In memoriam prof. dr. Liviu Oniciu

ELECTROREDUCTION OF CARBON DIOXIDE TO FORMATE ON BRONZE ELECTRODE

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ABSTRACT. This paper presents our data on the electrochemical reduction of carbon dioxide, on bronze electrode ($Sn_{85}Cu_{15}$) in aqueous medium (0.2 M K_2CO_3), under CO_2 atmosphere, $(12-25)^0C$. The current efficiency for main product (formate) depends on the current density and was found to be up to 74% at high negative potential (> - 1.6 V/SCE), decreasing with operating time and with temperature increase (72-74% at 12 ^0C and 60-65% at 25 ^0C).

Keywords: carbon dioxide, electroreduction, formate, bronze electrode.

INTRODUCTION

The electrochemistry of CO_2 is a continuously growing field because it is a remarkable process with respect to at least two reasons. Firstly, CO_2 is the ultimate by-product of all processes involving oxidation of carbon compounds. Secondly, CO_2 represents a possible potential source for C-feedstock for the manufacture of chemicals.

The electroreduction of CO_2 at various metal electrodes yields many kinds of organic substances, namely CO, CH_4, C_2H_6, EtOH, other alcohols, formic acid, etc. Sánchez-Sánchez et al. [1] summarized representative results for the direct electrochemical CO_2 reduction at solid electrodes. The various types of electrocatalytic behavior among metals can be related to their electronic configuration and can be grouped into sp and d metals [2, 3]. The electroreduction techniques had to overcome the difficulty of finding electrodes with both high electrocatalytic activity and satisfactory lifetime [3].

The thermodynamic requirements for various CO_2-reduction reactions should be considered, because of the stability and chemical inertness of CO_2. The necessary energy to carry out carbon dioxide transformations for the processing and recovery of the air carbon-based sources can be generated by high temperatures, extremely reactive reagents, electricity, or by light irradiation [1]. However, because of the close proximity of the hydrogen

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potential, hydrogen evolution may also occur, as a concurrent reaction, depending on the operating system. The electroreduction of carbon dioxide needs substantial overpotentials due to the kinetic barrier and the large difference in the HOMO and LUMO energies. Moreover, the cathodic reduction of carbon dioxide is normally accompanied by hydrogen evolution and often mixtures of reaction products are obtained.

The main competitive reactions (1-5) involve electrosorbed species with hydrogen atom participation. Thus, in the electrochemical reduction of CO_2 in water, the hydrogen formation competes with the CO_2 reduction reaction. Therefore, the suppression of hydrogen formation is very important because the applied energy is wasted on hydrogen evolution instead of being used for the reduction of CO_2.

$$H^+ + e^- \longrightarrow H_{ad} \tag{1}$$

$$CO_2 + H_{ad} \longrightarrow HCOO_{ad} \tag{2}$$

$$HCOO_{ad} + H_{ad} \longrightarrow HCOOH \tag{3}$$

$$HCOO_{ad} + CH_3OH \longrightarrow CH_3COOH + OH_{ad} \tag{4}$$

$$OH_{ad} + H_{ad} \longrightarrow H_2O \tag{5}$$

The large number of recent papers, published during the last ten years on electrochemical reduction of carbon dioxide are both fundamental and preparative interest [4-19].

According to the recent review of Gattrell and Gupta [4] the reaction product distribution strongly depends on conditions at which data has been reported. When used in the aqueous solution, most flat metallic electrodes yielded carbon monoxide and formic acid [5, 6-10]. Hori et al. [11] with regard to the hydrocarbons formation on copper cathode revealed extended aspects on the deactivation of copper. Many workers reported "poisoning" or "deactivation" of the copper electrode in 10-30 min after the start of the CO_2 electroreduction [11].

CO_2 can be reduced on the surface of Pd-Pt-Rh alloys in the potential range of hydrogen electrosorption [12, 13]. The presence of the adsorbed product of the electroreduction of CO_2 on the electrode surface does not block hydrogen absorption [1, 3, 13].

The electrocatalytic activity of bronze cathode for the electrochemical reduction of stable inorganic molecules (nitrates and NO) has been reported [14, 15]. An enhancement of the electrocatalytic activity of Cu by alloying with Sn was observed only in the composition region up to 15% (wt.) Sn. A further increase in Sn content results in a rapid decline of the electrocatalytic activity caused by changes in the phase structure of the alloy material [14].

136

The current efficiency for formate depends on the electrode nature [1,5], current density and CO_2 pressure. Other factors such the hydrogen overpotential [2] and mass transfer capacity of the cathode are important and depend on the operating time. During the experiments the tin was lost from the cathode surface [11,13] and this fact decreased the current efficiency for carbon electroreduction.

Several papers related to the electrochemistry of CO_2 are of technological interest [16-19]. Copper tube electrodes have been employed for the production of methanol and formic acid [16].

The idea of this work is to enhance the electrocatalytic activity of copper for reduction of carbon dioxide to formate, diminishing the competitive hydrogen formation in the presence of tin in Cu-Sn alloy cathode.

RESULTS AND DISCUSSIONS

Voltamperommetric response of system

The potential was scanned at a sweep rate of 25 - 250 mVs^{-1}. Typical current-potential curves are illustrated in Fig. 1. The starting potential of the cathodic current was observed at approximately -1.1 V. No voltammetric peak was observed in potential range down to $-$ 2.0 V. Further CO_2 reduction may proceed with increasingly negative potentials, inhibiting the hydrogen evolution.
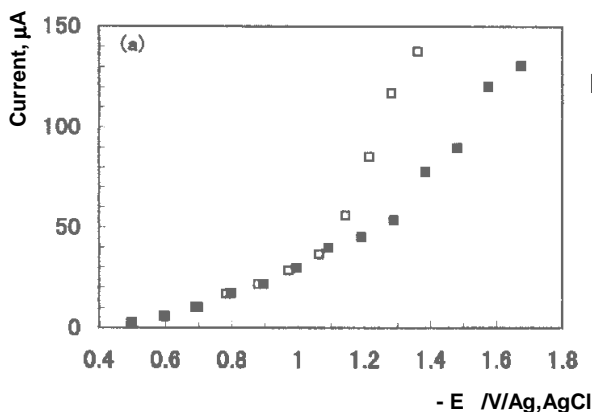

Figure 1. Current-potential curves for CO_2 reduction on bronze ($Sn_{85}Cu_{15}$) in 0.2 M K_2CO_3, saturated with CO_2 under CO_2 atmosphere at ambient temperature (20±0.4) ^{0}C.
€- Ar gas; ∎ – CO_2 gas.

From the polarization curves it was observed that the CO_2 reduction presented a Tafel slope corresponding to $n_e=1$, indicating that the first electronation of the CO_2 molecule to form the radical anion (CO_2^{-}), is the rate-controlling step.

Factors influencing the current efficiency

In absence of CO_2 in the cell, the current was used only for hydrogen evolution; no other reaction products were detected both in electrolyte and in cell atmosphere. In presence of CO_2, the main product detected (by HPLC Perkin-Elmer LC 200, ODS-18 column) and by gas chromatography (Hewlett-Packard 6890, TCD, FID, Porapac QS columns) was formic acid (formate and methyl formate, in the presence of methanol). Accordingly, only the formate has been determinated during our experiments. The influence of applied potential and temperature on the current efficiency for formic acid formation has been determinated.
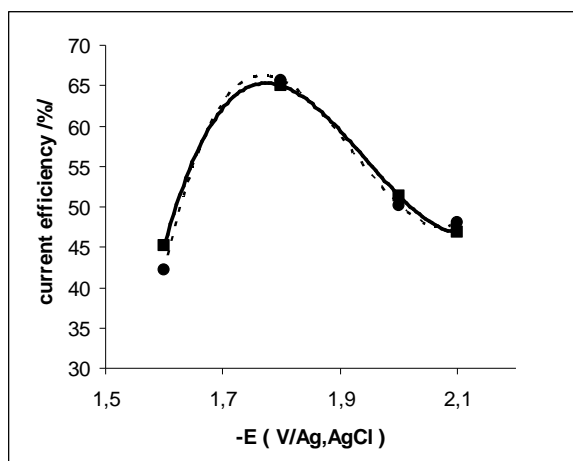
Influence of applied potential

Figure 2. Current efficiency - potential diagrams for CO_2 reduction on bronze ($Sn_{85}Cu_{15}$) in 0.2 M K_2CO_3, saturated with CO_2, under CO_2 atmosphere at ambient temperature (20 ± 0.4) ^{0}C.(● and ■) – two series of experiments

The maximum of the partial current density for the formation of formic acid on bronze electrode is 80-100 mAcm^{-2}, larger that with other reported electrode materials [1, 3].

Influence of temperature

The results of the temperature studies show (Fig. 3) that current efficiency achieved is in the range of 74% after 30 min. of electrolysis, carried out at the optimum reduction potential of -1.8 V (Fig.2).

It is well known that in aqueous electrolytes, the electroreduction of CO_2 not only to HCOOH is in competition with the H_2 evolution permanently [13].

138
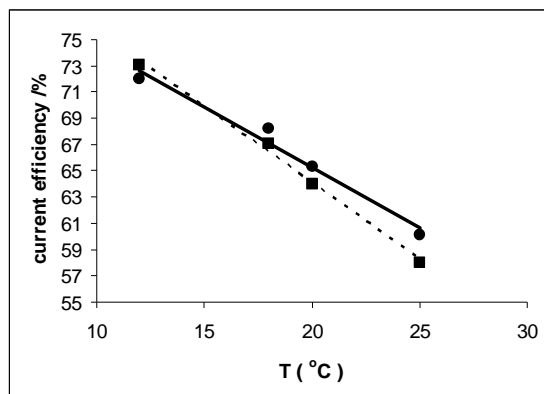
Figure 3. Current efficiency - temperature diagrams for CO_2 reduction on bronze ($Sn_{85}Cu_{15}$) in 0.2 M K_2CO_3, under CO_2 atmosphere, at 120 mA.cm^{-2}, ($\bullet$ and $\blacksquare$) – two series of experiments

The increase in the temperature under ambient conditions leads to a decrease of the current efficiencies for the HCOOH formation because of the decreasing CO_2 concentration in the electrolyte; thus the H_2 evolution becomes more dominant. In this small temperature range ($\Delta=13^0C$), the decrease was demonstrated. Probably, with the decrease of temperature under 12^0C, the competitive hydrogen evolution could be further diminished.

The preliminary data were obtained on the influence of electrolysis time and of the presence of methanol, on the current efficiency for formate formation (Table 1).

After 40-50 minutes of electrolysis, a cathode deactivation was observed (the corresponding current efficiencies decreased with 10-30%). A further increase in electrolysis time leads to a rapid decline in activity.

On the other hand, the presence of methanol up to 50% in volume leads to a smaller selectivity for formate formation, which becomes only (54-58) % at -1.8 V and low temperature (12 ^0C), comparing with (72-74) % in aqueous electrolyte.

The preliminary data in Table 1 are according to bibliographical information and with the supposed beneficial effect of Sn on the electro-catalytic activity of copper cathode, in bronze. Thus, when aqueous solution was used, copper was reported to be a suitable electrode for the formation of hydrocarbons. The electrochemical reduction of CO_2 with a Cu electrode in methanol-based electrolyte was investigated by other authors [6]. The main products from CO_2 were methane, ethylene, ethane, carbon monoxide and formic acid. On the other hand, very recent paper demonstrated the influence of added Sn on the electrocatalytic activity of copper, as the basic cathode material, on the electrocatalytic activity of the resulting material for nitrate (NO_3^-) reduction [15].

Table 1.

Current – efficiencies on bronze cathode depending on
electrolysis time and presence of methanol

Composition of electrolyte	Time of electrolysis (min)	Current Efficiency (%)
Aqueous 0.2 M K_2CO_3	30	72-74
	60	62-65
MeOH/water (1/2) + 0.2 M K_2CO_3	30	59-63
	60	49-52
MeOH/water (1/1) + 0.2 M K_2CO_3	30	54-58
	60	42-43

The current efficiency for HCOOH production increased after hydrogen was absorbed on the electrode surface. This fact was demonstrated using the bronze electrode after activation by H_2 evolution (10 minutes before the electrolysis in the presence of carbon dioxide). The participation of absorbed hydrogen in the reduction of CO_2 and the possibility of direct attack on the reaction intermediates by absorbed hydrogen could be involved.

CONCLUSIONS

The present paper demonstrated for the first time, up to our knowledge, that the bronze electrode is suitable for selective electroreduction of CO_2 to formate, especially in aqueous bicarbonate solution. The selectivity diminishes in the presence of methanol.

The important current efficiency for formic acid formation (up to 74%) have been obtained at reduction potential of -1.8 V and 12 ^{0}C, during the first 30 minutes of electrolysis.

According to our preliminary observations on the increase of current efficiency after the saturation of the electrode with adsorbed hydrogen (H_{ad}) the electrochemical hydrogenation can be also involved in the electroreduction mechanism.

The most important result of this work is the enhancing of the electrocatalytic activity of copper for reduction of carbon dioxide to formate, diminishing the competitive hydrogen formation, in the presence of tin of the Cu-Sn alloy cathode.

As perspectives, it is envisaged to use this procedure as a suitable alternative for testing other cathodes including modified materials, like nanocopper cathodes, modified with underpotential deposited stanium.

EXPERIMENTAL SECTION

Reagents and solution preparation

All reagents (potassium permanganate, potassium carbonate, potassium hydroxide, methanol, formic acid) were reagent grade from Fluka. The electrolytes were prepared from MiilQ water. To saturate the potassium bicarbonate the carbon dioxide (Fluka, quality sign 48) free of organics has been used.

Formate determination

The solution of the sample is treated with excess of standard potassium permanganate in alkaline conditions to form manganese dioxide. The manganese dioxide and excess potassium permanganate were determined iodometrically in acid conditions and the concentration of oxidizable impurities were calculated and expressed as formic acid.

Apparatus

Voltammetric measurements were made using a potentiostat-galvanostat system – BAS 100B (Bioanalytical Systems, USA) with the specific software BAS 100W and a classic three-electrode electrochemical cell. The electrochemical cell is comprised of a cell bottom of 20 mL capacity. A working electrode of ($Sn_{85}Cu_{15}$) (2 mm diameter) and a platinum plate auxiliary electrode were inserted through the cell top into the cell. During the voltammetry determination, a salt bridge for the protection of the reference electrode Ag/AgCl was used. The pH measurements were made with a pH-meter Basic 20 (Crison).

Procedure

Cyclic voltammetry and linear sweep potential voltammetry were performed in the usual way with a potential sweep rate of 5 mV/s at 25⁰ C. The sensitivity is 10 µA/V and the domain of potential was established after several determinations: -400 to 400 mV vs. Ag/AgCl.

The electroreduction of CO_2 was made in a laboratory divided bench-scale reactor (V= 200 ml; Nafion 424 membrane), equipped with bronze cathode (S= 2.2 cm^2) and Pt anode. The electrolyte was aqueous or hydro-alcoholic 0.2 M K_2CO_3 saturated with carbon dioxide. The catholyte was stirred magnetically. The faradic efficiency of formation for the main products were calculated from the total charge passed during batch electrolyses, which was set to 50 coulombs.

During the preparative electrolysis, samples were taken (in 30-min periods) with a volume of 5 mL from the electrolyte. The samples from the electrolyte were studied with respect to formate formation.

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