

– Supporting Information –

Multi-Layer Electrolyzer Stack Converts Carbon Dioxide to Gas Products at High Pressure with High Efficiency

B. Endrődi,^{1,} E. Kecsenovity,¹ A. Samu,¹ F. Darvas,² R. V. Jones,² V. Török,² A. Danyi,² C.*

Janáky^{1,}*

¹Department of Physical Chemistry and Materials Science, Interdisciplinary Excellence Centre, University of Szeged, Rerrich Square 1, Szeged, H-6720, Hungary

²ThalesNano Inc., Záhony u. 7, Budapest 1031, Hungary

AUTHOR INFORMATION

Corresponding Authors

*janaky@chem.u-szeged.hu (C. Janáky) & endrodib@chem.u-szeged.hu (B. Endrődi)

Experimental details

Methods and materials

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, VWR International), and were of at least analytical grade. These were used without further purification. MilliQ grade ($\rho = 18.2 \text{ M}\Omega \text{ cm}$) ultrapure deionized water was used to prepare all the solutions.

To prepare the cathode GDE, Ag nanoparticles ($d_{\text{avg}} < 100 \text{ nm}$, Sigma-Aldrich) were dispersed in a 1:1 isopropanol-water mixture at a concentration of 25 mg cm^{-3} . This dispersion also contained 15 wt% Sustainion XA-9 ionomer, with regards to the total amount of catalyst + ionomer. Similarly, Ir nanoparticles (Fuel-Cell Store) were also dispersed in a 1:1 isopropanol-water mixture in a concentration of 20 mg cm^{-3} . The ionomer content was also 15 wt% in this case. The Ir dispersion was homogenized in a regular ultrasonic bath for 20 minutes (carefully keeping the bath temperature below $35 \text{ }^\circ\text{C}$), while a high-power immersion sonotrode was used to disperse the silver nanoparticles.

The silver dispersion was spray-coated on Sigracet 39BC carbon diffusion layers, preheated on a hotplate at $100 \text{ }^\circ\text{C}$, using a hand-held airbrush and compressed air carrier gas ($\sim 100 \text{ cm}^3 \text{ min}^{-1}$). The anode catalyst was spray-coated similarly, on a porous titanium frit. The cathode catalyst loading was $3.0 \pm 0.1 \text{ mg cm}^{-2}$, while it was $1.0 \pm 0.1 \text{ mg cm}^{-2}$ for the anode.

A PTFE reinforced Sustainion anion exchange membrane was used to separate the anode and the cathode chambers. The membrane was activated before use for a day in 1 M KOH, which was exchanged to a fresh solution after the first 5 hours. Similarly, the Ag catalyst containing carbon papers were activated in 1 M KOH, for 1 hour before use.

Scanning electron microscopy (SEM) images were collected with a Hitachi S-4700 field emission scanning electron microscope.

Electrolyzer cell and test station

A custom-designed direct gas feed, zero gap cell was used for the measurements (**Figure S1**). The cell components were manufactured of high-quality stainless steel, while the insulating elements of the cell were formed of ZX-100 plastic. The electrolyzer stack were constructed from the following elements, in the following order: cathode endplate and current collector with gas inlets and gas flow pattern facing the GDE, cathode GDE, membrane, Ir catalyst on Ti frit, bipolar plate with liquid flow-channel facing the Ti frit, gas flow-channel on the other side. From this on, the same elements (from the GDE) were repeated in the same order to build multi-stack electrolyzers. After the last stack, the anode endplate and current collector with liquid flow-channel and anolyte in- and outlet was used to finish the cell. The proper gas and liquid sealing in the cell were ensured by Viton O-rings. While the presented cell-stack is completely scalable, the presented data were recorded with a stack which contained up to three electrolyzer layers (having 61 cm^2 /stack active area), connected through bipolar plates.

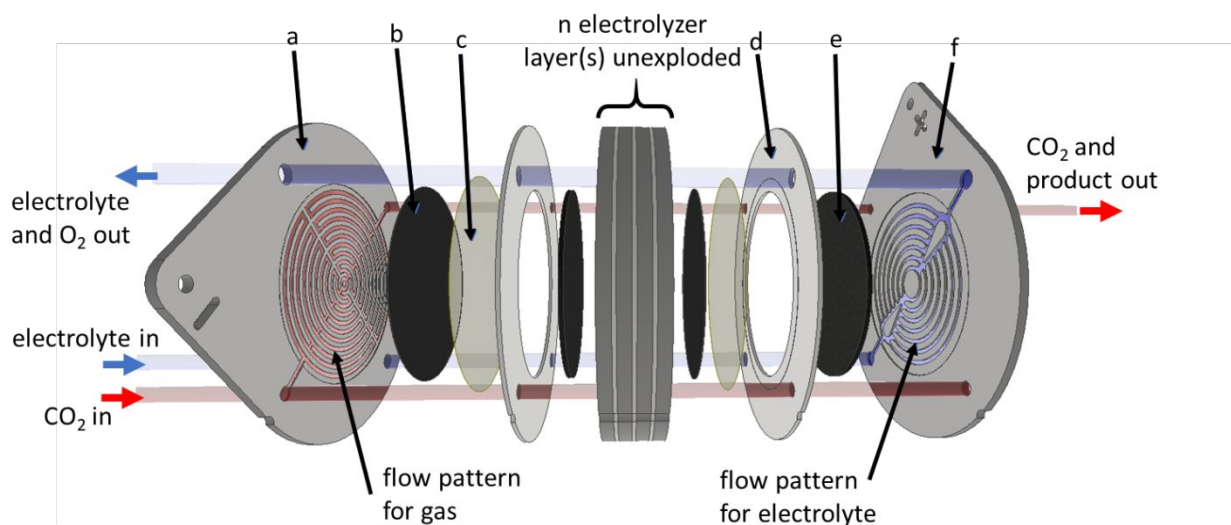


Figure S1. Schematic structure of the electrolyzer cell-stack with multiple layers, in the parallel configuration. The route of the CO_2 gas and the electrolyte in the cell are shown in red and blue, accordingly. a: cathode current collector; b: cathode GDE; c: ion exchange membrane; d:

membrane holder and insulator element; e: porous Ti frit with anode catalyst; f: anode current collector.

The cell design allows building multi-layer stacks, in which the cells could either be connected in parallel or in series in terms of gas-flow management (**Figure 1A** and **B** in the m/s, respectively). The parallel connection means that the CO₂ stream is evenly split between the layers, hence pure CO₂ is fed on each of them. In the serial connection the total CO₂ stream enters the first layer, and the remnant of this, together with the electrolysis products continue to the subsequent layer(s). The liquid flow channels were always connected in parallel, thus providing fresh electrolyte to each layer. Regarding the electrical connections, the layers were always contacted in series, hence the overall stack voltage was controlled. The individual cell voltages were measured periodically between the adjacent bipolar plates using a hand-held multimeter.

The cell-stack was fed with humidified (in $T = 22 \pm 2$ °C H₂O) CO₂ on the cathode side, while $T = 50$ °C 1M KOH was supplied to the anode (1.5 dm³ min⁻¹ feed rate). The CO₂ feed rate was controlled with a Bronkhorst F-201C type mass-flow controller, while an Agilent ADM G6691A type flow meter was used to measure the flow-rate of the cell gas outlet. The pressure of the CO₂ in the electrolyzer was controlled by a Swagelok back pressure regulator and measured using an analogue pressure gauge.

The electrochemical measurements were performed using a TDK Lambda GEN12.5-120 type power supply, driven by a custom developed LabVIEW software. The measurements were conducted in a two-electrode setup, and the cell voltage is given as the voltage difference between the cathode and the anode (hence the negative values). The recorded currents are shown as negative values as our focus is on the reduction processes (CO₂RR and HER). No IR-correction was applied on the voltage values presented throughout the manuscript.

The composition of the product stream was analyzed using a Shimadzu GC-2010 Plus type instrument, equipped with a barrier discharge ionization (BID) detector. A ShinCarbon ST column was used for the separation, with helium (99.9999%) as the carrier gas. Samples were taken in regular intervals through an automatized 6-port valve. All the instruments and the electrolyzer cell was incorporated in a custom designed test station (**Figure 1C** in the m/s). The tubing and the connections between the parts were built from Swagelok elements.

Structure of the cathode catalyst layers

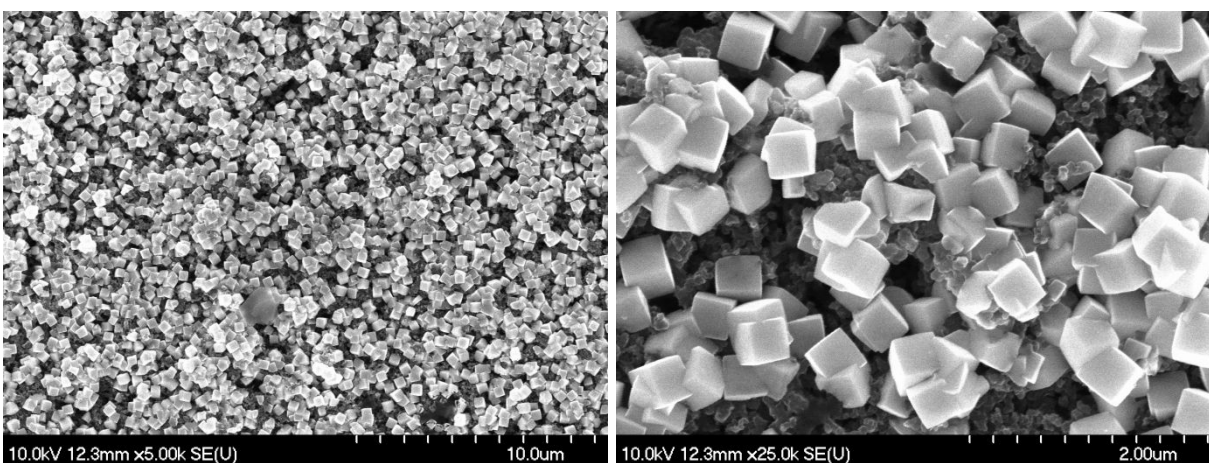


Figure S2. SEM images of the Cu catalyst electrodeposited on a Sigracet 39BC type GDL.

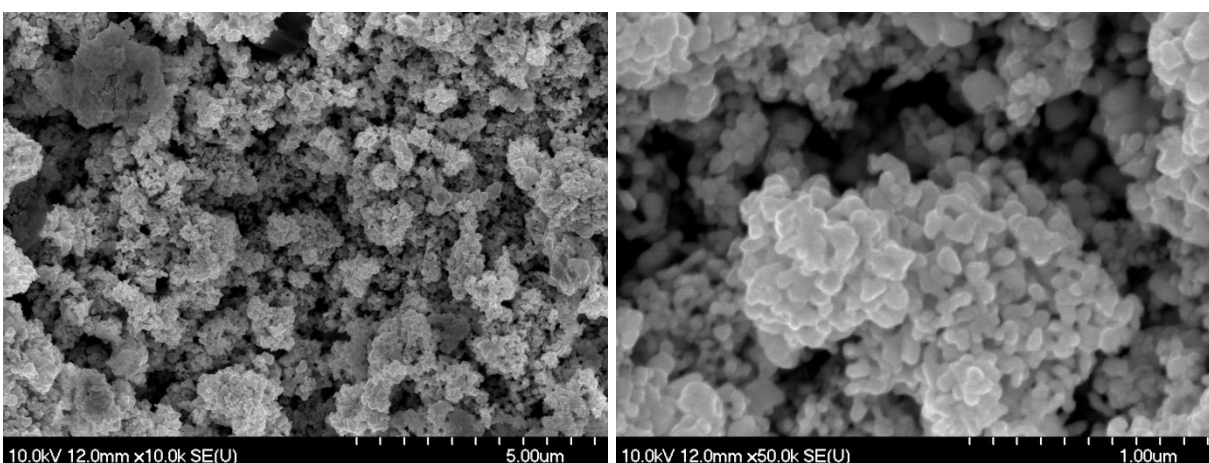


Figure S3. SEM images of the Ag catalyst spray coated on a Sigracet 39BC type GDL. The catalyst layer contained 15% ionomer.

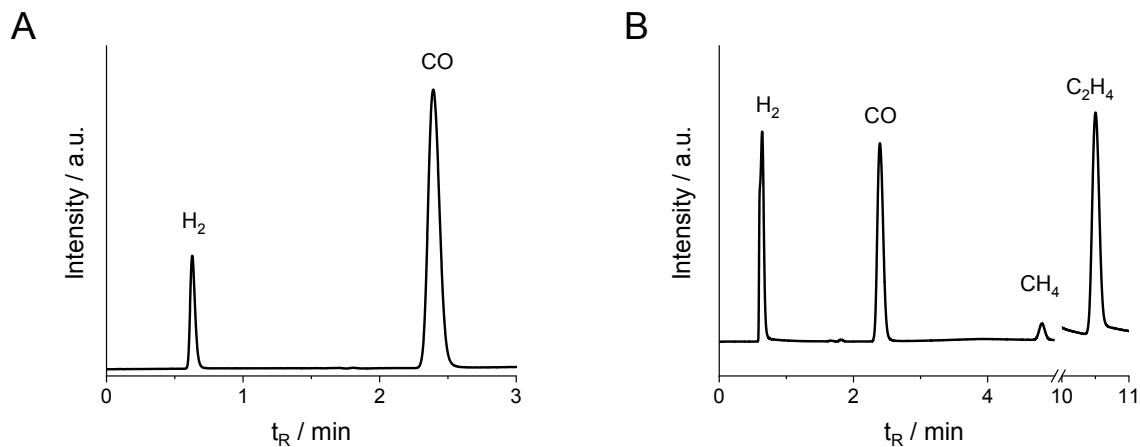


Figure S4. Gas chromatograms of the electrolysis product gas stream for Ag (A) and Cu (B) catalysts, during the measurements shown in Figure 2B in the manuscript.

Electrolysis of CO_2 to CO in a multi-stack electrolyzer

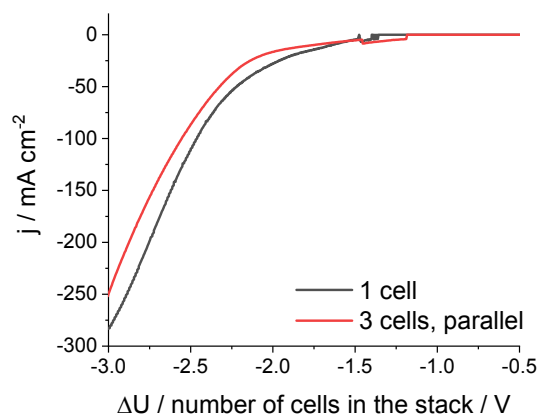


Figure S5. Comparison of the LSV curves recorded with a single-cell and a three-layer stack in the parallel configuration at $v = 10 \text{ mV s}^{-1}$ sweep rate, with $433 \text{ cm}^3 \text{ min}^{-1}$ CO_2 feed rate per layer at the cathode.