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Electrochemical reduction of CO_2 using Pb catalysts synthesized in supercritical medium

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ABSTRACT

Supercritical fluids have been used to obtain Pb/CNT catalysts consisting of Pb nanoparticles (5–10 nm of predominant size) deposited on CNT. The electrocatalytic activity of Pb/CNT catalysts has been studied by electroreduction of CO_2 in gas phase using a PEM type cell in continuous operation mode. The influence of current density (8–24 mA cm^{-2}), temperature (40–80 °C), CO_2 flowrate (0.02–0.08 L min^{-1}) and anolyte concentration (0.1–0.5 M $KHCO_3$) have been studied in terms of products formation rate. Formic acid has been the main CO_2 reduction product, followed by CO and methane, as well as methanol as minority product. The production of formic acid rises by increasing current density and CO_2 flowrate within the experimental ranges studied. High CO formation rates have been observed at 80 °C, but also at low CO_2 flowrate (0.02 L min^{-1}) and at high anolyte concentration (0.5 M $KHCO_3$). Formation rate of methane improves with increasing current density in the range studied. Regarding methanol, increasing temperature promotes its production, whereas it diminishes at higher anolyte concentration. A remarkable result that has not been reported yet for Pb electrocatalysts is the change in selectivity observed at 80 °C. At this temperature CO is the main CO_2 reduction product (instead of formic acid) and the selectivity to methanol formation increases. In addition, it has been observed that Pb/CNT catalysts yield CO_2 conversion rates (normalized by metal surface) 10% higher on average than Pt/CNT catalysts, and that the Pb electrocatalysts lead to larger selectivity to methanol formation. Specifically, using Pb catalysts the selectivity to methanol formation was up to 6.7%, which is almost 4 times higher than the maximum one observed with Pt catalysts.

1. Introduction

The continued use of fossil fuels as energy source in our society cause many problems related to pollution. In the last years, repeatedly, researchers have identified carbon dioxide as one of the main pollutants related to climate change problems and have warned of the importance of taking "immediate and efficient actions to reduce CO_2 emissions in the next decades" (Intergovernmental Panel on Climate Change, 2014) [1].

The main efforts nowadays to mitigate problems caused by climate change are related to the capture and conversion of CO_2. Among the conversion techniques, electroreduction seems to be one of the most promising [2]. It consists of the reduction of the carbon dioxide molecule on the cathode of an electrochemical cell thanks to the protons produced on the anode of the cell and the electrons supplied by an external energy source [3–5]. In this sense, it allows the efficient exploitation of electricity generated in excess from renewable sources for CO_2 conversion into fuels and value added chemicals [2].

There is a variety of useful products obtained from CO_2 electroreduction for instance formic acid, carbon monoxide, methane, ethylene, ethane, methanol, ethanol and even C3 compounds depending on the metal used as cathode (electrocatalyst) and the experimental conditions [6]. In this sense, metals such as Pb, Sn, Bi, Pd and Pt promote the conversion of CO_2 mainly to formic acid/formate, whereas Cu based electrodes favour the production of methane, ethylene and carbon monoxide (as well as alcohols in a lesser extent) [7,8], although none of them allow selective and effective CO_2 conversion.

Thus, the electrochemical reduction process involves the application of an electric potential between an anode and a cathode,

Abbreviations: CNT, carbon nanotubes; FID, flame ionization detector; GC, gas chromatograph; GDE, gas diffusion electrodes; ICP-AES, inductively coupled plasma atomic emission spectrometry; MEA, membrane electrode assembly; PEM, polymer electrolyte membrane; SPME, solid phase microextraction; TCD, thermal conductivity detector; TEM, transmission electronic microscopy.

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which is the electrocatalyst and the one promoting the activation of the CO_2 molecule. Regarding the electrocatalysts used, most of them have been produced through the deposition of metal nanoparticles onto the surface of a carbon support [9–11]. In the literature, several metals in nanoparticle form (among others copper [12,13], lead [14,15], platinum [4,5] or palladium [16,17],) and carbon supports (carbon black, carbon nanotubes or most recently graphene) [10,18] have been analysed and found to influence the process.

The synthesis processes of the metal-based catalysts usually consist of the reduction or decomposition of a metal precursor onto the surface of the carbon support. However, most of them usually employ high quantities of organic solvents for the synthesis what produce a large amount of wastes. A very interesting alternative to these methods consists of using supercritical CO_2 as reaction media for the metal deposition instead of an organic solvent [19,20]. The use of supercritical fluids has important advantages mainly related with their unique characteristics, namely, solvent properties very similar to liquids but transport properties similar to gases [21]. These properties favour the transport of the precursor to the fluid/solid interphase at high concentrations (at lower temperatures), as well as the removal of ligand decomposition products by desorption during decompression. In addition, the properties of the supercritical fluid can be simply adjusted modifying temperature or pressure [22]. Further, it is a technology environmentally friendly as the fluid used can be completely and easily recovered and reused in the process [20].

In most works reported in literature the electrochemical reduction has been carried out in liquid phase [14,23,24]. However, in the last years, several studies have developed reactors that operate in gas phase, an option that seems to improve the process avoiding problems related to the low solubility of CO_2 in water (around 30 mM at 1 atm and ambient temperature [11]). Especially important are those reactors using Gas Diffusion Electrodes (GDE) [12,25–29] although, in most cases, they work in batch mode [24,30] and/or with very small electrode surfaces (around 1 cm^2) [4,24,31,32].

For many years GDE have been used in Polymer Electrolyte Membrane (PEM) fuel cells that work with platinum as catalyst. In this sense, platinum has also been used for the electrochemical reduction of CO_2 in gas phase with very promising results [4,5,9]. In fact, in a previous work [5] we reported that the CO_2 conversion rate (per mg of metal catalyst) attained by Pt/CNT synthesized in supercritical medium was double than those obtained using Pt/CNT in a similar cell configuration by other authors [9]. However, platinum is a very expensive metal as well as a very scarce resource. For this reason, it is important to find catalysts able to combine availability and low price with good efficiency in the reduction of CO_2 molecule.

According to literature [33,34], lead seems to be the most suitable metal for industrial applications if compared with other electrodes that selectively reduce CO_2 to formate/formic acid (as Hg, Cd or Sn). Moreover, according to Vesborg and Jaramillo, 2012 [35], lead is between the 25 elements with higher global volume production ($4 \cdot 10^9$ Kg/yr), what is more than one order of magnitude higher than Sn ($2.5 \cdot 10^8$ Kg/yr) or two orders of magnitude higher than Cd ($2.1 \cdot 10^7$ Kg/yr). Moreover, it is cheaper (1.9 $/Kg) than both metals (Sn: 19.9 $/Kg; Cd: 2.5 $/Kg). For these reasons, and despite of its toxicity, lead can be an interesting alternative to platinum for the electrochemical reduction of CO_2. It is cheaper than platinum and earth abundant (Pt: global annual production, $2 \cdot 10^5$ Kg/yr; price, 50118.7 $/Kg) and it can lead to high efficiencies in the reduction of CO_2 molecule to formic acid [34,36].

In this context, the aim of this work has been to study the electrochemical reduction of carbon dioxide using Pb supported onto carbon nanotubes obtained by supercritical deposition. As far as we know, no results have yet been published on the use of Pb/CNT electrocatalysts synthesized in supercritical medium for the conversion of CO_2. In addition, the electrocatalytic reduction of CO_2 has been carried out in a PEM type reactor, in gas phase, and operating in continuous mode, as opposed to many studies. Thus, in this work we present the formation rates of CO_2 reduction products obtained as a function of current density, temperature, CO_2 flowrate and anolyte concentration. Carbon dioxide conversion rates attained with Pb/CNT have been compared to those previously obtained with Pt/CNT synthesized by supercritical deposition.

2. Material and methods

2.1. Experimental setup

2.1.1. Synthesis of Pb/CNT catalyst using supercritical CO_2

The experimental set-up used to accomplish the deposition of lead nanoparticles onto carbon nanotubes (Pb/CNT), the material used as electrocatalyst in the CO_2 reduction process, has been described in a previous work [5]. It involves an ad-hoc reactor of 90 mL volume made of stainless steel (DEMEDE Engineering and research, Spain), which comprises a temperature control through a thermocouple (placed inside the reactor), an electric resistance and a temperature controller (SOHO, TTM-204). The CO_2 stored in a cylinder is circulated through a refrigerated bath to liquefy it before entering a high pressure pump (P-50, Thar SFC, supplied by Productos de Instrumentación, S.A., Spain). The pump provides pressure to the fluid (CO_2) and therefore to the reactor. The experimental setup is also equipped with a tank for the addition of H_2 at 10 bar and a series of valves (and pressure gauges) that allow the fluid to circulate through the convenient parts of the installation (and the pressure monitoring). A filter of 1 μm is placed downstream of the reactor, in order to retain the particles that can be dragged during the decompression at the end of the experiments. Thus, the installation has been especially designed to work with supercritical fluids and allows fine-tuning of reaction conditions through appropriate control of pressure and temperature (up to 250 °C and 300 bar).

2.1.2. CO_2 electroreduction

The experimental set-up used to carry out the electrocatalytic reduction of CO_2 has been described in a previous work [5]. It consists of an electrochemical cell (single cell PaxiTech supplied by MICROBEAM, electrode area: 25 cm^2) analogue to a PEM (proton exchange membrane) fuel cell. The electrochemical cell has two compartments divided by a Nafion® 117 membrane assembled to two carbon cloths coated with the Pb/CNT electrocatalyst previously synthesized in the experimental assay described before. Each compartment consists of a graphite monopolar plate with a single channel serpentine flow field (1 mm × 1 mm).

A $KHCO_3$ aqueous solution is circulated through the anode using a peristaltic pump (DINKO-D21-V). Cell temperature is regulated with a temperature controller (EUROTHERM). CO_2 flowrate is fixed for each experiment with a mass flow controller (BROOKS, SLA5850). A potentiostat-galvanostat (PGSTAT302N, Metrohm AUTOLAB) is used to regulate the electrical current and to register voltage values.

2.2. Analytical methods

2.2.1. Characterization of Pb/CNT catalyst

The catalyst morphology and size distribution of lead nanoparticles deposited on the CNT have been determined by TEM (Transmission Electronic Microscopy) in a Jeol 2100 TEM