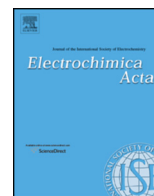




Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



Electrochemical reduction of carbon dioxide to formic acid at a tin cathode in divided and undivided cells: effect of carbon dioxide pressure and other operating parameters

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ARTICLE INFO

Article history:

Received 12 December 2015
Received in revised form 12 February 2016
Accepted 13 February 2016
Available online xxx

Keywords:

Carbon dioxide
Tin cathode
Electrochemical reduction
CO₂ Pressure
Formic acid
Carbon dioxide conversion

ABSTRACT

The reduction of carbon dioxide to formic acid at a tin cathode was studied in both divided and undivided cells. In the first stage of the study, the effect of some operating parameters, including the working potential and the nature of the supporting electrolyte and of the cathode, on both the cathodic reduction of CO₂ and the anodic oxidation of formic acid was investigated in a divided cell. In a second stage, the reduction of carbon dioxide was performed in an undivided cell with the aim of studying the effect on the generation of formic acid of various operating parameters such as current density, cathode to anode area ratio, mixing rate and nature of the anode and of the supporting electrolyte. A detailed investigation on the effect of the carbon dioxide pressure was also carried out. The utilization of relatively high CO₂ pressures (15–30 bar) allowed to achieve high concentrations of formic acid (up to 0.46 mol L⁻¹) working with high current density (up to 90 mA cm⁻²) and using cheap and simple undivided cell and electrodes.

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1. Introduction

The reduction of carbon dioxide is considered a relevant topic for both the synthesis of chemicals and/or fuels and the decrease of global warming. Indeed, the utilization of CO₂ as a feedstock for producing chemicals may contribute to alleviate global climate changes caused by the increasing CO₂ emissions and provide new opportunities for catalytic and industrial development [1]. Electrochemical processes could utilize excess electric energy from intermittent renewable sources to convert carbon dioxide in various products. CO, formate and formic acid, methane, ethylene and formaldehyde can be formed in water [2–5]. Oxalic acid, formic acid, CO [3,6] as well as carboxylic acids (by reaction with suitable reagents such as aromatic ketones [7,8] or benzylic halides [9,10]) can be obtained in aprotic solvents. It has been shown that the selectivity of the process dramatically depends on the nature of the cathode. Four distinct classes of metal catalysts have been identified on the basis of the main products obtained by the cathodic reduction of CO₂ in water: (i) metals that mainly form formic acid (Pb, Hg, In, Sn, Cd, Ti); (ii) metals that mainly form carbon monoxide (Au, Ag, Zn, Pd, Ga); (iii) metals that mainly form

H₂ (Pt, Ni, Fe, Ti); (iv) metals that form significant amounts of hydrocarbons such as methane and ethylene (Cu) [2–4,11]. Furthermore, Nakata et al. [5] have recently shown that the reduction of carbon dioxide in seawater at BDD cathode can lead to the formation of formaldehyde. In the last years, an increasing attention has been devoted to the electrochemical conversion of carbon dioxide to formic acid or formate in water [4,12–33]. Thus, formic acid has a broad market and wide application range in dyeing, textile and leather industries, in rubber production, as an intermediate in chemical and pharmaceutical industries, as an aid in the ensilage of green forage [34] and potentially as a fuel and energy-storage medium [14]. Formic acid can also be considered a good storage medium for hydrogen gas since it can be easily decomposed to H₂ and CO₂. At standard temperature and pressure, formic acid stores 580 times more H₂ than the same volume of hydrogen gas [35]. Furthermore, the bi-electronic reduction of carbon dioxide to formic acid seems more feasible and it is likely to present less extensive energetic inputs than its multi-electronic reduction to methanol, methane or more complex hydrocarbons [14]. Under proper conditions, formic acid can be formed in neutral or acidic solution, whereas formate ions are the main products in weak alkaline medium. The CO₂ reduction pathway to formate is likely to involve an initial CO₂ adsorption step and a subsequent electron addition to form the adsorbed intermediate species CO₂*—that evolves to formate through a protonation reaction followed by

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a second electron transfer [14,24]. This route is accompanied by the evolution of the adsorbed radical anion $\text{CO}_2^{\bullet-}$ to CO [24] and the hydrogen evolution.

Conventional catalysts for the electrochemical reduction of CO_2 to formic acid include metals such as Pb, Ru–Pd, Sn, Hg, In and Cd [14]. It has been shown that the utilization of tin cathodes allows the production of formic acid with good faradic efficiencies (FE) [4,16–33], that can be even higher, under suitable operating conditions, than that obtained at lead cathodes [19]. The engineering and economic feasibility of large-scale electrochemical reduction of carbon dioxide to formate salts and formic acid at tin cathodes was evaluated by Arun et al. [20] that concluded that this process could be operationally profitable. The effect of various operating parameters on the carbon dioxide reduction at tin cathodes was investigated by various authors [17–21,24,26,31]. Simple flat electrodes, gas diffusion ones and various kinds of alloys and nanostructured tin catalysts were used [17–33]. It was highlighted that the performances of the process strongly depend on the time passed. Various authors have shown that the FE of the process at Sn cathodes is quite high in the first stages of the electrolysis but that it decreases after few tens of minutes. The reason for this decrease was suggested to be the anodic oxidation of formic acid for undivided cells [16,21] or the deposition of substances (such as trace metals) on the surface of Sn electrode during the electrolysis [24]. However, Arun et al. [20] have shown that the faradic efficiency in formic acid presented quite high values also at the end of long experiments (about 50 h) performed in divided cells equipped with GLS (gas-liquid-solid) cathodic cell and 2 M KCl (pH 4–6) and 1 M KOH (pH 14) solutions for the catholyte and the anolyte, respectively [20].

In this work, a systematic study on the effect of numerous operating parameters on the reduction of carbon dioxide to formic acid at a Sn cathode is reported. The investigated parameters

include the working potential and the current density (for potentiostatic and amperostatic electrolyses, respectively), the pH, the nature of the cathode and of the supporting electrolyte and the mixing rate. A simple, flat cathode was chosen for its low cost and with the aim to highlight the effect of the above mentioned operating parameters. Both undivided and divided cells can be used for the electrochemical reduction of carbon dioxide. Divided cells allow an effective separation of anodic and cathodic processes, thus preventing or minimizing the anodic oxidation of the electrogenerated formic acid. On the other hand, the utilization of undivided cells would be appealing in order to avoid the potential and economic penalties given by the presence of the separator. Hence, the cathodic reduction of carbon dioxide was here studied in both divided and undivided cells to compare the performances of the process and the effect of operating parameters in both systems. Eventually, the effect of the carbon dioxide pressure, a key parameter that can affect drastically the performances of the process, was evaluated in detail.

2. Experimental

2.1. Electrolyses

Electrolyses were performed in three different systems. Systems I and II were bench-scale batch undivided and divided, respectively, glass cells equipped with a gas inlet, a SCE reference electrode, a tin sheet cathode, a compact graphite, a carbon felt or a Ti/IrO₂–Ta₂O₅ anode (DSA). Stirring of the electrolytic solution was performed with a magnetic stirrer. System III consisted in an AISI 316 stainless steel cell (Fig. 1) with a cylindrical geometry, described in detail in previous works [36,37], equipped with a gas inlet, a Sn cathode and a compact graphite anode from Carbon Lorraine. In order to try to increase the cathodic generation of

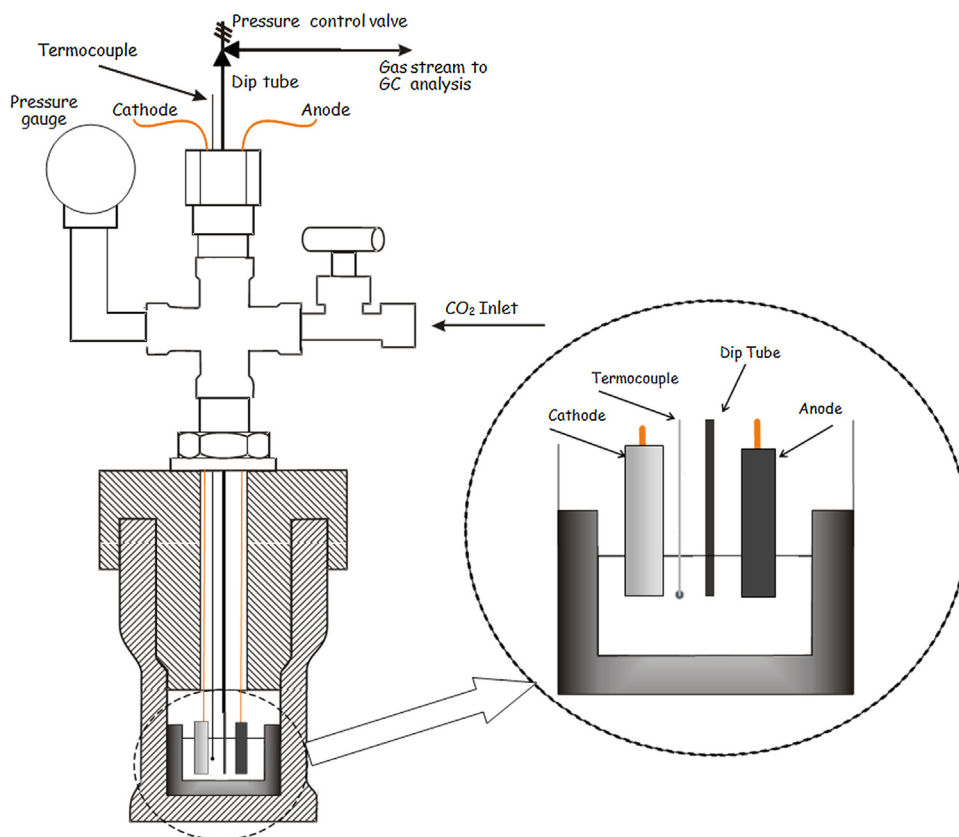


Fig. 1. Schematic diagram of the electrochemical reactor for experiments performed at pressure higher than the atmospheric value.

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