High Faradaic selectivity in the CO_2 electrocatalytic reduction to formate over Cu_2O-Cu hybrid nanoparticles on gas-diffusion-layer electrode

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Abstract: CO_2 is electrocatalytic reduced using a carbon diffusion layer decorated with copper oxide (I) nanoparticles (GDL/Cu_2O) electrode. The CO_2 reduction was studied during 18 h forming 4.30 mmol·L^{-1} of formate with 97% of selectivity. Electrode characterization after the CO_2 reduction indicates that the initial Cu_2O nanoparticles transformed to a hybrid Cu_2O-Cu system to which the high Faradaic selectivity is attributed. The cathode was used also in a full PEC cell, using TiO_2 nanotube array/CuO as photoanode with the formation of formate, acetate and hydrogen without external bias and sacrificial agents with Faradaic efficiency of 98%.

Keywords: Formate, Cu_2O-Cu/GDL, CO_2.

1. Introduction

The electrocatalytic conversion of CO_2 is an area of increasing interest, but still the development of high active and especially selective and stable electrocatalysts is an open problem.[1] In addition, the design of flow electrochemical cells to allow a continuous and easy recovery of the reaction products, a crucial aspect from a practical perspective,[2] requires a specific design of the electrodes not often considered in literature data. For example, the use of gas-diffusion-layer (GDL) type cathode for CO_2 reduction, and when combined with a photoanode to develop a photoelectrocatalytic (PEC) cell, to have specific nanostructure for the photoanode (such as an ordered array of vertically aligned nanotubes) to combine good light harvesting and charge separation to an efficient transport of the photogenerated electron and protons (from water photoelectrolysis) to the other side of the hemicell (where CO_2 electrocatalytic reduction occurs) separated through a proton membrane (Nafion, for example). The use of earth abundant elements is another aspect to consider, and in this sense copper can be an interesting element for the development of both anode and cathode sides in PEC cells for the direct reduction of CO_2 using sunlight.

We report here the performances of a cathode based on Cu_2O deposited over a GDL-type electrodes for the CO_2 electrocatalytic reduction, and its use also in an PEC cells (without external bias or use of sacrificial agents), where the photoanode is also based on copper, specifically CuO nanoparticles deposited over a titania thin film of vertically-aligned TiO_2 nanotubes (NtTiO_2).[3]

2. Experimental

Cu_2O nanoparticles were electrodeposited on the commercial GDL (Sigracet® GDL 25 BC). A three-electrode electrochemical cell arrangement was used with GDL as working electrode, platinum wire as counter electrode and Ag/AgCl, KCl (sat) as reference electrode, operating at 60°C. Copper sulfate was used as precursor and the pH of solution was adjusted to 12.0 with 12.0 mol·L^{-1} NaOH. A voltage of -0.40 V was applied for the oxide reduction by means of a Potentiostat/Galvanostat (AMEL 2049), and the time of the electrodeposition was investigated. After the electrodeposition, the material was washed with distillated water and dried with nitrogen. In order to compare the GDL/Cu_2O with GDL/Cu, the latter was prepared by electrodeposition using the same solution at pH 7, but applying -1.0 V. The samples, before and after tests, were characterized by different techniques: FE-SEM with EDS analysis, XRD, XPS and ciclic voltammetry, the latter carried out in 0.5 mol·L^{-1} $KHCO_3$ solution with and without CO_2 solubilized under 10 mV·s^{-1}.

The electrocatalytic CO_2 reduction was studied in a flow electrocatalytic cell, operating at room temperature and having a three-electrode configuration, with a Pt wire as counter-electrode and a saturated Ag/AgCl electrode as reference electrode. 0.5 mol·L^{-1} $KHCO_3$ was used as supporting electrolyte in both sides of the cell, saturated with CO_2 gas (gas flow rate of 10 mL·min^{-1}). A potentiostat/galvanostat (Amel mod. 2049A) was used to supply a constant voltage difference of -1.5 V between the electrodes. The liquid and gaseous products were analyzed during the reaction.

For PEC full cell tests, the photoanode ($CuO/NtTiO_2$) and the cathode (GDL/Cu_2O) were joint to the two sides of a Nafion® membrane. 1.0 mol·L^{-1} NaOH saturated with N_2 and 0.5 mol·L^{-1} $KHCO_3$ saturated with CO_2 were used as supporting electrolytes in the anodic and cathodic compartments, respectively. The solar illuminator used for the experiments is a Xe arc lamp (ORIEL, 300 W) equipped with a set of lenses for light collection and focusing, a water filter to eliminate the infrared radiation and a set of filters to evaluate the photoresponse in different light-absorption regions (ultraviolet or visible regions).

3. Results and discussion

The SEM, XRD and XPS data confirm the presence of flower-like (defective) Cu_2O particles (having preferred triangular (111) facets) with size between 800 nm to 1.20 µm in the Cu_2O/GDL electrode (60s electrodeposition, the one giving the better performances). In the electrocatalytic reduction of CO_2, formate, acetate and hydrogen are formed, with the sample electrodeposited for 60s giving the higher productivity to formate (3.84 mmol·L^{-1} after 240 min) with a selectivity (on C-bases) of 98,5% and a Faradaic selectivity of over 90%, the latter improving with time, due to a market reduction in H_2 formation. The Cu/GDL electrode, under the same conditions shows a lower formate formation and significantly higher H_2 formation. The behavior of Cu_2O/GDL was thus studied in longer (18h) performance tests (Fig. 1). The rate of formate production decreases with time (from about 1 to about 0.1 mmol·L^{-1}·h^{-1}), while that of acetate remains nearly constant (less than 0.01 mmol·L^{-1}·h^{-1}). The H_2 formation passes through a market maximum, becoming very low after 18h, with improvement of the Faradaic efficiency. Characterization of the electrocatalyst shows the co-presence of Cu and C_2O, but Cu alone is much less selective in formate, as shown by Cu/GDL tests. A core-shell Cu/Cu_2O, forming in situ during CO_2 electrocatalytic reduction, is thus likely responsible for the high Faradaic selectivity observed.

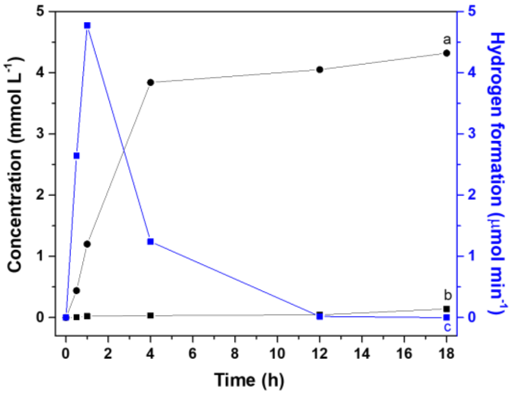

Figure 1. Production of formate (a), acetate (b) and H_2 (c) during CO_2 electrocatalytic tests using Cu_2O/GDL electrode (60s electrodeposition).

This Cu_2O/GDL was utilized as cathode in a flow PEC cell, where the photoanode is $CuO/NtTiO_2$, and the two electrodes on the two sides of a Nafion membrane. No bias was applied to the PEC cell, neither sacrificial agents utilized. The water splitting occurs in the anode compartment under $CuO/NtTiO_2$ illumination with a solar simulator. A change of the behavior was observed with time on stream (up to 24h) also in this case, with the H_2 evolution also passing through a maximum, but higher acetate formation that in only direct electrocatalytic CO_2 reduction and a less market decrease of the rate of formate production with time on stream. This difference from CO_2 electrocatalytic tests was due to the different potential at the electrocatalyst surface in PEC tests. The Faradaic efficiency was around 98% for 24 h of reaction, taking in consideration that are necessary $2e^-$ to hydrogen, $8e^-$ to acetate and others $2e^-$ to formate formation. The current generated was practically constant during the 24 h of reaction, reaching 0.2 mA.

References

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