

Communication

Direct Electrochemical Reduction of Bicarbonate to Formate Using Tin Catalyst

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Abstract: Nowadays, the self-accelerating increase in global temperatures strengthens the idea that the cutting of CO₂ emissions will not be enough to avoid climate change, thus CO₂ from the atmosphere must be removed. This gas can be easily trapped by converting it to bicarbonate using hydroxide solutions. However, bicarbonate must be converted into a more valuable product to make this technology profitable. Several studies show great efficiency when reducing bicarbonate solutions saturated with pure CO₂ gas to formate. However, those approaches don't have a real application and our objective was to obtain similar results without pure CO₂ saturation. The method consists of electroreduction of the bicarbonate solution using bulk tin (Sn) as catalysts. Tin is a relatively cheap material that, according to previous studies performed in saturated bicarbonate solutions, shows a great selectivity towards formate. The ¹H NMR analysis of bicarbonate solutions after electroreduction show that, without pure CO₂ gas, the faradic efficiency is around 18% but almost 50% for saturated ones. The formate obtained could be used to power formate/formic acid fuel cells obtaining a battery-like system, with greater energy density than common lithium batteries, but electroreduction efficiency needs to be improved to make them competitive.



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1. Introduction

Since the start of the industrial revolution, the atmospheric CO₂ levels increased drastically and exceeded the 400 ppm in 2016 [1]. For this reason, some studies indicate that just cutting off or reducing the CO₂ emissions will not be enough to avoid or mitigate the effects of climate change, and CO₂ removal from the atmosphere is going to be necessary [2]. One way to absorb atmospheric CO₂ is by transforming it into bicarbonate using hydroxide solutions, like the system developed by A. Nogalska and R. Garcia [3]. Bicarbonate is a product with low value and not many applications, but its conversion to more useful and valuable hydrocarbons is becoming an economically viable way to reuse it [4].

Many different direct CO₂ electroreduction techniques use bicarbonate solutions previously saturated with pure CO₂ gas to obtain hydrocarbons or alcohols showing significant selectivity. The main inconvenience of these techniques are its practical applications because CO₂ is present in the atmosphere at very low concentrations, and it is almost impossible to saturate a bicarbonate solution with CO₂ using atmospheric air, with just a few studies performing it on non-CO₂ saturated bicarbonate solutions [5–11]. Theoretically, direct CO₂ electroreduction is performed by CO₂ activation on a catalyst surface and its following reaction with two protons (2H⁺). Generally, the bicarbonate acts as an electrolyte, favoring the CO₂ dissolution and increasing the conductivity of the aqueous solution, but, since dissolved bicarbonate is always in equilibrium with dissolved CO₂, it is still not clear if the carbon source is bicarbonate or CO₂ [12–16].

The electrochemical reduction of CO₂ into formate performed with water as a proton source is a very attractive technology, due to the great energy density of formate that can be used to power formate fuel cells [17–19], as a future alternative to lithium batteries [20,21]. In addition, this liquid fuel may be easily stored and transported using existing infrastructures. This way, renewable energy, which is intermittent, unpredictable, and with irregular production peaks, could be stored as formate and released during low production periods without any additional emissions of CO₂ into the atmosphere.

Our goal is to study the viability of reducing a non-CO₂ saturated bicarbonate solution into formate using a bulk tin catalyst, which is a relatively cheap material, simple to use and with great selectivity towards formate in mild conditions [22–26]. For this purpose, electrochemical studies were performed with the use of potassium bicarbonate. Moreover, the influence of CO₂ saturation on faradic efficiency of conversion was evaluated.

2. Materials and Methods

2.1. Materials

Tin foil (99.8% trace metals basis), 0.25 mm thick, provided by Alfa Aesar (Haverhill, MA, USA), was used as a working electrode and highly pure KHCO₃ (Bio Ultra 99.5%), supplied by Sigma-Aldrich (St. Louis, MO, USA), with a content of iron lower than 5 mg/Kg was used for preparation of the electrolyte. Milli-Q water was used to prepare solutions. Proton exchange membrane was Nafion[®] 117 membrane (Sigma-Aldrich). Hydrogen peroxide 30% (v/v) (Sigma-Aldrich) and 95–97% H₂SO₄ (Serviquimia) were used to prepare cleaning solutions for Nafion membrane. To prepare a standard for ¹H NMR analysis, 99.8% D₂O from Panreac and 99.7% DMSO (Chromasolv Plus) from Sigma Aldrich were used. CO₂ gas used for the electrolyte saturation was pure liquid carbon dioxide (CO₂ Premier X10) purchased from Carbueros Metálicos.

2.2. Linear Sweep Voltammetry

Linear sweep voltammetry (LSV) was performed prior to electroreduction experiments to evaluate which is the lowest potential that is high enough to allow significant product formation, without experimenting excessive H₂ gas formation at high potentials. To study the effects of KHCO₃ concentration, three solutions with different concentrations (0.1, 0.5, and 1.5 M) were prepared. Finally, the 1.5 M KHCO₃ solution was submitted to saturation with CO₂ gas during 30 min at a flow rate of 14.47 sccm to test its effects. Constant stirring was applied to ensure homogeneous solution, improve bicarbonate migration to the electrode, and facilitate the release of residual gas bubbles formed during reaction.

All experiments were carried out in a gas-tight Teflon H-cell (Figure 1 and Figure S1), equipped with the standard three-electrode system. The counter electrode was a bulk Platinum (Pt) foil of 1 cm², the reference electrode was an Ag/AgCl/3M KCl (0.21 V), and the working electrode consisted of a tin (Sn) foil of 5 cm². A Nafion membrane was used to separate the working and counter electrode compartments (25 mL each) to prevent oxidation of the reduced products. The membrane was washed by immersion in an 80 °C aqueous solution, for 1 h each, in the following order: 0.5M H₂SO₄, H₂O₂ 3%, and distilled water to eliminate possible contamination (Figure S2). The working electrode was not pretreated before experiments, as the native SnO₂ layer is reported to increase the catalytic activity [27], and the whole system was leaned with distilled water between each experiment. An AutoLab PGSTAT 302N potentiostat (Metrohm, Autolab B.V.) was used in all the electrochemical experiments. All the LSV were conducted at a scan rate of 100 mV/s in a range of potentials between 0 and –2.0 V in the presence of the reference electrode.

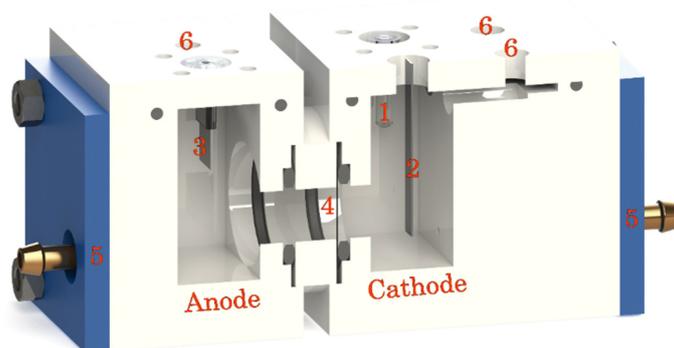


Figure 1. Cross section of Teflon H-cell used for the experiments. The cell consists of two compartments (Anodic and Cathodic) filled with the bicarbonate solution and separated by a proton exchange membrane (4) to prevent re-oxidation of reduced products on the anode. The cathodic compartment contains the working electrode (2), where the CO_2 is reduced and the reference electrode (1) (Ag/AgCl (0.21 V) is used to maintain a stable potential reading. In the anodic compartment, there is the counter electrode (3) (Pt foil) where water splitting takes place. For the saturation of solution with CO_2 , two inlets (5) and outlets (6) for gas were used.

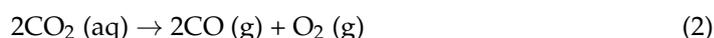
2.3. Electroreduction Experiments

The electroreduction experiments were carried out in potentiostatic conditions for 1.5 h in the same Teflon H-cell used for LSV analysis. In addition, constant stirring, CO_2 pre-saturation, and membrane-system cleaning were performed as described in the previous section and for the same purposes. The electroreduction potential was chosen based on the LSV analysis and set to -1.6 V. Beyond that, a significant increase of reduction current and gas bubble formation associated with CO (2) and H_2 (3) formation can be observed [28]. Some of those bubbles stayed in the working electrode surface, diminishing its active area, and reducing the efficiency of the reaction. The materials and the samples used are the same described in the voltammetry section.

The most probable electroreduction reaction of bicarbonate to formate in these conditions is showed (1), but formate formation from dissolved CO_2 is also possible [12–16]:



The most likely side reactions of CO and H_2 formation are:



2.4. Product Analysis

The analysis of the reaction's products was performed by ^1H NMR (VARIAN Mercury VX400). DMSO 0.010M in D_2O was used as an internal standard for quantification of the obtained products. Catholyte samples of 600 μL were mixed with 100 μL of standard. To obtain the peaks coming from products, we suppressed the water peak by irradiation.

Based on the determination of formate concentration through the NMR analysis with Mestrenova, Faradic efficiency FE (%) was calculated considering passed charge and electrons transferred with the following Equation (4):

$$\text{FE} (\%) = q_{\text{exp}} / q_{\text{theo}} \times 100 \quad (4)$$

Experimentally used charge [C] q_{exp} (5) is calculated by:

$$q_{\text{exp}} = Fnz \quad (5)$$

F stays for Faraday constant 9.6485×10^4 [C/mol], n is the amount of formate moles obtained by proton NMR, and z are electrons needed for bicarbonate conversion to formate based on chemical reaction ($2e^-$).

In addition, theoretical charge q_{theo} (6) [C] passed charge is obtained chronoamperograms by:

$$Q_{\text{exp}} = -It \quad (6)$$

where I is the total current [A] and t is the reaction time [s].

3. Results and Discussion

3.1. Linear Sweep Voltammetry (LSV)

The LSV measurements show a small peak between -0.9 V to -1.0 V corresponding to reduction of the small SnO_2 layer usually present on bulk Sn [21] (Figure 2). At potentials below -1.2 V, current density increases exponentially in all cases, probably associated with bicarbonate and hydrogen electroreduction. In addition, as current density increases, CO_2 bubbling on working electrode (Sn foil) is observed, probably associated with H_2 or CO and other residual gasses [29]. Furthermore, oxygen bubbles are observed on the platinum counter electrode. Current density is higher when CO_2 presaturation is used (Figure 2b), and the product analysis will determine if this is associated with more bicarbonate electroreduction or not.

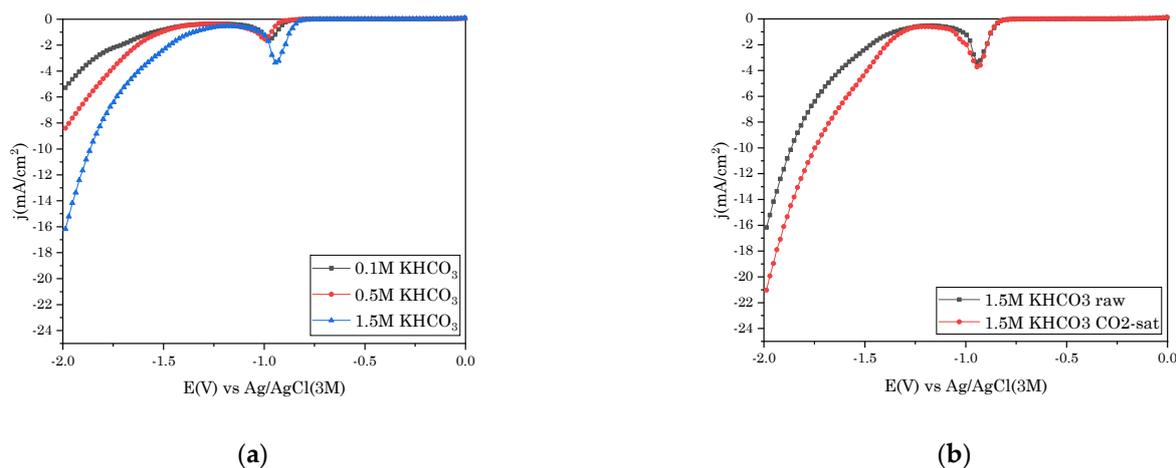


Figure 2. (a) LSV at different potassium bicarbonate (KHCO_3) concentrations of non- CO_2 saturated solutions; (b) comparison of a linear sweep voltammetry (LSV) between saturated with CO_2 and non-saturated potassium bicarbonate (KHCO_3) aqueous solutions.

3.2. Chronoamperometry

The working potential for electroreduction experiments was set at -1.6 V in order to obtain the greatest energy density without observing excessive formation of residual non-desired gasses (chronoamperograms shown in Figure 3). The current density should increase while augmenting KHCO_3 concentration, due to the improved conductivity of the solution and increased reaction rates. As expected, the results confirm an energy density six times higher for 1.5 M KHCO_3 solution respectively compared with 0.1 M KHCO_3 solution at -1.6 V (Figure 3a). For the CO_2 saturated experiments, the same trend is observed with a 33% increase on the current density at -1.6 V for the saturated solution (Figure 3b). The electroreduction current is stable during this interval of time for all experiments, slightly decreasing over time for experiments performed at 1.5 M KHCO_3 , which could be due to faster exhaustion of reactants, membrane poisoning, or catalyst degradation or even a reduction of solution volume. A small amount of noise most commonly present in experiments at higher currents are due to gas bubbles formation, which attach and detach from the catalyst surface affecting the active area.

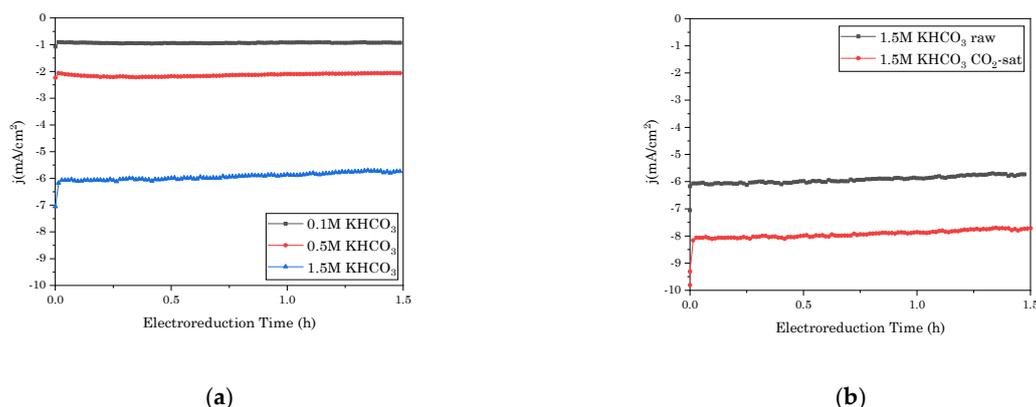


Figure 3. (a) Chronoamperogram at -1.6 V of different potassium bicarbonate (KHCO₃) concentrations of non-CO₂ saturated solutions; (b) chronoamperogram at -1.6 V of CO₂ saturated and non-saturated bicarbonate solution.

3.3. Analysis and Quantification of Products by ¹H NMR

The ¹H NMR spectra show three singlets at around 8.24, 4.63 and 2.50 ppm corresponding to HCOOK, DMSO, and H₂O, respectively (Figure S3). The slightly basic media (\sim pH 9) of the potassium bicarbonate solution, including the non-observation of an O-H bond of formic acid around 11 ppm, confirm that potassium formate (HCOOK) is the main product, and the acid form is not present for reaction conditions. The observation of only one product in the liquid phase indicates a high selectivity of tin foil towards formate production.

The faradaic efficiency towards formate shows a significant increase from 0% to 18% in 0.1 M and 1.5 M solutions as summarized in Table 1. With the saturation of CO₂, the efficiency increases from 18% to 47%, noting the importance of pre-saturating the solution with pure CO₂.

Table 1. Summary of the effects of the potassium bicarbonate (KHCO₃) concentration and the CO₂ pre-saturation on the faradaic efficiency of the electroreduction to formate.

KHCO ₃ (aq) Concentration (M)	0.1 M	0.5 M	1.5 M	1.5 M
CO ₂ pre-saturation	No	No	No	Yes
Faradaic efficiency (%)	n.d.	8	18	47

n.d.—not detected.

As we can see in Table 2, bulk Sn seems to have the highest efficiency compared with other similar bulk catalysts working in similar conditions.

Table 2. Summary of CO₂ electroreduction efficiencies towards HCOOH/HCOOK of similar bulk catalysts.

Electrode	Reference Electrode	Electrolyte	CO ₂ Saturation	Faradaic Efficiency (%) towards HCOOK/HCOOH	Ref.
Ag (99.98%) electrode	-1.6 V vs. Ag/AgCl saturated with KCl	0.1M KHCO ₃ aqueous solution	No	n	[30]
Au (99.95%) electrode				6	
Pd Metal	1.8 V vs. Ag/AgCl	0.1 M KHCO ₃ aqueous solution	No	4.4	[31]
Cu-Based catalysts	Ag/Ag+ with 0.01 M	0.5 M KHCO ₃ aqueous solution	Yes	3–15	[32]

4. Conclusions

During this brief study, we confirmed the possibility to reduce bicarbonate solutions to formate without using pure CO₂, with significant amounts for non-CO₂ saturated solutions (18%) and almost 50% for saturated ones.

Bicarbonate can be easily obtained from atmospheric air by CO₂ capture, and there is an unlimited stock of it. In addition, CO₂ pollutes the atmosphere and increases the greenhouse effect, with serious consequences for our planet and society, so pulling it out of the atmosphere will contribute to mitigate its negative consequences. The direct conversion of atmospheric CO₂ stored as bicarbonate will make this technology more competitive in the market, and to have an alternative for formic acid/formate production which is nowadays obtained by a non-renewable and very contaminating process. Another great application of formic acid is fuel cells because they have higher energy density than lithium batteries and they are safer than hydrogen fuels cells. Then, the possibility to have more competitive fuel cells with much higher energy density than current lithium batteries will also increase the competitiveness of renewable energies allowing the possibility to store more energy during its normally irregular energy production peaks.

To conclude, we can affirm that increasing the electroreduction efficiency and selectivity of bicarbonate to formate will become a great advance in energy storage systems, thus making renewable energies even more competitive, then investing in this technologies is a great way to fight climate change and take economical profit at the same time.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2673-3293/2/1/6/s1>, Table S1: List of abbreviations, Figure S1: 3D rendered design of Teflon H-cell used for the experiments, Figure S2: Nafion membrane cleaning procedure, Figure S3: 1H NMR spectra of products after electroreduction.

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