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Short Communication

Electrochemical Conversion of CO_2 into Aqueous-phase Organic Molecules Employing a Ni-nanoparticle-modified Glassy Carbon Electrode

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Electrochemical conversion of CO_2 into useable aqueous-phase organic molecules was investigated employing a glassy carbon (GC) electrode patterned with nickel nanoparticles (GC-Ni), in a batch electrochemical reactor operating at constant potential, room temperature and atmospheric pressure. The system was found to efficiently convert CO_2 into mostly ethanol (91 ± 1 mol.%), at a very high faradaic efficiency (221 ± 23% after 8 hours of electrolysis), indicating that the CO_2 reduction could most possibly be occurring both electrocatalytically and catalytically.

Keywords: Carbon dioxide; Electrochemical conversion; Aqueous electrolyte, Alcohols; Glassy carbon; Nickel nanoparticles, Faradaic efficiency

1. INTRODUCTION

Carbon dioxide plays a major role in producing the greenhouse effect [1-3]. It is estimated that the atmospheric concentration of CO_2 has significantly increased in the last 60 years [4]. As a result, the problem of global warming has escalated [5-8]. Therefore, it is extremely important to reduce the level of CO_2 in the atmosphere and, if possible, to convert it into useful organic molecules [6, 9-12].

Catalytic, photocatalytic and electrocatalytic methods have been used for the conversion of captured CO_2 into useful organic molecules [8]. Among them, the electrocatalytic conversion of CO_2 represents a simple, clean, and, if electricity is obtained from renewable sources, even potentially cost-effective method, which can be conveniently performed at atmospheric pressure and room temperature in an aqueous medium [7, 13-17]. However, there is currently no commercially-available process for the electrochemical conversion of captured CO_2. This is mostly due to the lack of efficient and selective electrocatalysts that could enable the CO_2 conversion process in aqueous electrolytes to proceed at a high faradaic efficiency [16, 18].

The main problem related to the electrochemical reduction of CO_2 is its high (electro)chemical stability. Hence, to reduce CO_2 electrochemically, a large overpotential is needed. This is because of the initial reduction of CO_2 molecule into surface adsorbed $CO^{-}_{2(ads)}$ radical (single electron reduction), which is the first and rate determining step [15, 19]:

$$CO_2 + e^- \rightarrow CO^{-}_{2(ads)} \qquad (1)$$

The formed radical further reacts with hydrogen to produce a final product, or intermediate(s) that is ultimately reduced to final products according to either the Eley-Rideal or Langmuir-Hinshelwood mechanism [20]:

$$nCO^{-}_{2(ads)} + ne^- + nH^+ / H_{ads} \rightarrow \text{Product} \qquad (2)$$

where H^+ is hydrogen ion in the solution and H_{ads} is hydrogen adsorbed on the electrode surface. However, the CO_2 reduction reaction in aqueous solution at higher cathodic potentials is always accompanied by the hydrogen evolution reaction (HER) [21, 22]:

$$H_{ads} + H^+ + e^- \rightarrow H_2 \qquad (3)$$

or

$$2H_{ads} \rightarrow H_2 \qquad (4)$$

This decreases the faradaic efficiency of the CO_2 reduction reaction. Therefore, it is quite difficult, both kinetically and thermodynamically, to reduce a very stable CO_2 molecule [15, 23]. The negative impact of the HER on CO_2 reduction can be minimized by using organic solvents, but since most organic solvents are not environmentally friendly, their use should be avoided. Another way of minimizing the negative impact of the HER is by designing new electrode materials that would promote reactions (1) and (2), but not (3) and (4).

Different electrodes have been used for the electroreduction of CO_2 such as bare metallic electrodes [15, 16, 23, 24] and several modified electrodes [25-29]. However, certain problems are associated with these systems such as high overpotential, electrode stability, electrode fouling, low selectivity, low product concentration and low faradaic efficiency [30].

We have recently reported results on the electrochemical conversion of CO_2 to certain organic molecules (mostly ethanol and methanol) at a faradaic efficiency of 85%, employing an Ir/Ru-oxide electrode operating in a batch electrochemical reactor in an aqueous electrolyte and atmospheric pressure and room temperature [31]. However, here we show that a significantly higher faradaic efficiency (221± 23%) can be achieved under the same experimental conditions (electrolyte type, pH, temperature, pressure), by employing a glassy carbon electrode patterned with nickel nanoparticles, indicating that the CO_2 reduction reaction, most probably, follows both an electro-catalytic and chemical-catalytic pathway [32]. The reader should note that only products in the liquid phase were analysed and discussed in the paper.

2. EXPERIMENTAL

Electroreduction of CO_2 using a nickel nanoparticle-modified glassy carbon (GC-Ni) electrode was studied in 0.4 M Britton Robinson buffer [33] at pH 5.82, atmospheric pressure and temperature 295±2 K. Formation of Ni nanoparticles (NPs) on a GC electrode surface was performed by electrochemical deposition of Ni as explained in a previous article [21].

Electrochemical reduction of CO_2 was performed in a three-electrode, two-compartment batch electrochemical reactor. The electrolyte volume was 80 mL. The geometric surface area of the GC-Ni working electrode (WE) exposed to the electrolyte was 6.25 cm^2. A mercury/mercurous sulphate electrode (MSE; +0.6 V *vs.* SHE) was used as a reference electrode (RE), and all potentials are expressed with respect to MSE. Two graphite rods were used as counter electrodes (CE). The CEs were separated from the WE and RE by a glass frit in order to prevent the oxygen gas evolved at the CE to get transported to the WE and be reduced, which would interfere with the CO_2 reduction reaction. In order to maintain an oxygen-free electrolyte, argon (99.998% pure) was purged through the electrolyte for 45 min prior to electrochemical measurements, followed by saturation of the electrolyte with CO_2 (99.99%, MEGS) for another 45 min. CO_2 was then continuously bubbled through the electrolyte during all electrochemical measurements, to maintain the electrolyte saturated with CO_2.

The surface morphology of the GC-Ni electrode was analyzed by a field-emission scanning electron microscope (FE-SEM). Identification of CO_2 reduction products dissolved in the liquid phase was done using mass spectrometry, and their concentration was determined by gas chromatography [31].

3. RESULTS AND DISCUSSION

3.1. Characterization of a GC-Ni electrode

The rationale for using a GC surface as an electrode substrate material for CO_2 reduction is related to the fact that GC is an inexpensive material, has large hydrogen evolution overpotential, and is a good substrate for adsorption of organic molecules [21, 22, 34]. On the other hand, to increase the kinetics of $CO_{2(ads)}^{-}$ radical protonation, it is desirable to have H_{ads} ("activated hydrogen") adsorbed at the neighbouring reaction site (close to the $CO_{2(ads)}^{-}$ radical formation site) so that the reaction follows the Langmuir-Hinshelwood mechanism, rather than having H^+ in the aqueous phase to directly react with the adsorbed $CO_{2(ads)}^{-}$ radical (the Eley-Rideal mechanism). Thus, taking into account that the Ni-H_{ads} bond is of intermediate strength [35], i.e. that H^+ can easily be adsorbed on the Ni surface to form H_{ads}, but can also be easily desorbed to react with the $CO_{2(ads)}^{-}$ radical adsorbed at the neighbouring GC electrode site, the choice of Ni to form nanoparticles on GC is reasonable (other metals, such as Pt, Ru, Ir can also be used for the same purpose, but these noble metals are significantly more expensive than Ni).

Fig. 1 shows a GC surface patterned with nickel nanoparticles (NPs). The NPs are uniformly / well dispersed on the GC surface, with a relatively narrow size distribution and good surface coverage. The corresponding mean particle size is 73±18 nm and the surface coverage is ca. 15%.

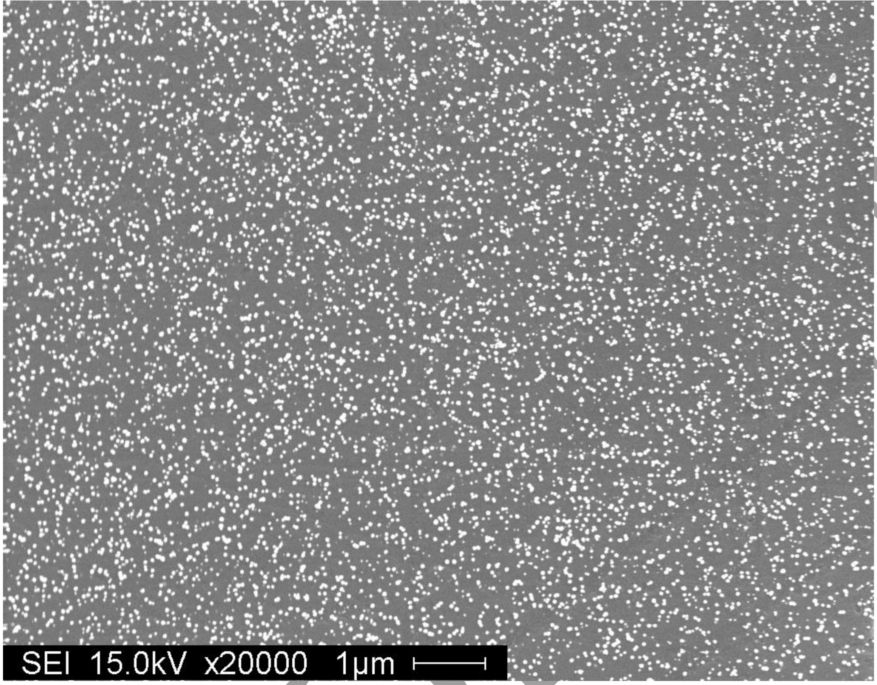

Figure 1. A SEM micrograph of Ni NPs deposited on a GC electrode surface.

3.2. Electrochemical reduction of CO_2

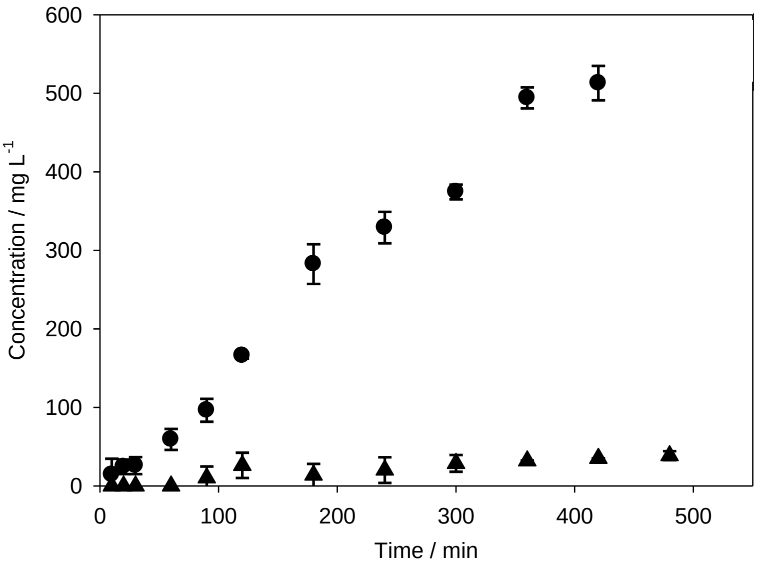

Figure 2. Concentration of (●) ethanol and (▲) methanol in the liquid phase produced by reduction of CO_2 on a GC-Ni cathode in a batch electrochemical reactor operating at electrode potential of -1.8 V_{MSE}. Small amounts of acetaldehyde were also produced (not presented).

In order to investigate the kinetics of CO_2 reduction on the GC-Ni electrode, electrolysis of a CO_2-saturated electrolyte was performed in a batch electrochemical reactor operating at constant potential. Fig. 2 shows the corresponding evolution of CO_2 reduction products (it should be noted that only products remained in the liquid phase at concentrations detectable by gas chromatography, are presented). Ethanol was identified as the major CO_2 electroreduction product in the liquid phase, with a minor contribution of methanol. Traces of acetaldehyde were also detected at longer electrolysis times (not presented). The corresponding electrochemical reactions can be presented as outlined below; note that these are complex reactions, composed of a number of elementary reaction steps that are currently now known:

$$\mathrm{CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O} \tag{5}$$

$$\mathrm{2CO_2 + 12H^+ + 12e^- \rightarrow CH_3CH_2OH + 3H_2O} \tag{6}$$

$$\mathrm{2CO_2 + 10H^+ + 10e^- \rightarrow CH_3CHO + 3H_2O} \tag{7}$$

Fig. 2 shows that the concentration of ethanol gradually increased with time and reached 574 ± 3 mg L^{-1} after 480 min. Methanol was first detected after 90 min of electrolysis, and its concentration reached only 38 ± 6.0 mg L^{-1} at the end of electrolysis time. The total alcohol production profile is, thus, governed by that of ethanol, and the average ethanol yield in the product mixture was 93±6 mol.% (taking into account the entire electrolysis time). It should be noted that the experiment in Fig. 2 was repeated in the absence of CO_2 in the electrolyte (control experiment), and none of the products presented in Fig. 2 was detected after 480 min of electrolysis. This demonstrates that the three products in Fig. 2 were indeed produced by the electrochemical reduction of CO_2.

As mentioned previously, one of the main obstacles in commercializing the CO_2 electroreduction process is its low faradaic efficiency in aqueous solutions. Consequently, the faradaic efficiency of the CO_2 reduction process performed on the GC-Ni electrode was determined by comparing the charge calculated using the Faraday law applied to the experimental data in Fig. 2 and Eqs.(5 - 7), to the experimentally-measured charge, and the results are presented in Fig. 3.

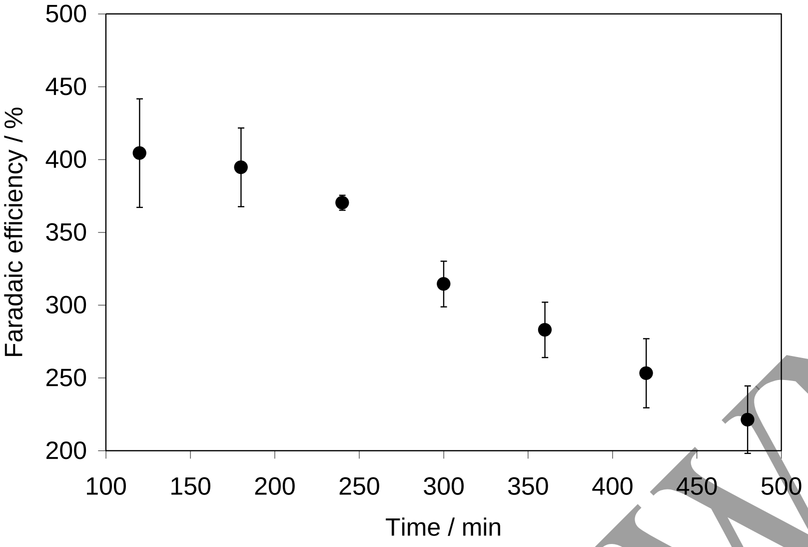

Figure 3. Faradaic efficiency of the CO_2 reduction reaction on GC-Ni calculated with respect to the production of ethanol, methanol and acetaldehyde dissolved in the liquid phase, in a batch electrochemical reactor operating at electrode potential of -1.8 V_{MSE}, 295 K and atmospheric pressure.

Surprisingly, during the first 120 min of electrolysis the total faradaic efficiency reached 404 ± 37%, and then gradually decreased to 221 ± 23% after 480 min. This decrease in efficiency may be due to the deactivation of the electrode caused by adsorption of CO_2 reduction products on the electrode surface, which partially blocked the electrode and reduced its electrochemically-active surface area. Our ATR-FTIR measurements (not shown) confirmed that organic molecules indeed adsorbed on the electrode surface at the experimental conditions employed.

Considering that the product analysis methodology used in this work was the same as that one published in our previous paper [31], in which the reported faradaic efficiency on an Ir/Ru-oxide electrode was significantly lower (85% under the same experimental conditions applied here), and considering that replicate measurements were performed and the corresponding error calculated (error bars in Figs. 2 and 3), we can eliminate a possibility of experimental and/or calculation error in determining the (high) faradaic efficiency values presented in Fig. 3.

The above-100% efficiency in Fig. 3 indicates that the formation of CO_2 reduction products proceeded not only through the electrochemical (electrocatalytic) pathway (Eqs. 5 - 7), but also through a chemical (catalytic) pathway. The authors currently do not have experimental evidence that would support this claim, but a possible explanation could be related to a so-called NEMCA (non-faradaic electrochemical modification of catalytic activity, also known as electrochemical promotion of catalysis, EPOC) effect [36-38]. This phenomenon has not yet been reported in the literature in the case of electrochemical reduction of CO_2 under the experimental conditions applied in this research (room temperature, atmospheric pressure), but it has been reported for other electrochemical systems operating under similar experimental conditions, where up to 500% faradaic efficiency values have been reported [37, 38]. However, further research is needed to verify the contribution of the NEMCA effect in CO_2 reduction.

4. CONCLUSIONS

The conversion of CO_2 into different organic molecules using a GC-Ni electrode in a batch electrochemical reactor operating at room temperature and atmospheric pressure and at a very high faradaic efficiency was demonstrated. We hypothesize that the >100% efficiency is possibly due to the contribution of the NEMCA effect. The GC-Ni electrode was found to be highly selective towards the conversion of CO_2 into ethanol (91±1 mol.% at longer electrolysis times).

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