

Electrochemical Reduction of Formic Acid on a Copper-Tin-Lead Cathode

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Abstract: The electrochemical reduction of formic acid in acidic solution (2 mol L⁻¹ HCl) on a Cu(88)Sn(6)Pb(6) cathode was studied. The main products of the reduction were methanol and ethanol having %Current Efficiencies (CEs) of 30.3 and 37.6% respectively at -0.8 V vs Ag/AgCl. Small amounts of methane and ethane were also detected. The rate of the reduction increased exponentially with the negative potential in the range -0.65 to -1.00 V and the maximum of the %CE was observed at -0.8 V. The rate of the reduction of HCOOH increased slightly with the concentration of HCOOH. In pure HCOOH as electrolyte a noticeable amount of CH₃CHO (17.1%) was detected. A possible reduction mechanism was proposed in which the adsorbed CO is the key intermediate for the formation of all the products.

Keywords: Copper, electrochemical reduction, ethanol, formic acid, lead, methanol, tin.

INTRODUCTION

The electrochemical reduction of carbon dioxide on the high overpotential metals for the hydrogen evolution, such as Sn, In and Pb gives formic acid or formate by a %Current Efficiency (%CE) near 100% [1-3]. Formic acid has limited uses and thus its conversion to more valuable organic products is of crucial importance for the efficient recycling of carbon dioxide. The conversion of HCOOH to other organic products is also important for the efficient utilization of biomass given that sugars such as glucose can be converted to formic acid by a high yield under mild hydrothermal conditions [4].

Among various products which can be produced from the reduction of formic acid methanol is the most attractive since it can be directly used either as fuel in internal combustion engines and fuel cells or as a raw material for the production of other chemicals. The energy density of formic acid is 285.5 kJ mol⁻¹ while that of methanol is 702.5 kJ mol⁻¹.

The standard potential for the conversion of formic acid to formaldehyde which is the first step of its reduction to methanol is only 0.056 V and corresponding for the conversion of formaldehyde to methanol is 0.232 V [5]. Although these reactions are apparently thermodynamically favorable the activation energy for the first step is quite high and this leads to a low reduction rate.

At the beginning of the 20th century a patent was published on the reduction of various monocarboxylic fatty acids on Pb, Ni, Fe, Co and Pt [6]. In 10% sulfuric acid as electrolyte the main products of the reduction of formic acid were formaldehyde at low current densities and methanol at higher current densities. The %CE was not mentioned. However, these results were not reproduced by a subsequent work [7].

Meller [8] found that formic acid can be reduced with low %CE (7-13%) on electrodeposited tin and with %CE 7.4-13.7% on liquid Cerrolow136 (alloy containing tin, bismuth, lead and indium). The maximum current density was 140 $\mu\text{A cm}^{-2}$, which is too low for commercial purposes. Russell and coworkers [3] showed that formic acid can be reduced to methanol in acidic solution in a narrow potential region between -0.68 and -0.72 V vs. SCE on Sn and between -0.9 and -1.0 V on Pb, where a %CE of 99% on Sn and 11.9% on Pb was achieved. The current density of the reduction was also quite low (less than 4 $\mu\text{A cm}^{-2}$). The low rate of the reduction was attributed to the limited adsorption of formic acid on the electrode surface near the pzc, which was considered as the rate determining step. Kapusta and Hackerman [2] achieved a similar %CE on tin at low current densities but the poor efficiency was attributed to the formation of organometallic complexes on the surface of tin which accelerate the hydrogen evolution reaction.

Cyclic voltammetry experiments by Miles et al [9, 10] on a variety of metal cathodes and TiO₂ showed that the cathodic current increased linearly with the concentration of formic acid. They proved that the increase in the current was not due to the reduction of formic acid but to the acceleration of the hydrogen evolution reaction in the presence of formic acid, which simply served as a conveyor of protons to the electrode surface.

The reduction of formic acid by chemical methods is also difficult. The only efficient chemical method for the reduction of formic acid to formaldehyde has been proposed by Grand [11]. It includes its reduction by hydrogen produced from metallic magnesium in acidic solution and this is one of the methods of its analysis. In a previous work [12] from our laboratory it was found that the reduction of HCOOH takes place on a CuSnPb cathode in 2 mol L⁻¹ HCl and gives methanol (19.5%) and CH₄ (6.3%).

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The present work shows for the first time that formic acid can be reduced to ethanol and acetaldehyde with remarkably high %CEs on a CuSnPb cathode.

EXPERIMENTAL

The experiments were carried out in a Teflon cell having a total volume of 24 mL. The two equal volume compartments were separated by a Nafion 117 (H^+ form) cation exchange membrane. The cathode was a foil of a Cu(88)Sn(6)Pb(6) alloy having an apparent area of 7 cm^2 and the anode was a platinized Pt foil (Alpha Metal) of equal area. The electrode was polished before each experiment in a Struers DP-U2 grinding equipment with a No. 1200 polishing paper and subsequently rinsed with ultra-pure water. The cyclic voltammetry experiments were performed in a three-compartment glass cell which had a Cu(88)Sn(6)Pb(6) cathode with a geometric area of 0.5 cm^2 .

The potential was controlled by a Wenking POS 73 (Bank Elektronik) potentiostat and the reference was a saturated Ag/AgCl electrode. In the electrolytic experiments the solution was degassed for about 10 min before its entrance to the electrolytic cell and the desirable potential was applied before the entrance of the electrolyte in the cell in order to avoid the corrosion of the cathode due to the high acidity. A stream of He having a flow rate of 10 mL min^{-1} was used to withdraw the gaseous products and a part of the produced methanol from the cell during the electrolysis. The escaped liquids from the cell by the gaseous stream were collected in three tubes containing cold water. By this way the esterification of methanol with HCl in the catholyte was minimized. No significant volume loss of the catholyte was observed at the end of electrolysis. Formic acid (purity 98%) was supplied from Baker and the other chemicals from Fluka. The solutions were prepared using ultra pure water from a Sation 9000 apparatus. All the experiments were performed at ambient temperature conditions.

A gas chromatograph (GC) with a Plot Q, 30 m long, 0.530 mm diam. column equipped with TCD and FID detectors connected in series was used for the analysis of all the products. The gas chromatograph were calibrated with Air Metal standards and tested periodically. Tests for the possible production of formaldehyde were performed by the chromotropic acid method [11].

The detection limit for methane and methanol was 1 ppm and the reproducibility of the experimental results was established to be within $\pm 5\%$. The %CEs of the products were calculated by assuming that the number of electrons is 4 for CH_3OH , 8 for CH_3CH_2OH , 6 for CH_3CHO and CH_4 and 10 for C_2H_6 .

The rate of the reduction of formic acid was calculated as the sum of the rates of formation of the products of its reduction which were determined analytically.

RESULTS AND DISCUSSION

Study by Cyclic Voltammetry

Fig. (1). shows the cyclic voltammograms of formic acid and that of the supporting electrolyte. The voltammograms were taken in the potential region between -0.65 and -0.90 V , because at less negative potentials the electrode undergoes corrosion whereas at more negative potentials than -0.9 V massive hydrogen evolution takes place. The current in the presence of formic acid was higher than that of the background electrolyte in all potential region examined. The increase in the concentration of formic acid resulted in corresponding, but not linear, increase in the cathodic current density. A similar reduction wave was observed by Miles et al [9] on various electrodes. Closer examination showed that this wave was mainly due to the increased rate of H_3O^+ reduction in the presence of formic acid and not to the reduction of formic acid. Therefore, the cyclic voltammetry is not capable to provide reliable data on the reduction of formic

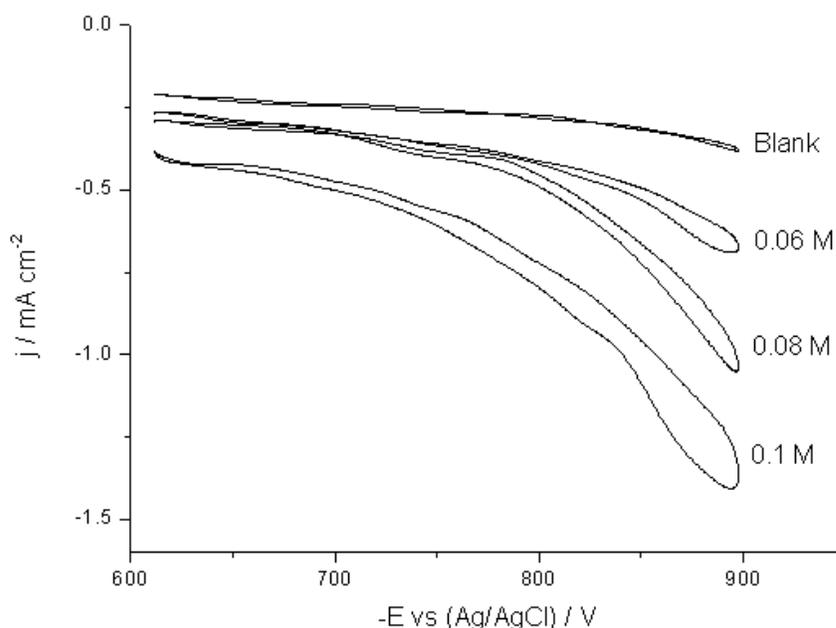


Fig. (1). Cyclic voltammograms of the background electrolyte and that of formic acid 0.06, 0.08 and 0.1 mol L⁻¹. Scan rate 5 mV s⁻¹.

acid. After that our work was based mainly on steady state electrolysis experiments.

Steady State Electrolysis Experiments

Table 1 shows the effect of cathodic potential on the rate of the reduction and the %CE of the products. The main products of the reduction were methanol, ethanol as well as small amounts of methane and ethane. The %CEs of methanol and ethanol displayed a common maximum of 30.3 and 37.6% respectively at -0.8 V. It is worth mentioning that a similar maximum was observed on tin cathode at -0.68 V, but in this case the only product was methanol [3]. As far as we know it is the first time that ethanol was found to be a main product of the reduction of HCOOH. It is worth mentioning that ethanol was formed only at the first electrolysis

steps (~15 min) and its amount was constant thereafter. In all experiments traces of carbon monoxide were detected a fact which will be discussed later in this article.

In some experiments the sum of %CEs was lower than 100%. This was attributed apart from the experimental error to the possible formation of other organic compounds which were not detectable under our experimental conditions.

The rate of the reduction increased exponentially by increasing the negative potential as it is shown in Fig. (2) and this implies that a charge transfer reaction is involved in the rate determining step. Unfortunately, the increase in the rate of the reduction of HCOOH with the negative potential is accompanied with a much higher increase in the rate of the hydrogen evolution reaction, which leads to a significant decrease of the %CE of HCOOH reduction as it is shown in

Table 1. %CEs of the Products and Rate of Reduction of 0.5 mol L⁻¹ HCOOH vs. Cathodic Potential in 2 mol L⁻¹ HCl Solution. Electrolysis Time 120 min

| E/ V | %CE | | | | | Total CE | Total Charge/C | Reduction Rate $\mu\text{moles/h}$ |
|-------|--------------------|------------------------------------|-----------------|-------------------------------|----------------|----------|----------------|------------------------------------|
| | CH ₃ OH | CH ₃ CH ₂ OH | CH ₄ | C ₂ H ₆ | H ₂ | | | |
| -0.65 | 21.6 | 24.5 | 5.9 | 2.1 | 25.1 | 79.2 | 3.1 | 3.4 |
| -0.70 | 22.4 | 33.8 | 7.2 | 2.3 | 24.9 | 90.6 | 3.1 | 3.5 |
| -0.75 | 25.5 | 35.5 | 5.4 | 0.4 | 25.8 | 92.6 | 3.3 | 3.8 |
| -0.80 | 30.3 | 37.6 | 4.4 | 1.2 | 27.3 | 100.8 | 3.6 | 5.9 |
| -0.85 | 16.1 | 11.3 | 2.0 | 0.3 | 46.7 | 94.4 | 18.5 | 6.9 |
| -0.90 | 3.1 | 2.3 | 0.5 | tr | 86.6 | 92.5 | 104.2 | 9.1 |
| -1.00 | 0.5 | 0.1 | 0.1 | tr | 93.1 | 93.8 | 652.2 | 14.4 |

tr = traces

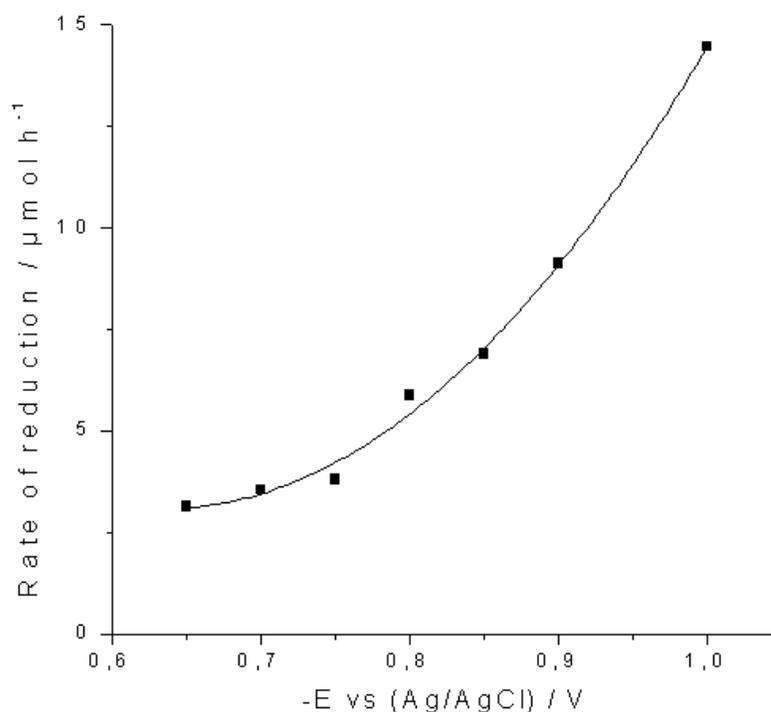


Fig. (2). Rate of the reduction of HCOOH against the cathodic potential, in a 2 mol L⁻¹ HCl solution. Electrolysis time 120 min.

Table 1. Therefore, the main problem which must be faced is the suppression of the hydrogen evolution reaction.

Influence of the Concentration of Formic Acid

Table 2 shows that the increase in the concentration of formic acid from 0.1 mol L⁻¹ to 100% (pure HCOOH) leads to an increase of %CE for the hydrogen evolution from 32.5 to 55.1%. The %CE of methanol was in the range 12-30% in all concentrations studied. The %CE of ethanol displayed a maximum 37.6% in a 0.5 mol L⁻¹ solution but in pure HCOOH it was not detectable. On the contrary acetaldehyde was not detectable at low concentrations, but in pure HCOOH solution had a noticeable %CE of 17.1. Apart from the above mentioned products in some experiments traces of methyl formate were detected which probably resulted from the esterification of the produced methanol with formic acid. The rate of the reduction of HCOOH increased from (5.1 to 10.3 μmols/h) as the concentration of HCOOH increased from 0.1 mol L⁻¹ to pure HCOOH.

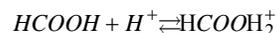
As it results from Fig. (1), the current density of the reduction of formic acid, which was assumed to be the difference between the current density of a solution of formic acid (0.1 mol L⁻¹) from that of the background electrolyte (at -0.8 V) was 0.44 mA cm⁻². From the electrolytic experiment performed under the same conditions, the current density of formic acid, which is the sum of the partial current densities of all the detected organic products, was found to be 0.41 mA cm⁻². The fact that these values are similar within the experimental error leads to the conclusion that the observed increase in the current density in the presence of formic acid in Fig. (1) actually corresponds to the reduction of formic acid and not to the acceleration of hydrogen evolution from formic acid.

Some experiments were also performed in supporting electrolyte containing trivalent lanthanum cations as well as higher concentrations of hydrochloric acid. In both cases, no significant difference in the rate of the reduction of formic acid was observed.

DISCUSSION

The detected products (apart from ethanol) during the reduction of HCOOH and their distribution were similar to

that found during the reduction of CO₂ under the same conditions [12]. This suggests that the reduction of both formic acid and carbon dioxide proceeds through common intermediates. According to this the following reduction scheme can be proposed: It is known that formic acid can be partially converted to its protonated form in acidic solution [13]:

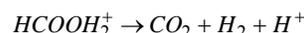


which then decomposes either to CO or CO₂ :



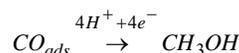
(decarbonylation)

or

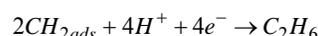
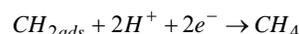
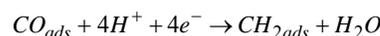


(decarboxylation)

The fact that in our experiments a small amount of CO was detected in the gaseous stream but not CO₂, implies that under the experimental conditions used the decarbonylation reaction is the dominant. The produced CO is further adsorbed on the electrode surface to give CO_{ads}. The CO_{ads} intermediate can give either methanol:



or after its hydrogenation CH_{2ads}, which is the key intermediate for the formation of the other products according to the reactions:



According to Hori *et al.* [14-16] the formation of acetaldehyde and ethanol takes place through the reactions:

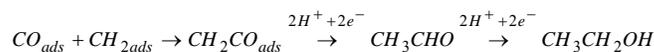


Table 2. %CEs of the Products and Rate of Reduction vs. Concentration of HCOOH in 2 mol L⁻¹ HCl Solution at a Cathodic Potential of -0.8 V. Electrolysis Time 120 min

| Electrolyte | %CE | | | | | | Total CE | Total Charge /C | Reduction Rate μmols/h |
|-------------------------------|--------------------|------------------------------------|---------------------|-----------------|-------------------------------|----------------|----------|-----------------|------------------------|
| | CH ₃ OH | CH ₃ CH ₂ OH | CH ₃ CHO | CH ₄ | C ₂ H ₆ | H ₂ | | | |
| 0.1 mol L ⁻¹ HCOOH | 23.5 | 19.6 | tr | 4.2 | 1.1 | 32.5 | 80.9 | 3.2 | 5.1 |
| 0.5 mol L ⁻¹ HCOOH | 30.3 | 37.6 | tr | 4.4 | 1.2 | 27.3 | 100.8 | 3.6 | 5.8 |
| 2.0 mol L ⁻¹ HCOOH | 24.4 | 18.7 | 3.1 | 4.9 | 1.6 | 33.2 | 85.9 | 4.1 | 7.0 |
| 5.0 mol L ⁻¹ HCOOH | 21.7 | 15.9 | 6.4 | 5.2 | 2.1 | 42.8 | 94.1 | 4.9 | 7.7 |
| 100 % HCOOH | 12.4 | tr | 17.1 | 1.3 | 1.7 | 55.1 | 87.6 | 8.6 | 10.3 |

tr = traces

Assuming such a tentative reaction scheme the formation of ethanol and acetaldehyde during the reduction of formic acid can be reasonably explained.

CONCLUSIONS

The electrochemical reduction of HCOOH acid in acidic solution on a Cu(88)Sn(6)Pb(6) cathode gives CH₃CH₂OH (37.6%CE), CH₃CHO (17.1%CE) and CH₃OH (30.3%CE) as main products. Both the rate of the reduction and the distribution of the products depend on the cathodic potential. The rate increases by a factor of 2 with the increase in the concentration from 0.1 mol L⁻¹ to pure HCOOH. The main problem for the efficient reduction of formic acid is the suppressing of the hydrogen evolution reaction which has an inhibiting effect on the reduction of formic acid. This work shows for first time, at our best knowledge, that ethanol and acetaldehyde can be produced from the reduction of formic acid.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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None declared.

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