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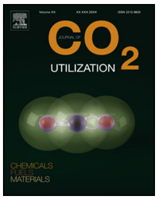

Sn nanoparticles on gas diffusion electrodes: Synthesis, characterization and use for continuous CO_2 electroreduction to formate

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ABSTRACT

Electrochemical reduction of CO_2 has been pointed out as an interesting strategy to convert CO_2 into useful chemicals. In addition, coupling CO_2 electroreduction with renewable energies would allow storing electricity from intermittent renewable sources such as wind or solar power. In this work, an easy and fast method is adapted for the synthesis of pure and carbon supported Sn nanoparticles. The resulting nanoparticles have been characterized by transmission electron microscopy and their electrocatalytic properties towards CO_2 reduction evaluated by cyclic voltammetry. Carbon supported Sn nanoparticles have been subsequently used to prepare Gas Diffusion Electrodes (Sn/C-GDEs). The electrodes have been characterized by scanning electron microscopy and also by cyclic voltammetry. Finally, the electrodes were tested on a continuous and single pass CO_2 electroreduction filter-press type cell system in aqueous solution, to obtain formate at ambient pressure and temperature. These Sn/C-GDEs allow working at high current densities with low catholyte flow. Thus, for instance, at 150 mA cm^{-2}, a 70% Faradaic Efficiency (FE) was obtained with a formate concentration of 2.5 g L^{-1}. Interestingly, by increasing the current density to 200 mA cm^{-2} and decreasing the flow rate, a concentration over 16 g L^{-1} was reached. Despite the high concentrations obtained, further research is still required to keep high FE operating at high current densities.

1. Introduction

CO_2 emissions are one of the major contributors to the greenhouse effect and climate change [1]. Among the different alternatives that are being considered to upgrade carbon dioxide, electrochemical reduction appears as an interesting strategy to convert CO_2 into valuable chemicals such as fuels or raw material for industries [2]. Particularly attractive is the coupling of this electrochemical transformation with renewable energy, allowing the storage of the excess of electricity from intermittent sources such as wind or solar power in form of chemical products with value-added [3–6]. The storage of electricity is a critical point for the development and wide implementation of renewable energy, since these types of sources have the disadvantage of energy displacement: the energy is often produced in places or at times that do not necessary match with electric demand [7].

There are several pathways to convert CO_2 into useful products [8–15]. Among all the products, formic acid or formate is particularly interesting. Previous studies suggest that the electrochemical conversion of CO_2 in formic acid is a suitable reaction to be used at industrial scale despite some drawbacks still need to be solved [16–18]. Formic acid is a raw material for industries such as pharmaceutical synthesis, textile finishing or paper and pulp production, among others [19]. Furthermore, formic acid has been proposed as a suitable fuel for low temperature fuel cells and also as a promising chemical for hydrogen storage [20–23]. The current production process of formic acid is mainly the carbonylation of methanol followed by the hydrolysis of methyl formate, with negative environmental impacts. A novel and economic electrochemical process could allow to increase the use of formic acid at industries and on new applications such as fuel cells [24].

Several metals have been used as electrocatalysts for CO_2 electrochemical reduction to formic acid/formate, such as Pb [25,26], In [27], Ir [24], Cu [28], Pd [29,30], Co [31] or, specially, Sn [32–42]. These metals are usually deposited in form of particles to maximize the active surface with the minimum amount of metal,

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and recent studies show that the structure and size of these particles have a great influence on the selectivity and behaviour of the electrochemical reduction [32–34].

Particularly, in recent years, very promising results on CO_2 electroredution to formate have been obtained using Gas Diffusion Electrodes (GDEs) with Sn nanoparticles (NPs) [43–54]. This type of electrode presents a high electroactive surface which allows working at higher current densities than those used with plate electrodes. A GDE also enhances the three phase boundary area, avoiding mass transfer limitations and promoting the CO_2 electroreduction, which increases the Faradaic Efficiency (FE), formate rate of production and formate concentration in comparison with plate electrodes [44,46,52].

Most of the studies on CO_2 electroreduction to formate using GDEs with Sn have been carried out in batch [46,54] or semibatch mode [47,50] obtaining FE to formate from 70% to 85% working at current densities between 10 and 40 mA cm^{-2}. Some references report electrodes working at high current densities, above 100 mA cm^{-2} with FEs over 85% [48,49]. However, details about rates of formate production are not reported. The concentration of product formate achieved is another important aspect that is usually neglected. High current density operation, high product concentration and continuous operation mode are basic requirements for the scale up and industrial implementation of this process [16,49].

In this context, the aim of this work is to develop an easy and fast method for the synthesis of Sn pure and carbon supported NPs with which preparing Sn-GDEs for a continuous process of CO_2 electrochemical conversion into formate. The performance of the Sn-GDEs electrodes is finally tested using an experimental electrochemical reactor in continuous mode, which is closer to a practical application of the electrochemical process.

2. Methods

2.1. Synthesis and characterization of Sn NPs

The Sn NPs were prepared at room temperature using a chemical reduction procedure adapted from a previous contribution by Chee and Lee [55]. However, several aspects, including the nature of the solvent, the specific concentration of the chemicals and the order of their addition, among others, were modified in comparison with the original procedure [55] to facilitate both the synthesis of the nanoparticles and the incorporation of the carbon substrate. In detail, 0.5 g of $SnCl_2{\cdot}2H_2O$ (Sigma–Aldrich Co.) and 0.15 g of polyvinylpyrrolidone (PVP) (molecular weight 55,000, Aldrich Chemical Co.) were dissolved in 100 ml of ethyleneglycol (EG) (Sigma–Aldrich Co.). Subsequently, 0.5 g of sodium borohydride ($NaBH_4$) (99.99%, Sigma–Aldrich Co.) were directly added to the solution under continuous magnetic stirring. After the addition of the reducing agent, the solution turns from pale yellow to black thus suggesting an effective chemical reduction. The solution was kept under continuous stirring for at least 30 min and then about 100 ml of acetone were added. The incorporation of acetone gives rise to the destabilization of the colloidal suspension and the NPs precipitate. The so-prepared Sn NPs were filtered, washed with acetone (at least 3 times) and finally dried overnight at 70–80 °C.

Carbon supported Sn NPs were prepared using the same methodology. The required amount of carbon powder (0.614 g of Vulcan XC72R, Cabot Corp corresponding to obtain a Sn metal loading of 30 wt%) was incorporated to the solution before the addition of the reducing agent and continuously mixing, alternating both magnetic and ultrasonic for about 1 h, until getting an uniform suspension. After the reduction step is carried out, the sample was then filtered, washed and dried as previously described.

Transmission Electron Microscopy (TEM) experiments were performed with a JEOL JEM-1400 Plus working at 120 kV. The samples were prepared by dispersing a small fraction of the sample in isopropyl alcohol, IPA ($\geq$99.7%, Sigma–Aldrich), and placing a drop of the IPA solution onto a Formvar-covered copper grid. The solvent is allowed to evaporate in air at room temperature. For each sample, usually about 200 particles from different parts of the grid were used to estimate the mean diameter and size distribution of the NPs.

The samples were also electrochemically characterized in presence and absence of CO_2. The electrochemical characterization was performed by cyclic voltammetry in a standard three electrode electrochemical cell. A graphite rod and an AgCl/Ag electrode were used as counter and reference electrodes, respectively. The electrode potential was controlled using a PGSTAT302N AUTOLAB system (Metrohm Autolab, B.V.). The electrolyte was an aqueous solution of 0.45 M $KHCO_3$ + 0.5 M KCl saturated with Ar or with CO_2 at room conditions. The catalytic ink was prepared by dispersing the samples in a Nafion solution (Perfluorosulfonic acid-PTFE copolymer 5% w/w solution, Alfa Aesar) at a Sn/Nafion mass ratio of 70:30. The mixture was then diluted to 3% in isopropyl alcohol, IPA (P99.7%, Sigma–Aldrich). Ultrasonic agitation was used to homogenize the ink for at least 30 min. An aliquot (20 μL) of the catalytic ink was deposited on a vitreous carbon collector electrode (3 mm diameter, model EM-EDI-CVJ, 0.071 cm^2 geometrical area, Radiometer) and dried under an Ar atmosphere. The vitreous carbon electrodes were mechanically polished with alumina, sonicated and rinsed with ultra-pure water before each experiment to make sure that all the NPs from previous experiments were removed. The samples were cycled between −0.2 V and −1.8 V at a scan rate of 50 mV s^{-1}.

2.2. Sn-GDE fabrication and characterization

For the preparation of the Sn-GDEs, the Sn NPs prepared as previously described in Section 2.1 were used. In brief, a Toray carbon paper was used as carbonaceous support (Toray Paper, TGPH-90). A carbon microporous layer (MPL), formed by Vulcan XC72R and PTFE in a mass ratio 40/60, was firstly air-brushed onto the carbonaceous support. This layer was sintered at 623 K during 30 min. Subsequently, the catalytic layer (CL) was prepared by air-brushing a catalytic ink similar to that previously mentioned. Using these conditions, homemade Sn-GDEs electrodes with a geometric surface area of 10 cm^2 and a Sn loading of 0.75 mg cm^{-2} were prepared. Additionally, smaller portions of these Sn-GDEs (about 1 cm^2) were cut and electrochemically characterized as above mentioned. To characterize them, these electrodes were held with clamps by the portion of carbon paper excess. The clamps were not in contact with the electrolyte solution. The Sn-GDEs were also characterized with a scanning electron microscope (SEM, HITACHI S-3000N microscope) working at 20 kV. The electrodes were sectioned and scanning electron micrographs of the cross section were obtained and analyzed. In this way, thickness and morphology of the different layers forming the homemade Sn-GDE can be properly evaluated. For sake of comparison two types of electrodes were prepared: a Sn-GDE with pure Sn NPs (Sn/P-GDE), and Sn-GDE with carbon supported Sn NPs (Sn/C-GDE).

2.3. Filter press tests

The fabricated electrodes were tested on a continuous filter-press cell in such a way that both the catholyte and the anolyte only passed once through the cell. This experimental set up was similar to the set up used in previous works [53]. The catholyte was a 0.45 mol L^{-1} $KHCO_3$ + 0.5 mol L^{-1} KCl aqueous solution and the