



Doctoral Dissertation.
Doctoral Program in Science and Technology of Materials (36th Cycle)

Study of electrode fabrication and cell configuration for CO₂ reduction

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Summary

During my Ph.D., I concentrated my investigations on the electrochemical characterization of catalysts for the CO₂ Reduction Reaction (CO₂RR). This technology can obtain high valuable products converting the CO₂. The more demanded products are carbon monoxide, formic acid and ethylene. The investigation has been focused on develop catalysts and fine the optimal reaction conditions to specifically produce these products.

Initially, the research involved studying tin oxide catalysts grown by anodic oxidation reaction. This research started during my master's thesis, and throughout the early stage of my Ph.D. The catalysts production and their reaction performances were optimized and enhanced. The main products of this catalyst are CO and HCOOH as reaction products.

Then electrode obtained by direct sputtering deposition have been explored, thanks to their easy fabrication procedure and absence of any binder. Using this technique the properties of two different catalyst have been studied silver and copper. Silver electrodes were known to be primarily active for CO production, and the research was directed towards defining the optimal electrode deposition parameters and its performances, maximising the catalyst activity. Copper electrodes produced several products, the most appealing was C₂H₄. In this case the research was focused on identifying the catalyst and the optima electrochemical cell condition, then a selectivity switch has been noticed during the investigations. The study highlights the importance of the copper oxide presence for C₂H₄ production and the effects of the pH and the electrolyte concentration on it stability and products production.

A Bi-based catalyst grown using a microwave reactor has been developed and investigated. The main reaction product of this catalyst is HCOOH. An advantage of this catalyst is its ability to operate over a wide pH range of electrolytes while maintaining optimal performances.

The investigation started with the uses of an H-cell then move to a batch cell electrolyser, but the larger research has been focused on the uses of the flow cell reactor. At the end some investigation has been done also on the uses of half MEA set up. To identify the optimal reaction conditions several electrolytes have been used, especially KHCO₃ with different concentrations. But not only also very

strong alkaline electrolyte like KOH and strong acidic one like K_2SO_4 with the addition of H_2SO_4 have been studied.

The goal of this thesis is to improve the production of the CO, HCOOH and C_2H_4 , finding the optimal conditions to enhance the catalyst performances and its stability.