a virtual single-layer fibrous sheet, consisting of straight fibers with an identical distribution of fiber diameters. Next, we made the assumption that single-layer fibrous sheets stack in the Z direction with uniform interlayer spacing and random angular displacement between layers. The interlayer spacing was adjusted according to the intrinsic permeability for CO\(_2\) from experiments. With these two assumptions, a virtual three-dimensional fibrous model was generated.

The FlowDict module of GeoDict (Math2Market) was used for pressure and flow simulations.

The Reynolds number \((R)\) is the ratio between the fluid’s inertial force \((F_{inert})\) to its viscous force \((F_{visc})\), which can be expressed as:

\[
R = \frac{F_{inert}}{F_{visc}} = \frac{\rho v D}{\mu}
\]

(S4)

where \(\rho\) is the fluid density, \(v\) is the velocity, \(D\) is the diameter of the pipe, and \(\mu\) is the viscosity of the fluid. In this study, the fluid was assumed to be viscous, uncompressed, and
stationary. Thus $F_{\text{inert}}$ was much smaller than $F_{\text{vis}}$, and the dimensionless Reynolds number, $R$, was assumed to be much smaller than 1. Gas flow through a porous material was considered as Stokes flow. The LIR (left-identity-right) solver was employed in a non-uniform adaptive grid to calculate the flow in the virtual fibrous three-dimensional structure. Periodic boundary conditions were applied in flow direction, and in tangential direction. The computational domain size was $1500 \times 1500 \times L_1$ voxels for Sn/Cu-PVDF and $700 \times 700 \times L_2$ voxels for Sn/Cu-nylon. $L_1$ and $L_2$ were proportional to the thickness of the two electrodes, respectively. The voxel length was 0.01 µm. CO$_2$ face velocities from 10 to 100 cm·min$^{-1}$ were used for simulations. Each simulation led to a pressure drop. All pressure drops were plotted against CO$_2$ face velocities.

8. Electrochemical measurements and product analysis

Anion exchange membranes (AEM, Sustainion™, PTFE Supported) were purchased from Dioxide Materials. Sn/Cu-nanofiber electrodes were pressed on an AEM at 125 °C for 10 s. Then the membrane-electrode assembly (MEA) was encapsulated in a Teflon tape (No.75100, CMC Klebetechnik GmbH) with an exposed electrode area of 0.196 cm$^2$. A Cu current collector contacted the edges of the electrode.

For the electrochemical CO$_2$ reduction reaction (CO$_2$RR), a home-built two-compartment cell, made of polyetheretheretherketone (PEEK), was used. The MEA was placed between the two compartments. The electrode side was exposed to gaseous CO$_2$. Here we refrained from using a pressurized electrolyzer design to avoid gas crossover from the cathodic to the anodic compartment. The AEM side contacted the aqueous electrolyte of CO$_2$-saturated 0.1 M KHCO$_3$. The use of CO$_2$-saturated 0.1 KHCO$_3$ aims at making the results comparable with our previous work [7]. A Pt-gauze (2 cm$^2$) counter electrode was assembled parallel to the MEA with a distance of 12 mm. A leakless miniaturized Ag/AgCl electrode (ET072-1, eDAQ) was inserted in the anodic compartment as the reference. Electrochemical
measurements were performed by a potentiostat (SP240, BioLogic). Accurate potentials were obtained by compensating the measured potential with the ohmic potential drops in the system (IR-compensation).

The CO$_2$ flow in the cathodic compartment was regulated by a mass flow controller (Red-y MFC, Voegtlin). During electrolysis, pure CO$_2$ gas flowed into the cathodic compartment at a flow rate of 4 to 20 ml·min$^{-1}$, and diffused across the gas diffusion electrode (GDE) towards the electrode/membrane interface, where the CO$_2$RR takes place. CO$_2$ flow rates were adjusted to maintain the mole fraction of CO$_2$ in the total gas mixture as measured by gas chromatography at the outlet of the cathodic compartment above 98% (i.e. mole fraction of products lower than 2%). The pressure at the outlet of the cathodic compartment was kept at ambient pressure.

The anolyte was circulated in a loop for separating produced O$_2$ and saturating the anolyte with CO$_2$. The circulation was propelled by a peristaltic pump (Reglo Digital, I smatec). A gas chromatograph (3000A µGC, Agilent) with a Plot Q (Ar carrier gas) and a Plot U (He carrier gas) column was used to determine the volume fraction of gaseous products. The volume fraction of each product was converted to the concentration via a molar volume of gas of 24.2 l·mol$^{-1}$ (1 atm. and 22 °C). The faradaic efficiency for the gaseous product $k$ ($FE_k$ (%)) was evaluated according to Equation S5 shown as below:

$$FE_k(\%) = \frac{z_kF \cdot dn_k}{I} \cdot 100(\%) = z_kF \frac{C_kQ_{CO_2}}{I} \cdot 100(\%)$$  \hspace{1cm} (S5)

where $z_k$ is the number of exchanged electrons, $F$ is the Faraday constant (96485.3 A·s·mol$^{-1}$), $dn_k$ is the production rate with a unit of mol·s$^{-1}$, $I$ is the current at the moment for gas sampling, $C_k$ is the concentration of the product $k$ characterized by GC, and $Q_{CO_2}$ is the volumetric flow rate of CO$_2$. 
Liquid phase products were quantified using $^1$H nuclear magnetic resonance spectra (NMR, Avance III 400 NMR spectrometer, Bruker) recorded at 400.1 MHz at 298 K, following the same procedure in Ref. [7]. Samples were prepared by mixing 1500 µL of the solution of interest with 150 µL of a 10 mM dimethyl sulfoxide (DMSO, 99.8+ %, Alfa aesar) standard solution and with 300 µL of D$_2$O. The $^1$H NMR spectra of 700 µL of these solution mixtures were recorded with lock on D$_2$O / H$_2$O using the gradient selected composite Bruker pulse sequence “zgcpgppr” with presaturation of the water resonance at 4.7 ppm. Relaxation delays of 60s were applied since formic acid as the main species of interest showed a rather long T$_1$ relaxation time in the order of 20 s in accordance with published data [8]. Additionally, the presaturation on the water resonance was switched on for 4 s only, since we observed that an NOE type signal enhancement from the irradiated H$_2$O signal over the acidic protons onto the aldehyde resonance at 8.4 ppm of formic acid when presaturation was switched on during the whole relaxation delay of 60 s.

9. Impact of CO$_2$ diffusion on the CO$_2$ conversion rate

We employed Darcy’s law (Equation S6) to estimate the flux of CO$_2$ to the electrode/membrane interface, where CO$_2$RR takes place:

$$Q = \frac{kA}{L \mu} \Delta P$$  \hspace{1cm} (S6)

where $k$ is the permeability of the GDE, $\mu$ is the fluid viscosity, which is 1.48×10$^{-5}$ Pa·s for CO$_2$ at 20 °C [6], $A$ is the cross-sectional area to flow, which is 0.196 cm$^2$ for all measurements, and $L$ is the thickness of the GDE. In this work, the Sn/Cu-PVDF GDE has a CO$_2$ gas permeability of 1.8×10$^{-14}$ m$^2$, and a thickness of 8 µm, while the Sn/Cu-nylon GDE has a CO$_2$ gas permeability of 3.5×10$^{-15}$ m$^2$, and a thickness of 2.5 µm. Assuming a comparable pressure drop across the GDE, the ratio of CO$_2$ flux across the Sn/Cu-PVDF ($Q_{PVDF}$) and that across the Sn/Cu-nylon ($Q_{nylon}$) can be expressed as:
Conversely, we also estimated the CO$_2$ consumption rate at the electrode/membrane interface from the production rates of the two major carbon-based gaseous products (CO and C$_2$H$_4$), when operated under identical conditions (-1.2 V vs RHE, CO$_2$ flow rate of 20 ml·min$^{-1}$, resulting in average current densities of 122 mA·cm$^{-2}$ for the Sn/Cu-PVDF GDE and 87 mA·cm$^{-2}$ for the Sn/Cu-nylon GDE). The CO$_2$ consumption rate at Sn/Cu-PVDF ($R_{PVDF}$) is 1.912 mmol·h$^{-1}$·cm$^{-1}$, and that at Sn/Cu-nylon ($R_{nylon}$) is 1.238 mmol·h$^{-1}$·cm$^{-1}$. The ratio of the two CO$_2$ consumption rates can be expressed as:

$$\frac{R_{PVDF}}{R_{nylon}} = \frac{1.912}{1.238} = 1.55 \times 10^{-2} \text{ mmol·h}^{-1} \text{·cm}^{-1}$$

which is in excellent agreement with the ratio of CO$_2$ fluxes determined above, indicating that the production rate is limited by CO$_2$ diffusion to the reaction zone at the electrode/membrane interface.
Figure S4. (a) Size distributions applying Gaussian fittings for diameters of PVDF nanofibers before (blue circles) and after polydopamine, Cu and Sn coating (red diamonds). (b) XRD patterns with assigned reflexes of PVDF, polydopamine-coated PVDF, and Sn/Cu-PVDF. Top-view (c) and cross-sectional (d) SEM images of a Sn/Cu-PVDF electrode. (e) CO$_2$ flow field simulated based on a virtual three-dimensional fibrous model (inset) at a CO$_2$ face velocity of 80 cm·min$^{-1}$. 
Figure S5. (a) Top-view SEM image of a Sn/Cu-PVDF electrode, and the elemental mapping for carbon (C), and oxygen (O) by EDS (scale bar: 1 µm), and (b) EDS spectrum with assigned peaks of the Sn/Cu-PVDF electrode.

Figure S6. Cross-sectional SEM image of a Sn/Cu-PVDF electrode encapsulated in an epoxy resin (scale bar: 1 µm), and the elemental mapping for Cu, C, and F.
Figure S7. (a–g) Chronoamperograms and corresponding faradaic efficiencies for H₂ (FE_{H₂}), CO (FE_{CO}), C₂H₄ (FE_{C₂H₄}), and the sum of all gaseous products (FE_{total}) at sampling points for a Sn/Cu-PVDF electrode at potentials from -0.6 to -1.2 V. (h) Summary of all chronoamperograms at applied potentials.
**Figure S8.** (a) Chronoamperogram, (b) ohmic resistance of the electrolytic system, and (c) pH values of anolyte for a Sn/Cu-PVDF / AEM assembly during a 135 h stability test. Red dashed lines in (a) mark the moments of replacing used anolyte with fresh CO$_2$-saturated 0.1 M KHCO$_3$.

**Figure S9.** $^1$H NMR spectrum of anolyte used for electrochemical CO$_2$ reduction catalyzed by a Sn/Cu-PVDF electrode. The anolyte was employed for 24 hours (in the last interval in Figure S8a). Chemical species assigned according to ref. [9].
Figure S10. (a) Top-view and (c) cross-sectional SEM images of a Sn/Cu-nylon electrode. (b) Size distributions applying Gaussian fittings for diameters of nylon nanofibers before (green circles) and after polydopamine, Cu and Sn deposition (purple pentagons). (d) XRD patterns with assigned reflexes of nylon, polydopamine-coated nylon, and Sn/Cu-nylon.
Figure S11. (a) Virtual three-dimensional fibrous model for a Sn/Cu-nylon electrode. (b) Measured and simulated CO$_2$ pressure drops through a Sn/Cu-nylon electrode at CO$_2$ face velocities from 10 - 90 cm·min$^{-1}$. The simulation is based on the model in (a). (c) CO$_2$ flow field and (d) pressure field for a 139.1-Pa pressure drop through the electrode at a CO$_2$ face velocity of 80 cm·min$^{-1}$.

Figure S12. Pore size distribution in a Sn/Cu-PVDF electrode (red diamonds) and a Sn/Cu-nylon electrode (blue circles). The pore size is determined by fitting spheres into the pore volume based on the virtual fibrous model.
**Figure S13.** (a) Cross-sectional SEM images of a Sn/Cu-nylon / AEM assembly, and (b) electrode / electrolyte interface. The cross-section was prepared by freeze fracture in liquid nitrogen.

**Figure S14.** (a) Faradaic efficiencies, (b) current densities, and (c) production rates for electrochemical CO$_2$ reduction at a Sn/Cu-nylon GDE at -0.5 to -1.2 V.
Figure S15. (a-h) Chronoamperograms and corresponding faradaic efficiencies for H$_2$ (FE$_{H2}$), CO (FE$_{CO}$), C$_2$H$_4$ (FE$_{C2H4}$), and the sum of all gaseous products (FE$_{total}$) at sampling points for a Sn/Cu-nylon electrode at potentials from -0.5 to -1.2 V. (i) Summary of all chronoamperograms at applied potentials.
References


