SYNTHESIS OF NANOSTRUCTURED ELECTRODES FOR THE CATALYTIC ELECTROREDUCTION OF CO₂

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INTRODUCTION
Environmental emissions caused by the combustion of fossil fuels has been widely linked to global warming processes. Renewable energy sources could be an effective alternative but, due to their intermittent nature, they require extensive and complex accumulation systems. A promising solution is represented by the electroreduction of carbon dioxide (ERCO), where CO₂ is electrochemical reduced to produce chemical products and fuels. This process could allow the simultaneous abatement of CO₂ emissions and the storage of renewable-based energy. ERCO is characterized by the wide amount of possible products, mostly carbon monoxide (used as syngas) and C₁-C₃ hydrocarbons. In order to reach exploitable grades of conversion and selectivity, ERCO requires catalytic electrodes.

In this study, we evaluate the synthesis and the catalytic proprieties of nanstructured metallic electrodes. Our catalysts are composed of a micrometric layer of nanoengineered copper supported on a conductive, gas permeable surface made of carbon paper (Cpap). The role of synthesis conditions was analyzed in order to tune the electrodes nanostructure and thus their catalytic activity.

SYNTHESIS
Catalysts are synthesized by galvanostatic electrodeposition of the copper from an aqueous plating bath. Deposition solutions contained copper sulphate, nanostructuring additives and sulphuric acid as pH regulator. Electrodeposition has been preferred to other kind of nanosynthesis in order to obtain a simple, inexpensive and scalable process. Synthesis conditions has been analyzed and linked to their nanostructuring effects. The effect of deposition parameters, such as current density, amount of charge, additives and pH were considered.

CHARACTERIZATION
Electrodeposited nanostructures were analyzed both by Scanning Electronic Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). SEM images represent a double benefit: they allow us to make a qualitative organization of the nanostructures, an estem of the structure distribution on the support and a quantitative comparison between the dimensions of various nanostructures. EDX mapping confirms the identification of the metallic nanostructures.

Catalytic properties are tested in a double compartment, three-electrode cell. ERCO is here tested in an aqueous electrolyte based on potassium hydroxide electrolyte. Catalysts are subjected to Linear Sweep Voltammetry, an electrochemical analysis designed to evaluate redox reactions by applying a potential which increase or decrease at a constant ratio. Afterwards, electrodes were tested in a potentiostatic setup and gaseous products were analyzed by gas chromatography (GC).

REAGENTS EFFECT
Additives with surfactant proprieties, such as n-Dodecylcycrimethylammonium Bromide (DTAB), allow the wetting of the hydrophobic surface of the carbon paper, increasing the deposition uniformity.

CURRENT DENSITY AND CHARGE
The amount of metal reduced during an electrodeposition is approximately proportional to the charge passing into the deposition cell. Our electrodes show no exception.

HYDROGEN
OXYGEN
METHANE
CARBON MONOXIDE
ETHANE
HYDROGEN
OXYGEN
METHANE
CARBON MONOXIDE
ETHANE

On the other side, compounds like the 3-Diamino-1,2,4-Triazole (DAT), a copper complexant, act as nanostructuring agent bound to the depositing copper atoms, its molecule inhibit the lateral growth of the metallic structure, allowing the creation of a nanowires/nanogrid pattern.

Linear Sweep voltammograms obtained from electrodeposited electrodes. The catalytic behavior of the nano-structured electrode is compared with a copper foil (in red). Voltammograms were recorded in the same kind of CO₂ saturated electrolyte. (A) DTAB-assisted electrode; (B) Cu Foil. Both DTAB and DAT electrodes show a decrease in reduction current with respect to the copper foil.