



Electrocatalytic conversion of CO₂ to added-value chemicals in a high-temperature proton-exchange membrane reactor



N. Gutiérrez-Guerra^a, J.L. Valverde^a, A. Romero^a, J.C. Serrano-Ruiz^b, A. de Lucas-Consuegra^{a,*}

^a Department of Chemical Engineering, School of Chemical Sciences and Technologies, University of Castilla-La Mancha, Avda. Camilo José Cela 12, 13005 Ciudad Real, Spain

^b Department of Engineering, Universidad Loyola Andalucía, Energía Solar, 1. Edifs E, F y G, 41014 Sevilla, Spain

ARTICLE INFO

Keywords:

PEM
Cu catalyst
CO₂ electroreduction
Electrolysis
Solar fuels
Electrocatalytic hydrogenation

ABSTRACT

We have developed a novel gas-phase electrocatalytic system for the conversion of CO₂ into added-value chemicals. The system is based on a high-temperature proton-exchange membrane reactor containing a Cu cathodic catalyst supported on carbon nanofibers (CNFs) and an H₃PO₄-doped polybenzimidazole polymer electrolyte membrane (PBI). The resulting Cu–CNFs/PBI/IrO₂ membrane electrode assembly (MEA) allowed the utilization of higher temperatures (110 °C) than has been previously reported. The application of a low current density (– 0.8 mA/cm²) permitted the direct transformation of CO₂ into various organic compounds in the C₁–C₃ range, acetaldehyde being the most common product (85% selectivity). The application of a higher current density (– 1.6 mA/cm²) increased the overall electrocatalytic activity of the system, producing lighter and more saturated compounds. The novel electrochemical cell proposed in this work allows the conversion of CO₂ into valuable products under mild conditions (i.e., room pressure, 110 °C) with no requirement for H₂ and using electrical energy that could potentially be obtained from renewable energy sources.

1. Introduction

The electrocatalytic reduction of CO₂ has been recognized as an interesting approach for converting CO₂ into high-energy-density products (electrosynthesis) rather than being seen as a method for the large-scale reduction of the level of this greenhouse gas in the atmosphere [1]. The reaction provides a cheap source of carbon for synthesis and can also be used to detect CO₂ in clinical and industrial environments. In this regard, gas-phase electrocatalytic cells (similar to those used in proton-exchange membrane (PEM) fuel cells based on a Nafion polymeric membrane and carbon electrocatalysts) have been previously studied and proposed as a plausible route for production of hydrocarbons and oxygenates [2,3–6]. Gas-phase electrocatalytic reduction studies are very scarce in the literature compared to liquid phase reduction routes, and all employed low-temperature protonic conductor membranes (e.g., Nafion membranes) that are limited to a maximum operating temperature of 90 °C, thereby negatively affecting the kinetics of the overall process.

In this work, we propose a novel gas-phase electrocatalytic cell involving a high-temperature proton-exchange membrane (i.e., H₃PO₄-doped polybenzimidazole-polymer electrolyte membrane (PBI)) which makes it possible to work at higher temperatures, thereby improving

the CO₂ electroreduction rates. With this aim, a Cu cathodic catalyst supported on functionalized carbon nanofibers (CNFs) was fabricated while the PBI membrane was used as a solid polymer electrolyte. PBI is a basic polymer (pK_a = 5.5) that can be easily doped with strong acids to form a single-phase polymer electrolyte [7]. The main reaction products of the gas-phase electrocatalytic reduction of CO₂ at 110 °C were analyzed. Additionally, the influence of the applied current on electrocatalytic activity and product selectivity was investigated.

2. Experimental

2.1. Preparation, characterization, and assembly of the catalysts and electrodes

Copper supported on functionalized CNFs (Cu–CNF) was used as the cathodic catalyst, while IrO₂ was selected as the anodic catalyst because of its superior ability towards water oxidization [8]. First, the CNFs were synthesized by a catalytic chemical vapor deposition (CVD) method in a fixed-bed reactor at atmospheric pressure, following the procedure described elsewhere [9]. The CNFs were functionalized via an oxidative treatment with HNO₃ with the aim of introducing oxygen-containing groups onto the carbon surface. The Cu metal particles were

* Corresponding author.

E-mail address: Antonio.lconsuegra@uclm.es (A. de Lucas-Consuegra).

subsequently deposited on the CNF support by impregnation using an ethanol–water solution containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as a precursor. The solvent was subsequently removed by vacuum evaporation at 90 °C, dried at 120 °C, calcined for 2 h at 350 °C in a N_2 atmosphere, and finally reduced in H_2 at 300 °C for 2 h (heating rate: 5 °C/min). The total Cu loading (nominal Cu metal loading on the powdered catalyst: 50 wt %) was determined by atomic absorption spectrophotometry using a SPECTRA 220FS analyzer.

The cathodic and anodic catalyst inks were subsequently prepared by mixing appropriate amounts of Cu–CNF and IrO_2 (Alfa Aesar, 99%), respectively, with PBI ionomer (5 wt% PBI in *N,N'*-dimethylacetamide, DMAc), with DMAc serving as a solvent. The inks were applied on carbon paper substrates (Fuel Cell Earth) at 130 °C until a metal loading of 0.5 mg/cm² was obtained for both electrodes. The geometric surface area of both electrodes was 12.56 cm² (circular electrode 4 cm in diameter). The electrodes were then wetted with a 10% H_3PO_4 solution at a loading of 30 mg/cm², and the electrodes were left to absorb the acid overnight. The commercial PBI membrane was removed from a 85 wt% phosphoric acid bath and the membrane electrode assembly (MEA) was prepared as follows. The anode/membrane/cathode assembly was mounted by hot-pressing using a press at 1 metric ton and 130 °C for 15 min. Transmission electron microscopy (TEM) observations were conducted for the powder cathodic catalysts on a JEOL JEM-4000EX unit with an accelerating voltage of 400 kV. The Cu-based cathodic electrode was also characterized before the reaction tests by X-ray diffraction (XRD) on a Philips PW-1710 diffractometer using Ni-filtered Cu K α radiation ($\lambda = 1.5404 \text{ \AA}$).

2.2. Electrocatalytic activity measurements

The electrocatalytic conversion of CO_2 was carried out in a lab-scale continuous atmospheric-pressure electrochemical cell reactor, which has been described in detail elsewhere [10]. The anode side of the cell was fed with a 1 M $\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ solution while protons (H^+) were subsequently supplied across the PBI membrane to the Cu–CNFs cathodic catalyst. The cathodic side of the cell (Cu–CNF) operated with a gas flow of CO_2 which was controlled by calibrated mass flowmeters. The $\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ anodic solution was introduced into the feed stream by means of a saturator. The electrocatalytic experiments were carried out at atmospheric pressure and 110 °C with an overall gas flow rate of 0.5 NmL/min for the cathode and 6 NmL/min for the anode. A potentiostat/galvanostat (Voltalab 21, Radiometer Analytical) was used to apply a constant current between the electrodes, which were connected with gold wires. The reactant (CO_2) and the products (H_2 , CH_4 , CO , acetaldehyde, methyl formate, methyl acetate, methanol, ethanol, 2-propanol, and *n*-propanol) were analyzed using a double-channel gas chromatograph (Bruker 450-GC) equipped with Hayesep Q-Molsieve 13 \times consecutive columns and thermal conductivity (TCD) and flame ionization (FID) detectors.

3. Results and discussion

Fig. 1 shows the XRD pattern of the Cu–CNF cathodic catalyst deposited on the carbon paper and a TEM image of the Cu–CNF cathodic powder catalyst. Four diffraction peaks were observed at $2\theta = 43.3^\circ$, 50.4° , 74.1° and 90° , and ascribed to metallic copper with a face-centred cubic (FCC) crystalline structure (JCPDS, 85-1326). Additionally, minor peaks were detected at $2\theta = 32.5^\circ$ and 86.6° and ascribed to CuO (JCPDS, 78-2076). However, the intensity of these peaks was very low, indicating that Cu was almost completely in its reduced form and was not oxidized during the deposition of the catalyst ink on the carbon paper support. The TEM micrograph of the Cu cathodic catalyst revealed the presence of carbon nanofibers and Cu particles with sizes ranging from 30 to 50 nm, in good agreement with previous studies using similar preparation methods [2,10,11].

Fig. 2 shows the dynamic response of the different production rates

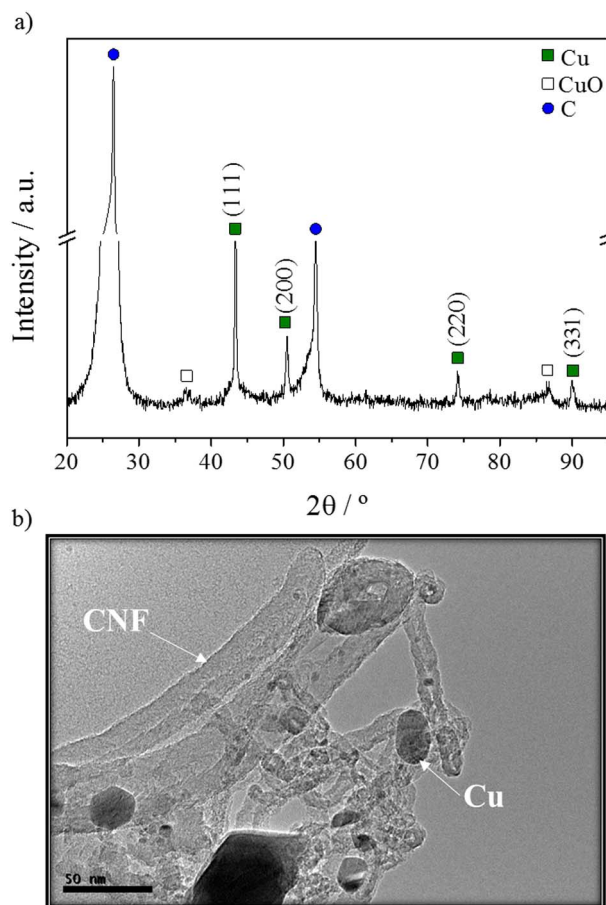
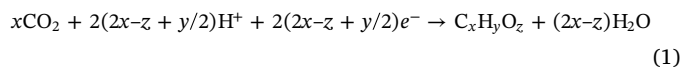


Fig. 1. XRD (a) and TEM analysis (b) of the fabricated Cu–CNF cathodic catalyst.

normalized by the area of electrode for a constant applied current density of -0.8 mA/cm^2 at 110 °C and the variation of the cell potential as a function of time. First, no activity was observed under open circuit conditions (OCC), i.e. with no current applied. In contrast, under polarization conditions, a large variety of products was obtained. The gas-phase electrocatalytic reduction of CO_2 is a complex multistep reaction involving shared intermediates and multiple reaction pathways. The formation of the different products can be described by the following general reaction involving the reaction of CO_2 with H^+ on the Cu–CNF cathodic catalyst:



As shown in Fig. 2, acetaldehyde was the main reaction product followed by methyl formate, with minor amounts (one order of magnitude lower in concentration) of methane, carbon monoxide, methyl acetate, methanol, ethanol, 2-propanol, and *n*-propanol. The wide variety of reaction products obtained can be attributed to the presence of functional oxygen groups on the CNF support [2]. After ca. 350 min of reaction, steady-state conditions were reached for all products. The slow dynamic response of the system can be attributed to the long residence times of CO_2 and the products in the cathodic chamber. The highest rate of production of acetaldehyde was $0.0242 \mu\text{mol/h cm}^2$ (i.e. $63.64 \mu\text{mol/h g}$) at 110 °C. This value is significantly higher than that reported by Liou et al. [12] ($0.3 \mu\text{mol/h g}$) for the photocatalytic reduction of CO_2 at 70 °C on a $\text{NiO}/\text{InTaO}_4$ catalyst. Gangeri et al. also reported a lower acetaldehyde production rate of $0.0013 \mu\text{mol/h}$ at 60 °C over Fe and Pt carbon nanotubes during the electrocatalytic conversion of CO_2 [3]. Remarkably, a significantly higher value of $0.3 \mu\text{mol/h}$ was obtained in this work at 110 °C under similar applied polarization conditions. Thus, the characteristics of the system (i.e., a

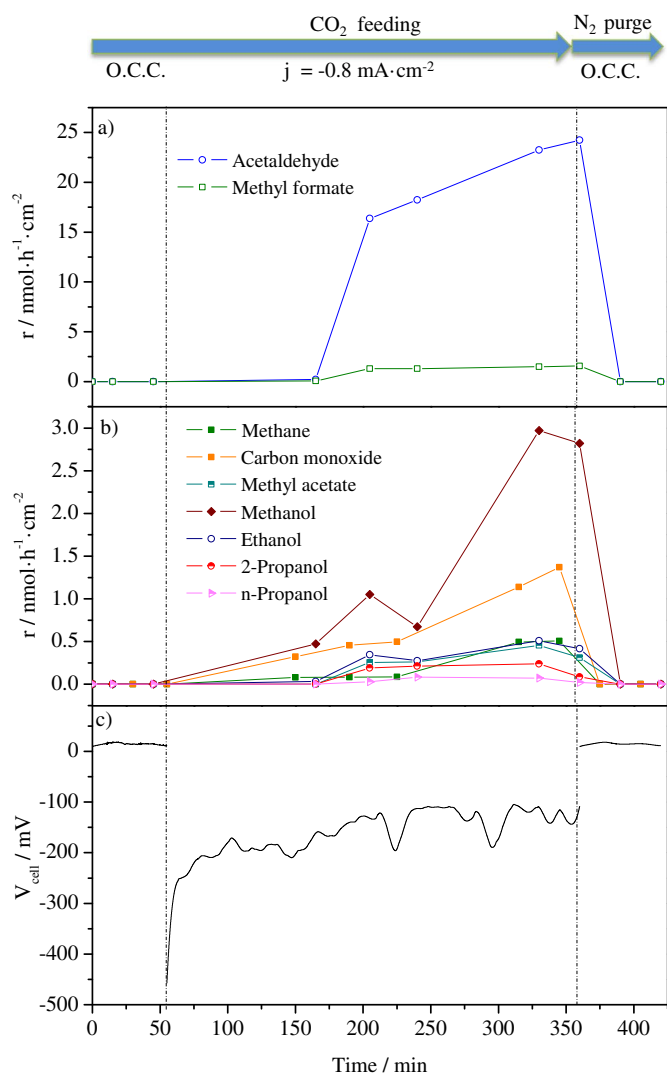


Fig. 2. Time-on-stream variation of the reaction rates of the different obtained products (a and b) and potential variation (c) under open circuit conditions (OCC) and under polarization conditions.

functionalized Cu–CNF cathodic catalyst and the utilization of higher reaction temperatures and higher reaction kinetics) led to an increase in the electrocatalytic activity of the system compared with that reported in similar studies. At the end of the experiment, the cathodic side of the cell was purged with N_2 under OCC conditions in order to remove all the products for subsequent experiments. The variation of the potential with time during the galvanostatic operation is shown in Fig. 2c. The current increased with time-on-stream within the first 200 min and then levelled off at ca. -200 mV . These results indicate the stability of the electrodes and the entire MEA during the operation of the system. The low value of the cell potential obtained under the galvanostatic imposition of 10.048 mA ($-0.8 \text{ mA}/\text{cm}^2$) indicates that proton pumping from the anode to the cathode is the main electrochemical process vs. the water splitting reaction.

Fig. 3 shows the effect of the applied current density on the steady-state production rates and selectivity towards different products at 110°C . As shown in Fig. 3a and b, larger applied current densities led to higher production rates for the different hydrocarbon products, and this was attributed to a larger number of H^+ ions being electrochemically supplied to the cathodic catalyst. However, overall CO_2 conversion and Faradaic efficiencies were below 2% in all cases, indicating that the H_2 evolution reaction is the main cathodic process. Further work on reactor designs and new catalyst configurations may improve these

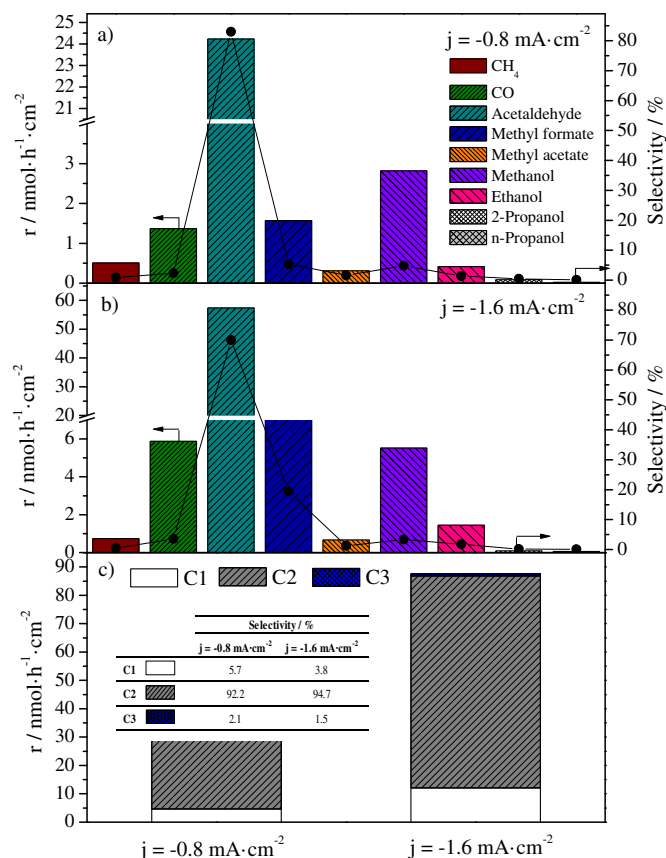


Fig. 3. Effect of the applied current density on the steady-state production rate and selectivity at $j = -0.8 \text{ mA}/\text{cm}^2$ (a) and $j = -1.6 \text{ mA}/\text{cm}^2$ (b), and on the C_1 – C_3 production and selectivity (c).

numbers.

Selectivity towards the different products was calculated by the following equation:

$$X_i \text{ selectivity (\%)} = \frac{F_{X_i}}{F_{\text{CO}_2}^0 - F_{\text{CO}_2}} \cdot 100 \quad (2)$$

Low applied current densities ($-0.8 \text{ mA}/\text{cm}^2$) favored the production of acetaldehyde (selectivity over 85%, compared to 70% at $-1.6 \text{ mA}/\text{cm}^2$). Higher values resulted in larger supply rates of H^+ , which shifted the selectivity towards lighter and more saturated compounds [13,14]. In particular, the increase in the applied current increased the selectivity towards methyl formate (from 5% to 20% at $-1.6 \text{ mA}/\text{cm}^2$) at the expense of acetaldehyde. Thus, the compounds produced can be potentially controlled by varying the applied polarization conditions. Finally, selectivity towards C_1 – C_3 compounds during the electroreduction of CO_2 at the two current density values studied is also shown in Fig. 3c. The overall selectivity towards C_1 – C_3 products remained nearly unchanged with changes in current density, C_2 being the most common fraction. Therefore, under the conditions explored in this work, increasing the amount of supplied H^+ did not alter the hydrocarbon chain growth mechanism. Further experiments will be performed to better understand the mechanism and type of products generated under a wider variety of conditions (e.g., polarization, temperatures, and flow rates).

4. Conclusions

This work demonstrates that the use of a Cu–CNFs/PBI/ IrO_2 MEA allowed the conversion of CO_2 into high-added-value products. The use of a PBI membrane also made it possible to work at higher temperatures than in previous studies using Nafion membranes, thereby enhancing

the CO₂ electroreduction kinetics. The utilization of a Cu–CNF functionalized cathodic catalyst resulted in a wide variety of products, mostly acetaldehyde (selectivity over 85%). The application of higher currents increased the overall electrocatalytic activity of the system while shifting the selectivity towards more saturated hydrocarbon products (i.e., methyl formate). However, the overall selectivity towards C₁–C₃ products did not change with the current, and C₂ was the most common fraction. The electrochemical reactor configuration described here seems to be an interesting alternative to the conventional catalytic CO₂ hydrogenation route, producing similar added-value products from CO₂ under significantly milder temperature and pressure conditions and with no hydrogen requirements.

References

- [1] D. Pletcher, The cathodic reduction of carbon dioxide—what can it realistically achieve? A mini review, *Electrochem. Commun.* 61 (2015) 97–101.
- [2] C. Genovese, C. Ampelli, S. Perathoner, G. Centi, Electrocatalytic conversion of CO₂ on carbon nanotube-based electrodes for producing solar fuels, *J. Catal.* 308 (2013) 237–249.
- [3] M. Gangeri, S. Perathoner, S. Caudo, G. Centi, J. Amadou, D. Bégin, C. Pham-Huu, M.J. Ledoux, J.P. Tessonnier, D.S. Su, R. Schlögl, Fe and Pt carbon nanotubes for the electrocatalytic conversion of carbon dioxide to oxygenates, *Catal. Today* 143 (2009) 57–63.
- [4] C. Genovese, C. Ampelli, S. Perathoner, G. Centi, A gas-phase electrochemical reactor for carbon dioxide reduction back to liquid fuels, *AIDIC Conference Series* 11, 2013, pp. 151–160, <http://dx.doi.org/10.3303/ACOS1311016>.
- [5] C. Genovese, C. Ampelli, S. Perathoner, G. Centi, Electrocatalytic conversion of CO₂ to liquid fuels using nanocarbon-based electrodes, *J. Energy Chem.* 22 (2013) 202–213.
- [6] C. Jiménez, J. García, R. Camarillo, F. Martínez, J. Rincón, Electrochemical CO₂ reduction to fuels using Pt/CNT catalysts synthesized in supercritical medium, *Energy Fuel* 31 (2017) 3038–3046.
- [7] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, Testing a vapour-fed PBI-based direct ethanol fuel cell, *Fuel Cells* 9 (2009) 597–604.
- [8] J.C. Tokash, B.E. Logan, Electrochemical evaluation of molybdenum disulfide as a catalyst for hydrogen evolution in microbial electrolysis cells, *Int. J. Hydrog. Energy* 36 (2011) 9439–9445.
- [9] V. Jiménez, A. Nieto-Márquez, J.A. Díaz, R. Romero, P. Sánchez, J.L. Valverde, A. Romero, Pilot plant scale study of the influence of the operating conditions in the production of carbon nanofibers, *Ind. Eng. Chem. Res.* 48 (2009) 8407–8417.
- [10] N. Gutiérrez-Guerra, L. Moreno-López, J.C. Serrano-Ruiz, J.L. Valverde, A. de Lucas-Consuegra, Gas phase electrocatalytic conversion of CO₂ to syn-fuels on Cu based catalysts-electrodes, *Appl. Catal., B* 188 (2016) 272–282.
- [11] A. Karelavic, P. Ruiz, The role of copper particle size in low pressure methanol synthesis via CO₂ hydrogenation over Cu/ZnO catalysts, *Catal. Sci. Technol.* 5 (2015) 869–881.
- [12] P.-Y. Liou, S.-C. Chen, J.C.S. Wu, D. Liu, S. Mackintosh, M. Maroto-Valer, R. Linforth, Photocatalytic CO₂ reduction using an internally illuminated monolith photoreactor, *Energy Environ. Sci.* 4 (2011) 1487–1494.
- [13] V.R. Rao Pendyala, G. Jacobs, J.C. Mohandas, M. Luo, W. Ma, M.K. Gnanamani, B.H. Davis, Fischer–Tropsch synthesis: attempt to tune FTS and WGS by alkali promoting of iron catalysts, *Appl. Catal., A* 389 (2010) 131–139.
- [14] M.E. Dry, The Fischer–Tropsch process: 1950–2000, *Catal. Today* 71 (2002) 227–241.