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Supporting Information

Enhanced formation of $>$C1 Products in Electroreduction of CO_2 by Adding a CO_2 Adsorption Component to a Gas-Diffusion Layer-Type Catalytic Electrode

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1. Description of the electrocatalytic cell and related electrodes

The electrochemical cell for CO_2 reduction working in gas-phase (under electrolyte-less conditions) is designed to operate under a continuous flow of CO_2 diffusing through the GDL to arrive to the surface of the electrocatalyst. The homemade cell (built in Plexiglas) is located within an oven to operate also at higher temperatures (up to about 70-80°C). At temperatures higher than 80°C, the conductivity of Nafion® membrane sharply decreases and different kinds of membraned should be used (such as polybenzimidazole-based membranes) [1]. However, all the tests reported in this paper were carried out at room temperature to be comparable to the more common liquid-phase reported in literature. Figure 1S shows a schematic drawing and a picture of the experimental apparatus.

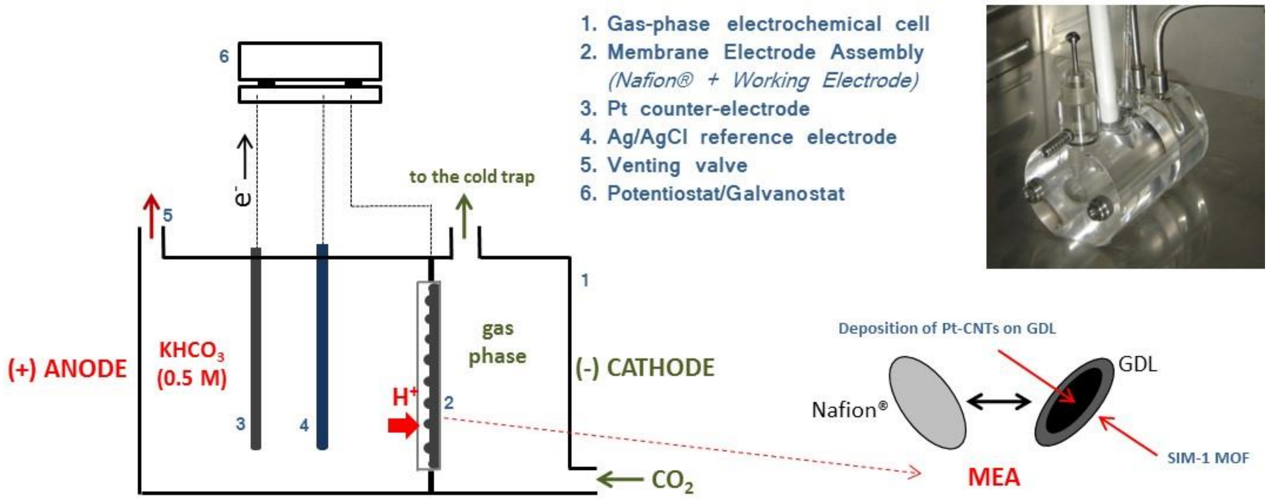

Figure 1S: Schematic drawing and picture of the experimental apparatus for electrocatalytic tests of CO_2 reduction in gas-phase (electrolyte-less conditions). Adapted from Reference [2].

The cell has a three-electrode configuration, with a Pt rod as the counter-electrode and a Ag/AgCl electrode as the reference electrode, both submerged in the anode compartment. The working electrode, prepared by the method reported in the experimental section, is a Gas Diffusion Electrode (GDE) with SIM-1 MOF and Pt-CNTs deposited onto the two opposite sides of a commercial Gas Diffusion Layer (Sigracet® GDL 25 BC).

The main properties of commercial GDL and CNTs are reported in Table 1S.

Table 1S: Properties of the as-produced commercial materials used to prepare the electrocatalyst.

Properties of GDL 25 BC Sigracet®	
thickness	235 μm
areal weight	86 g/m^2
porosity	80 %
air permeability	1.0 cm^3/(cm^2 s)
electrical resistance (through plane)	<12 mΩ cm^2

Properties of CNTs PR-24-XT-PS Pyrograf®	
Fiber diameter (average)	100 nm
Surface area	45 m^2/g
Dispersive surface energy	85 mJ/m^2:
Moisture	<5 wt.%
Iron	<14,000 ppm
Polyaromatic hydrocarbons	<1 mg PAH/g fiber

The resulting composite catalytic layer (SIM-1/GDL/Pt-CNTs) was assembled with a Nafion® membrane (Nafion® 115, supplied by Ion Power) by hot pressing at 80 atm and 130°C for 90 s, to form a Membrane Electrode Assembly (MEA), in analogy to fuel cells. The SIM-1 MOF layer is thus on the GDL side at direct contact with CO_2 in gas-phase, while the electrocatalyst (Pt-CNTs) is on the other side of the GDL in direct contact with the Nafion® membrane. The GDL is also electrically connected through a wire with the other side of the electrocatalytic cell. The active area of the GDE is around 2 cm^2. The MEA separates the cell into two compartments. The anode side is filled with an electrolyte aqueous solution ($KHCO_3$ 0.5 M) and it is in direct contact with one side of the Nafion® membrane. A gas flow of pure CO_2 (10 ml/min) is continuously fluxed into the cathodic compartment.

A potentiostat/galvanostat (Amel mod. 2049A) was used to supply a constant current (-10 mA) between the electrodes. At the end of the reaction (1 h), the current polarity was inverted to facilitate desorption of the products from the working electrode. The liquid products were collected in a cold trap from the gaseous stream leaving the cathodic part of the cell. They were analysed by a gas chromatograph equipped with a mass detector (Thermo Scientific GC Trace 1310 – ISQ MS). The gaseous stream was also periodically sampled (every 20 min) and analysed by a gas chromatograph equipped with a Thermal Conductivity Detector (Agilent 7890A, TCD) to detect the formation of H_2, CH_4 and CO.

The structural and morphological characterization of the MOF-based GDL was performed by a scanning electron microscope (SEM) with Quanta 250 FEG FEI high resolution field emission gun, equipped with energy dispersive x-ray (EDX) analyser, at the "Centre Technologique des Microstructures" (CTμ, Villeurbanne, France).

The electrocatalytic tests were performed in galvanostatic mode, by applying a constant current (-10 mA) and reading the voltage. Figure 2S shows the voltage profile during the first hour of reaction in presence of SIM-1/GDL/Pt-CNTs as Gas Diffusion Electrode. After 30 min the voltage reached a plateau of about -1.5 V.

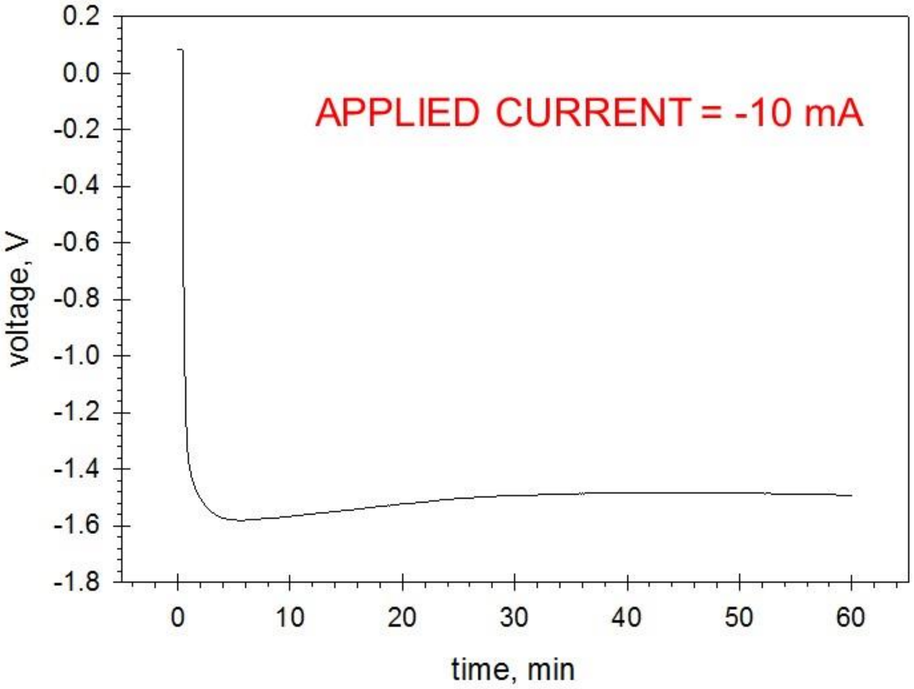

Figure 2S: Voltage vs. time profile during the electrocatalytic reduction of CO_2 in gas-phase with MOF-doped GDL/Pt-CNTs as electrocatalyst (Galvanostatic mode, Set current = -10 mA).

References

[1] A. Chandan, M. Hattenberger, A. El-kharouf, S. Du, A. Dhir, V. Self, B. G. Pollet, A. Ingram, W. Bujalski, High temperature (HT) polymer electrolyte membrane fuel cells (PEMFC) - A review, Journal of Power Sources, 231 (2013) 264-278.

[2] C. Ampelli, C. Genovese, B. C. Marepally, G. Papanikolaou, S. Perathoner, G. Centi, Faraday Discuss. 2015, 183, 125-145.