

# Electrocatalytic conversion of CO<sub>2</sub> to fuels using advanced materials

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1. Introduction – In the last decades, carbon dioxide emissions have become an important environmental problem, which is aggravating mainly due to the use of fossil fuels as energy source. In this context, the capture and conversion of CO<sub>2</sub> into synthetic fuels is a promising approach to contribute to stop these emissions. This technology can be used to convert excess electricity produced by intermittent renewable energy sources in “electro-fuels” that can be easily stored and transported [1], although nowadays, the challenge is finding stable and selective catalysts. In this sense, this work focuses on the electrocatalytic conversion of CO<sub>2</sub> in gas phase to fuels using advanced materials as catalysts.

2. Experimental – The electrocatalysts used consist of metal nanoparticles (Pt, Pb or Cu) supported on carbon nanotubes (CNT), being the main novelty of this work the method for metal deposition which has been carried out in supercritical media (CO<sub>2</sub>) through the use of organometallic metal precursors (Pt-, Pb- and Cu-acetylacetonate) [2]. ICP-AES, XRD, TEM and particles size distribution techniques were used to characterize the catalysts obtained. On the other hand, these electrocatalysts have been used as electrodes assembled to a proton exchange membrane (Nafion®) in a continuous electrochemical PEM type cell (25 cm<sup>2</sup> geometric area) where CO<sub>2</sub> gas is fed to the cathodic flow channel for its reduction. The metal load of membrane-electrodes assembly was 0.4 mg/cm<sup>2</sup> on each electrode (anode and cathode). During CO<sub>2</sub> electroreduction experiments, gas products have been quantified by GC-FID-TCD, whereas liquid reduction products were pre-concentrated by SPME to analyse them by GC-FID.

3. Results and Discussion – The supercritical method allowed attaining metal deposition yields ranging from 60 % for lead to 100 % for copper. As well, different particles size distributions were obtained deposited on CNT: Pb nanoparticles mainly had diameters of 5 nm, whereas Cu principally formed nanoparticles around 2-3 nm. In case of Pt, main particles diameter was 8-9 nm with important contribution of 3-4 nm size particles. Regarding the electrocatalytic conversion of carbon dioxide, the main reduction products have been formic acid, carbon monoxide and methane; in addition to methanol and small amounts of acetone and isopropanol (ethylene and ethanol were not detected in the experimental conditions tested: 16 mA cm<sup>-2</sup>, 0.05 SL CO<sub>2</sub> min<sup>-1</sup>, 60 °C, anolyte 0.1M KHCO<sub>3</sub>). Nevertheless, the comparison of the formation rate of these products revealed different electrocatalytic behaviour of these catalysts: formic acid is the main CO<sub>2</sub> reduction product with Pt/CNT and Pb/CNT, which attain similar conversion rates (near 0.015 mmol CO<sub>2</sub> h<sup>-1</sup>). However, methane predominate over carbon monoxide as second CO<sub>2</sub> reduction product with Pt, contrary to what happens with Pb. Very different results are observed in case of Cu/CNT, whose main CO<sub>2</sub> reduction product in the experimental conditions tested is carbon monoxide, reaching CO<sub>2</sub> conversion rate 5 times higher than those obtained with Pt/CNT and Pb/CNT.

4. Conclusions – Supercritical deposition of Pt, Pb and Cu on CNT allows obtaining electrocatalysts with metal nanoparticles size ≤ 6 nm. These catalysts (Pt/CNT, Pb/CNT and Cu/CNT) are active in the electrocatalytic reduction of CO<sub>2</sub> in gas phase in a PEM type electrochemical cell, where CO<sub>2</sub> is mainly converted to formic acid, methane, carbon monoxide and small amounts of methanol. Pb/CNT and Pt/CNT favour the production of formic acid with similar conversion rates, whereas Cu/CNT is able to reduce CO<sub>2</sub> five times faster than Pb and Pt, promoting the formation of carbon monoxide.

5. References [1] I. Ganesh, *Renew. Sust. Energ. Rev.*, 59, (2016) p. 1269. [2] C. Jiménez, J. García, R. Camarillo, F. Martínez, J. Rincón, *Energy Fuels*, 31(3), (2017), p. 3038.