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Enhanced formation of >C1 Products in Electroreduction of CO₂ by Adding a CO₂ Adsorption Component to a Gas-Diffusion Layer-Type Catalytic Electrode

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The addition of a CO₂-adsorption component (substituted imidazolate-based SIM-1 crystals) to a gas-diffusion layer-type catalytic electrode enhances the activity and especially the selectivity towards >C1 carbon chain products (ethanol, acetone, and isopropanol) of a Pt-based electrocatalyst that is not able to form products of CO₂ reduction involving C–C bond formation under conventional (liquid-phase) conditions. This indicates that the increase of the effective CO₂ concentration at the electrode active surface is the factor controlling the formation of >C1 products rather than only the intrinsic properties of the electrocatalyst.

There is increasing interest for the electrocatalytic reduction of CO₂,[1–5] not least because this approach represents a key way to develop renewable energy-based technologies for the conversion of carbon dioxide into chemicals and to utilize CO₂ as an energy vector,[6] including in artificial-leaf type devices.[7] Although the electrocatalytic reduction of CO₂ has often been focused on simple $2e^-$ reactions, such as the formation of CO or formic acid, there is a need to address more challenging reactions leading to the direct formation of >C1 products through electrocatalytic reduction of CO₂. This is necessary for process and energy intensification. For example, in the direct electrocatalytic reduction of CO₂ to acetic acid[8] the process is four-to-five times more energy-efficient than the industrial multistep process starting from fossil fuels, with an equivalent enhancement in terms of CO₂ emission savings. Owing to the reduction in the number of steps and the formation of higher added-value chemicals, such processes are economically advantageous over simple reactions such as CO or formic acid formation.

We have reported that operations carried out in electrolyte-free conditions, also called "gas-phase conditions",[9] can allow enhanced formation of >C1 products in relation to the more conventional CO₂ electrochemical reductions in the presence of a liquid electrolyte. The electrode in this case, in contrast to liquid-phase operations in the presence of a liquid electrolyte, is composed of the electrocatalyst deposited over a gas-diffusion layer (GDL), which is used as an electron-conductive substrate and to sandwich the electrocatalyst between the GDL and the proton-conductive membrane.[5, 9]

We proposed that the enhanced formation of >C1 products under "gas-phase" conditions is due to the enhanced concentration of CO₂ at the electrode surface. Recently, Bajracharya et al.[10] reported that the use of gas-diffusion electrodes enhanced the mass transfer of gaseous molecules, such as CO₂, to the electrocatalytic sites, in comparison with electrodes submerged in a liquid electrolyte. Albo and Irabien reported that CO₂ concentration in the vicinity of a Cu₂O-based gas-diffusion electrode (GDE) was able to influence the product selectivity.[11] Moreover, they observed that the process of CO₂ reduction was limited by the internal diffusion of reactants through the porous structure of the GDE. In general, the gas-phase approach is advantageous with respect to operations at high pressure, since it avoids fixed and operative costs linked to high-pressure electrochemical cells and the known problem of fast deactivation in high-pressure operations with CO₂.

The concept that the surface concentration of CO₂ at the electrode is the key factor determining the possibility of forming >C1 products contrasts with the common indication in earlier reports that only specific electrocatalytic metals, such as Cu, are able to give this type of products.[12] To refute this indication and to further support the idea that the surface concentration of CO₂ at the electrode is key, we report herein a novel approach, based on the deposition of a CO₂ adsorption component onto the GDL to enhance the concentration of CO₂ at the electrocatalyst surface. Deliberately, an electrocatalyst based on Pt nanoparticles supported on carbon nanotubes (Pt/CNTs) was used, because this electrocatalyst is not able to

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form >C1 products in the electrocatalytic conversion of CO_2 under conventional operations in the presence of a liquid electrolyte[9a] and Pt metal has been reported to be unable to give >C1 products.[12] It is thus possible to proof the concept that the surface coverage rather than metal surface characteristics only determines the possibility to form >C1 products in the electrocatalytic conversion of CO_2. We report herein that gas-phase electrocatalytic reduction (i.e., that in the absence of a liquid electrolyte, in contrast to the majority of reported data), in which the gas-diffusion layer (GDL) is modified by depositing a component that enhances the CO_2 adsorption, leads to a significant promotion of both the activity and the selectivity of the Pt/CNTs electrocatalyst, and particularly to the formation of >C1 products that are not detected under conventional conditions. This finding indicates that the selectivity and nature of the products in the electrocatalytic reduction of CO_2 considerably depend on the concentration of CO_2 at the electrocatalytic sites, and not only on the type of electrocatalyst.

As the CO_2 adsorption component, we used substituted imidazolate-based metal–organic framework SIM-1, developed at IRCELYON for CO_2 separation membranes.[13] SIM-1 belongs to the class of zeolitic imidazolate framework (ZIF) materials also known as ZMOFs.[14] The zinc imidazolate SIM-1 is isostructural to ZIF-8 (SOD) and consists of Zn tetrahedra linked by 4-methyl-5-carboxylimidazolates. SIM-1 crystallites were grown selectively on only one side of a commercial gas-diffusion layer (Sigracet GDL 25 BC, a non-woven carbon paper with a microporous layer having a total thickness of 235 μm). The SEM cross-section image of such GDL layer (Figure 1 a) shows that the SIM-1 crystals form a layer of around 20 μm on the bottom side of the carbon paper support, corresponding, on average, to 2–3 layers of MOFs. The coverage appears uniform over the carbon fibers (Figure 1 b,c), on which the SIM-1 crystals have a cubic morphology (Figure 1 d,e) and an average crystallite size of 7.5 μm.

This SIM-1-covered gas-diffusion layer was loaded with Pt-doped carbon nanotubes (Pt/CNTs) on the MOF-free side of the GDL. The resulting composite catalytic layer (SIM-1–GDL–Pt/CNTs) was assembled with a Nafion proton membrane to form a membrane electrode assembly (MEA, in analogy with fuel cells) by hot pressing. The GDL is also electrically connect-

ed through a wire with the other side of the electrocatalytic cell.

CO_2 electrocatalytic tests were carried out in a three-electrode electrochemical cell under a continuous gas flow of pure CO_2 (10 mL min^{-1}) and without a liquid electrolyte at the cathode (gas-phase), as schematically depicted in Figure 2. The
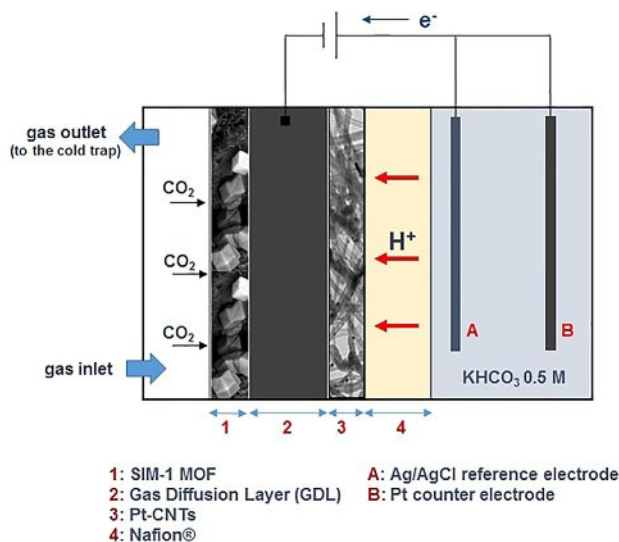

Figure 2. Schematic depiction of the membrane electrode assembly (SIM-1–GDL–Pt/CNTs–Nafion) in electrolyte-free (gas-phase) electrocatalytic reduction of CO_2.

anode operates in the liquid phase and is used to provide the protons (through the Nafion membrane) required for the CO_2 reduction process. The anode compartment is filled with an aqueous electrolyte solution (0.5 M $KHCO_3$) and is in direct contact with one side of the Nafion membrane.

A galvanostat was used to supply a constant current (−10 mA) between the electrodes. This current allows a quite constant voltage (ca. −1.5 V) between the electrodes during the first hour of testing, thus overcoming the open circuit voltage of the cell (+0.4 V). Then, the current polarity was inverted (from −10 mA to +10 mA) to facilitate product desorption from the working electrode. The products were then collected in a cold trap from the outlet gas stream leaving the cathode. The inversion in polarity acts as an electric pulse and modifies the flow of electrons, favoring desorption of the reduction products. After the current inversion, no partial oxidation of the adsorbed products was observed. A more detailed description of the experimental apparatus is reported in the Supporting Information. The electrolyte-free approach and the location of SIM-1 MOF layer on the cathode side of the GDL working in gas-phase can also circumvent the issues related to the general fast deactivation of MOF materials in presence of a liquid aqueous electrolyte.

Table 1 collates the results obtained for the SIM-1–Pt/CNTs, compared with the analogous data collected on a similar SIM-1-free Pt/CNTs electrocatalyst. The setup was also tested on SIM-1-coated GDL without the Pt/CNTs, but the activity was very low (only traces of methanol and ethanol were detected).
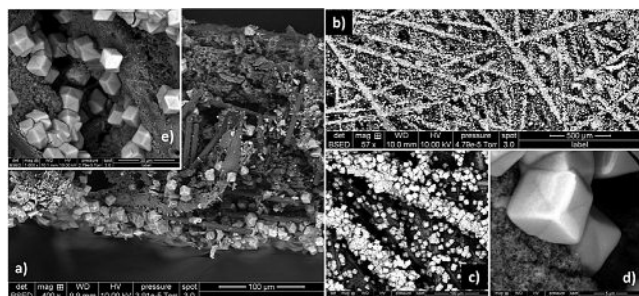

Figure 1. SEM images of SIM-1 deposited on the fibers of the GDL showing: a) A cross-section of the GDL; b,c) top views of the SIM-1-covered carbon fibers; d,e) cubic morphology of the SIM-1 crystals at different magnifications.

Table 1. Production rate ($\mu mol\,h^{-1}$) of liquid products in gas-phase CO_2 electrocatalytic reduction (standard deviations are reported in brackets). Testing conditions: -10 mA, pure flow of CO_2 in the cathode, $KHCO_3$ 0.5 M in the anode.

Electrocatalyst	Methanol	Ethanol	Acetone	Isopropanol	Total
Pt/CNTs	1.30 (± 0.07)	–	–	0.15 (± 0.01)	1.5
SIM-1–Pt/CNTs	1.50 (± 0.08)	0.41 (± 0.01)	0.0016 (± 0.0003)	0.41 (± 0.01)	2.3
SIM-1	trace	trace	–	–	n.a.

A blank test without CO_2 (which was replaced by a constant flow of Ar) was also performed to exclude CO_2 formation directly from MOF decomposition. Finally, for reference it should be indicated that, under conventional liquid-phase operation, this Pt/CNTs electrocatalyst forms only formic and acetic acid,[9a] but with a rate nearly one order of magnitude lower than in the gas phase and only slightly higher than the activity of CNT support itself (functionalized by oxidative treatment).

The SIM-1–Pt/CNTs electrode led to a 1.5-fold increase in the net carbon products (total) in comparison to the SIM-1-free Pt/CNTs electrode. The selectivity shifted towards ethanol and isopropanol. Small amounts of acetone were also detected. The faradaic selectivity to >C1 products strongly increases when the SIM-1 crystallites are present, thus showing the improvement in selectivity towards organic products with longer C chains in the presence of the MOF layer (Figure 3). The faradaic selectivity was calculated as the number of electrons exchanged to give >C1 products (i.e., ethanol, acetone, and isopropanol, requiring 12, 16, and 18 electrons, respectively) divided by the total number of electrons exchanged to give all liquid products (i.e., also including methanol).

The total faradaic efficiency, that is, by considering that electrons are also used to generate H_2 by water electrolysis (instead of using the protons/electrons to reduce CO_2), is about 5.8% at a voltage of -1.5 V. However, by decreasing the applied voltage from -1.5 V to -0.5 V, the faradaic efficiency to the products of CO_2 reduction strongly increased to about

70%, although at this voltage the current density (and thus the productivity) is quite low.

Figure 4 shows the time-on-stream evolution of H_2 and CO during the electrocatalytic tests on the two MEA assemblies,
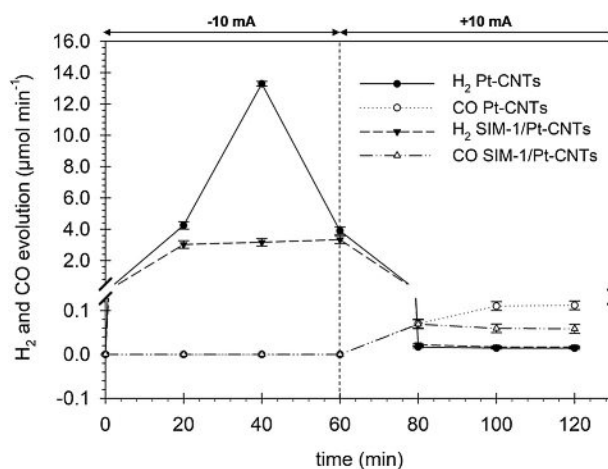
Figure 4. Hydrogen and CO evolution rates versus time for SIM-1–Pt/CNTs electrode in comparison with the same electrode but without MOF (Pt/CNTs).

with and without the SIM-1 layer. Initially, hydrogen was the main detected product of the reaction. This behavior is similar for the two cases, but the presence of MOF strongly diminished the total H_2 production. When the polarity was inverted after 1 h of reaction, H_2 formation completely stopped and CO_2 reduction products (CO, together with methanol, ethanol, isopropanol, and acetone) were detected. The CO evolution is related to the desorption of strongly chemisorbed CO on Pt and the presence of the SIM-1 layer halves the CO release. As discussed above, the Pt/CNTs-free setup—that is, that containing only the GDL and SIM-1—showed no carbon-based products (only traces), indicating that the MOF is not responsible for the observed carbon-based products and corroborating the fact that such products are genuinely due to CO_2 reduction.

The addition of SIM-1 on the external face (the one exposed to gas-phase CO_2) of the GDL has the following effects on the electrocatalytic behavior of Pt/CNTs in CO_2 reduction: an increase by about 103% of the electrons used to produce liquid fuels in the electrocatalytic reduction of CO_2; an increase in the faradaic selectivity to the formation of >C1 products from less than 26% to over 58%; a decrease in the side formation of H_2 by recombination of H^+ and e^-.

The SIM-1 component is itself not active in the electrocatalytic reduction of CO_2 and the Pt/CNTs electrocatalyst is the same in the two cases. It is thus well proof the concept that a modification in the CO_2 concentration at the electrocatalyst surface (induced by the presence of the CO_2 adsorption component, even if physically separated from the electrocatalyst, being present in the GDL layer exposed to gas phase) has a dramatic influence on the selective performances of the electrocatalyst. The presence of SIM-1 on the external surface of the GDL enhances the effective concentration of CO_2 within
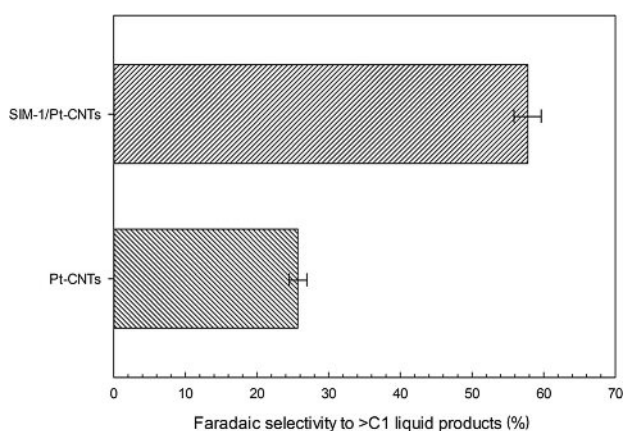

Figure 3. Faradaic selectivity to >C1 liquid products for SIM-1–Pt/CNTs electrode in comparison with the same electrode without MOF component (Pt/CNTs).

the GDL layer, where the electrocatalyst (Pt/CNTs) is located at the contact with the Nafion membrane. Upon adsorption by the MOF, the carbon dioxide diffuses on the surface of the GDL (a porous structure made by pressing carbon fibers together into a carbon paper) to reach the Pt nanoparticles, where the reduction of CO_2 occurs in the presence of protons and electrons.

Even if the GDL is porous and permeable to CO_2, and a pure CO_2 stream is fed continuously to the electrochemical gas-phase hemi-cell (Figure 2), the effective surface concentration of CO_2 at the Pt nanoparticles is likely controlled by diffusion through the Helmholtz double layer. The presence of surface transport, providing an additional transport mechanism, can increase the effective concentration of CO_2 at the Pt nanoparticle surface. The higher surface concentration of CO_2 could explain the increased formation of C—C bonds, as demonstrated in the case of acetic acid synthesis,[8] and the reduced surface concentration of CO (reacting to give >C1 products). The higher surface concentration of CO_2 can explain also the more efficient reaction of protons and electrons with surface carbon species, limiting the side reaction of H_2 formation. Alternatively or concomitantly, the SIM-1 component could also alter the exo diffusion of the products from the electrocatalyst. Regardless of the mechanism(s) at hand, the consequence is an increase in productivity and in the selectivities to longer C chains.

Although further evidence of the mechanism is necessary, these data do indicate that cell design parameter(s) other than exclusively the nature of the metal can increase the possibility to form >C1 products in the electrocatalytic reduction of CO_2. Previous studies, including various theoretical studies, suggested that, to date, only Cu surfaces have been able to give rise to products with C—C bond formation.[12, 15] As shown here, also Pt-based electrocatalysts are able to form products involving C—C bond formation during the electrocatalytic reduction of CO_2, provided that a novel component (SIM-1 in this case) can promote the enhanced surface concentration of carbon dioxide.

In conclusion, we have reported herein the positive effect of a CO_2-capturing component (SIM-1) present in the GDL of a gas-phase electrode in enhancing the activity and especially the selectivity to >C1 products in the electroreduction of CO_2. The results indicate that the surface concentration of CO_2— and not just the nature of the electroactive metal, as commonly reported—can become a key factor in steering the selectivity. This aspect should therefore become a new parameter to be considered, especially in modeling the electrocatalytic behavior in CO_2 reduction.

Experimental Section

A commercial gas-diffusion layer (Sigracet GDL 25 BC, supplied by Ion Power), with one side protected by a Teflon mask, was immersed in a suspension of $Zn(NO_3)_2 \cdot 4 H_2O$ (0.71 g) and 4-methyl-5-imidazolecarboxaldehyde (1.2 g) in dimethylformamide (20 mL). After solvothermal treatment at 85 °C for 48 h, the resulting supported GDL (with SIM-1 selectively deposited on one side of the

GDL) was washed with ethanol (ca. 15 mL) to remove unreacted precursors and fine unsupported SIM-1 particles, and then dried at room temperature. The final loading of SIM-1 was about 3.5 mg cm^{-2} of the geometrical area of the GDL. The microscopy characterization was performed by scanning electron microscopy (SEM), using a FEI Quanta FEG 250, at the "Centre Technologique des Microstructures" (CTμ, Villeurbanne, France). The Pt/CNTs were prepared starting from commercial CNTs (PR-24-XT-PS, Pyrograf). The CNTs were first treated in concentrated HNO_3 (65 %, 50 mL g$_{CNTs}^{-1}$) under reflux at 100 °C for 3 h, to introduce oxygen functionalities on the external carbon surface. Then, Pt was deposited on the CNTs by using an ethanolic solution containing the metal precursor ($H_2PtCl_6 \cdot 6 H_2O$). The relative quantities of reactants were chosen to yield 10 wt % Pt with respect to CNTs. The samples were annealed for 2 h at 350 °C and finally reduced in H_2 at 400 °C for 2 h. The as-prepared Pt/CNTs, in the form of an ethanolic ink, were deposited on the free side of the GDL (the opposite side to the SIM-1 MOF). Finally, the composite layer SIM-1–GDL–Pt/CNTs was assembled with a Nafion membrane (on the Pt/CNTs side) to form the MEA.

Conflict of interest

The authors declare no conflict of interest.

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