**Insight into the practical challenges of membrane-electrode assembly for the CO2 electrochemical reduction and its advantages**

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**1.Introduction**

The heat-trapping nature of carbon dioxide (CO2) makes its ever-increasing concentration in the atmosphere a growing threat to global security. The International Energy Agency (IEA) recently found that the CO2 emissions rose by over two billion tons in 2021, that is after the pandemic impacted the world economy, reaching their highest ever level[1]. Then, efforts are needed to counteract this trend and to avoid the irreversible consequences of climate change. In this context, several alternatives have been proposed to convert CO2 to valuable products: the electrochemical reduction of CO2 (ECR-CO2) represents one of the most promising routes, allowing to employ renewable resources and to obtain a wide spectrum of gaseous and liquid products, in accordance with sustainable development and circular economy. In this work, the ECR-CO2 has been carried out in gas diffusion electrodes (GDE)-based systems, where the limitations of mass transport associated with the CO2 diffusion in electrolyte solutions can be overcome by directly feeding CO2 in gaseous form to the electrode surface[2]. Copper (Cu)-based catalysts[3] have been employed in our alkaline continuous flow cell, in which a potassium hydroxide solution has been selected as electrolyte both in the cathodic and the anodic chambers. Moreover, the two liquid chambers have been separated by an anion exchange membrane (AEM). In view of an industrial deployment, CO2 electrolysers must provide modest cell voltages during operations as well as they must selectively produce concentrated target products at high rates[4]. This challenge is being currently met by researchers moving from a so-called three chambers configuration towards a membrane-electrode assembly (**Figure 1**). The purpose of this work is therefore to demonstrate the benefits of reducing the distance between the electrode surface and the membrane to reach a zero-gap system, analyzing also the critical issues which might have to be addressed.



**Figure 1.** Schematic layouts of the GDE (left) and MEA (right) configurations.

**2. Methods**

A porous and conductive support was employed for the manufacturing process of the GDEs, where the Cu-based catalyst was deposited by means of a spray coater (automated technique). In the case of MEA, the electrode was successively hot-pressed to the AEM according to our own optimized procedure[5]. The characterization of the electrodes was performed by X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM) analytical techniques. On the other hand, the electrochemical behavior of the electrodes was assessed by conducting cyclic and linear sweep voltammetry measurements (CV, LSV). Furthermore, two hours-chronopotentiometry (CP) tests were carried out to investigate on the stability and the CO2 reduction performance of the GDEs. With reference to the latter aspect, the gaseous products were monitored continuously during the CP, while the liquid products analysis was conducted at a later time by means of high-performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS) methods.

**3. Results and discussion**

The findings highlight a general suppression of the hydrogen evolution, the main competitor for the electrochemical CO2 reduction in aqueous electrolytes, when migrating from GDE to MEA configuration. In addition, the formation of C2+ products was enhanced (with an increase in FE towards C2+ of about 13%), leading to a more efficient process in energy terms. Moreover, the MEAs required lower applied cell potentials for sustaining two-hours experiments than GDEs, under the same operating conditions (i.e., current density, catalyst loading, electrolyte solutions, gas and liquid(s) flow rates, etc.). However, the process of getting a well-made MEA is not a straightforward task as well as finding the most suitable working conditions: going by order, one first need to identify the temperature and pressure conditions of the hot-pressing step which on the one hand allow the complete transfer of the catalytic layer onto the membrane, and on the other hand do not cause unwanted breakage/cracks of either the carbon support or the membrane itself; subsequently, the proper moisture content of the CO2 feed gas must be found in order to optimize the water balance in the components of the MEA (herein, we obtained a humid stream by sending CO2 in a water source at 80°C); ultimately, the operating conditions and the cell design aspects need to be deeply studied to avoid delamination and, thus, the worsening of the performance during operation.

**4. Conclusions**

The challenging need to move towards low-carbon emitting technologies has pushed researchers in the last period to focus not only on the catalyst development but also on the overall system design, with the aim to minimize the potential losses while keeping high selectivities at sustained rates. Accordingly, due to the low solubility of CO2 in aqueous solutions and to mass transfer limitations, the attention is currently being drawn towards GDE-based systems, where shorter diffusion pathways and higher CO2 concentration than in traditional devices can lead to commercially-relevant current densities. The intent of the present work is to prove the advantages that result from the use of a membrane-electrode assembly, i.e., reducing the gap between membrane and electrode up until reaching a distance equal to zero, not neglecting but rather discussing the experimental challenges that the worker potentially has to deal with. In particular, we observed that switching from GDE to MEA is possible to promote the CO2 reduction reactions at the expense of hydrogen production and with lower energy consumption.

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