**Electrocatalytic reduction of CO2 to solar fuels: Insight into product distribution by varying the current density**

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**Highlights**

* The influence of current density on CO2 reduction product distribution is studied.
* 27.4 % carbon Faradaic efficiency is obtained under industrial relevant conditions.
* CO and formic acid are the main products obtained at high current density.
* Current density directly affects the C-C bond formation.

**1. Introduction**

The (photo-)electrocatalytic reduction of CO2 to energy-dense chemicals is an emerging route for storing the intermittent renewable energy produced by sunlight and closing the cycle of CO2 production/consumption [1]. To achieve higher efficiencies towards hydrocarbons and oxygenates, and limit the side-reaction of water electrolysis, many efforts have been made on designing the electrodes and the related cell [2]. The selective distribution of CO2 products, in fact, depends not only on the catalytic materials used for assembling the electrodes, but it is strongly influenced by the operational conditions (i.e. electrolyte, pressure, current density, cell configuration). Generally, high current densities are often required for industrial application, in which high space-time yields are mandatory, for reasons related to stoichiometry (the specific rate of an electrode reaction is proportional to the current density by Faraday’s law) and economics (to support the capital cost of the electrochemical reactors). Thus, the products may be greatly different by changing the current density and this should be taken into account in scale-up industrial operation.

In this context, the main objective of this contribution is to show the influence of current density on product distribution in CO2 electroreduction, by testing copper-doped carbon nanotubes deposited on a gas diffusion layer, thus opening the route towards a practical implementation of CO2 electroreduction process with low-cost and earth abundant materials as electrocatalysts.

**2. Methods**

Copper nanoparticles (Cu NPs) were deposited on pre-functionalized carbon nanotubes (CNTs) by incipient wetness impregnation. The total amount of Cu loaded onto the CNTs was 5 wt.%. The as-prepared Cu NPs-CNTs were then deposited on a carbon gas diffusion layer (GDL) and finally joined to a proton exchange membrane (Nafion) to form a Membrane Electrode Assembly – MEA (in analogy with fuel cells) [3]. The electrodes were fully characterized by different advanced techniques (such as XRD, SEM, HR-TEM) to study their morphological and structural characteristics, as well as by Linear Sweep and Cyclic Voltammetry to evaluate their electrochemical properties. Finally, Cu NPs-CNTs/GDL electrodes were tested in the process of CO2 electroreduction using a homemade compact device working in a three-electrode configuration, by processing pure CO2 in 0.1 M KHCO3 electrolyte.

**3. Results and discussion**

The tests were carried out at different applied potentials (from -0.5 to -1.7 V vs. Ag/AgCl), corresponding to different current densities (from 0.1 to 2.3 mA cm-2, respectively). A further test was carried out in amperometric mode applying directly 10 mA cm-2, in order to evaluate the catalytic performance under industrial relevant conditions.



**Figure 1.** Faradaic efficiency (%) vs. current density.

As shown in Figure 1, the total Faradaic efficiency values are all ranging from 75 to almost 90 %, except when the current density is very low (0.11 mA cm-2). At this current density, no hydrogen was detected, as the applied voltage (-0.5 V vs. Ag/AgCl) was not sufficient to activate water reduction. However, under industrial relevant conditions (10 mA cm-2), the carbon Faradaic selectivity was quite high (27.4 %), indicating Cu NPs-CNTs/GDL as a promising electrocatalyst for CO2 reduction process. Formic acid was the main carbon product formed, while carbon monoxide started to form at 2.25 mA cm-2 and became even higher than formic acid at 10 mA cm-2. At low current density, the product distribution was quite different: methanol, ethanol and isopropanol (especially at 0.25 mA cm-2) were formed, while acetic acid and oxalic acid were produced at -0.5 V vs. Ag/AgCl (0.11 mA cm-2). These are examples of products involving C-C bond formation.

**4. Conclusions**

These results showed that the current density strongly affects the product distribution. Specifically, acetic acid, ethanol, formic acid, oxalic acid, methanol, and isopropanol are the main products obtained at lower current density, while the production of formic acid, CO and H2 increased at higher current density, evidencing a direct influence of this parameter on C-C bond formation.

**Acknowledgments:** *This work was funded by the European Union’s Horizon 2020 project A-LEAF (Grant Agreement No. 732840).*

**References**

1. B.C. Marepally, C. Ampelli, C. Genovese, E.A. Quadrelli, S. Perathoner, G. Centi, in: S. Albonetti, S. Perathoner, E.A. Quadrelli (Eds.), Stud. Surf. Sci. Catal. 178 (2019) 7–30.
2. C. Ampelli, F. Tavella, S. Perathoner, G. Centi, Chem. Eng. J. 320 (2017) 352–362.
3. C. Genovese, C. Ampelli, S. Perathoner, G. Centi, Green Chem. 19 (2017) 2406–2415.