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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

COUPLED VOLTAMMETRIC AND ELECTROGRAVIMETIC INVESTIGATION OF COPPER BEHAVIOR IN CARBONATE-BICARBONATE SOLUTIONS

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ABSTRACT. Among other alternatives, CO_2 electroreduction on copper electrodes exhibits formation of desirable reduction products with reasonable high yield. However, passivation of the electrocatalyst prevents a long time operation, limiting the economical efficient applicability. Aiming an investigation of the occurring phenomena, a coupled voltammetric and electrogravimetric investigation is further presented.

Keywords: *CO_2 electroreduction, copper, voltammetry, electrogravimmetry.*

INTRODUCTION

Known as global warming gas, carbon dioxide can be reduced by electrochemical methods because of two main reasons: (1) selectivity towards formation of convenient gaseous or liquid products on employed cathode materials and (2) the experimental equipment required is rather inexpensive because neither high vacuum nor high reaction temperatures are needed. In this way, CO_2 have been converted into potential energy sources such as CH_4, C_2H_4, HCOOH, CH_3OH, etc. [1,2]. Products distribution and yield of the CO_2 electroreduction process is strongly influenced by the nature of employed cathode material. Formation of CO and HCOOH is preferential on Ti cathode, with additional formation of H_2 on Ag, Au and Sn [3]. On Cu-Ag alloys, high yield formation of C_2 compounds (especially C_2H_4, C_2H_5OH, and CH_3CHO) [4] while on Cu, CO and hydrocarbons (CH_4 and C_2H_4) were mainly obtained [5-8].

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Among the above-mentioned cathode materials, copper and its alloys are important alternative for CO_2 electroreduction because of their cost, reasonable corrosion resistance and important yield towards formation of valuable products. However, influenced by the nature of solvent and employed electrolyte, a passivation phenomenon decreases significantly the catalytic activity [9,10]. The present work aims investigation of charge and mass changes on copper/carbonate aqueous solution in the conditions identical to those employed during CO_2 electroreduction.

In this work, the electrolyte solution was chosen a mixture between sodium carbonate and bicarbonate, acting as precursor for CO_2 reduction and with significant supporting electrolyte contribution, using water as solvent. Avoiding the use of a high pressure experimental setup, this electrolyte solution is commonly reported.

The determination of electric charge is a common issue in electrochemical measurements, achievable either instrumentally, by chronocoulometry, or computationally, by integrating the current in potentostatic and galvanostatic techniques, solely the methodology of the determination of mass change will be discussed further in detail [11].

The resonance frequency of the quartz resonator depends on its mass and the mechanical forces applied upon. By choosing conditions in which the latter are invariable, the resonance frequency will be influenced mainly by the mass addition or removal from the resonator. By construction, the resonator has two conductive electrodes, one functioning as working electrode, being immersed into solution, as the second remains in air. In this way the mass changes (Δm) of the electrode immersed into solution can be correlated to the frequency variation (Δf) of copper coated quartz resonator by using the Sauerbrey equation [9]:

$$\Delta f = -2f_0^2\ \Delta m/A(\mu_q\rho_q)^{1/2} = -C_f\ \Delta m \qquad (1)$$

where f_0 is the fundamental (in air) resonant frequency (9 MHz) of the quartz resonator, A is the geometric area (0.196 cm^2) of the metallic plate, μ_q is the quartz shear modulus (2.947 10^{11} g $cm^{-}1$ s^{-2}), and ρ_q is the quartz density (2.648 g cm^{-3})]. For the used resonator the theoretical value of the Sauerbrey constant (C_f) is 945.6 Hz μg^{-1} whereas the calibration that uses copper electrodeposition from Oettel solution (see [12] for details) give an experimental value of 943.7±1.2 Hz μg^{-1}. As the validity of Sauerbrey equation is restricted to relative small frequency variation ($\Delta f/f_0 < 0.01$), the chosen thickness (150nm) of electrodeposited copper layer assures the operation well inside the validity domain ($\Delta f/f_0 = 0.0028$) allowing a significant margin to a potential formation of a film during investigation.

For describing the electrochemical processes at the electrode surface, the primary Δf vs. potential (E) electrochemical quartz crystal microbalance data can be treated in different ways. In this paper was used a straight-to-forward method, based on a Q *vs* Δm correlation. Using Faraday's law it is possible to calculate the parameter ΔM/n:

$$\Delta M / n = F \ \Delta m / |Q| \tag{2}$$

where ΔM is the stoechiometric molecular (or atomic) mass variation of the solid phase species involved in reaction, n the number of exchanged electrons, Q the charge consumed by the reaction and F the Faraday constant (96,485.31 C mol^{-1}). Usually, the ΔM/n parameter is specific for a given reaction. By comparing these values with the experimental found ones, it is possible to identify the reactions taking place at the electrode.

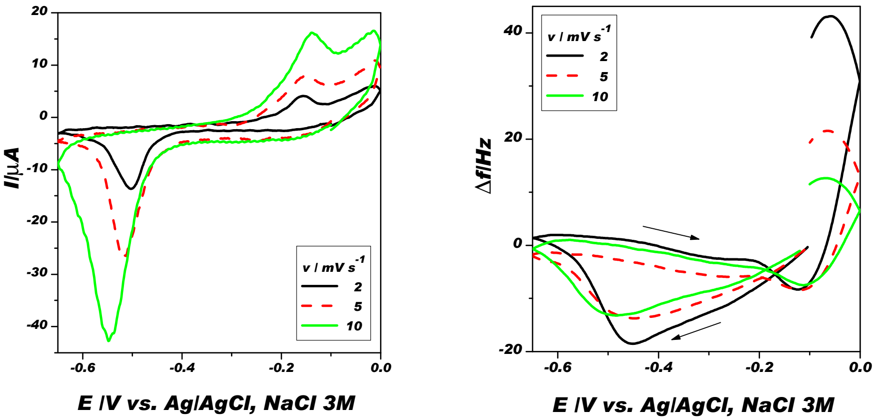
RESULTS AND DISCUSSION

The measurements were carried out with a mixture of carbonate and bicarbonate in order to modify the pH while keeping the sum of the two mentioned CO_2 precursors concentration constant. In that way, a more mechanistic approach is allowed for the study, since allows discrimination between pH-independent and dependent elementary reaction steps.

All the measurements were carried out using relative small scan rate of electrode potential, between 2 and 10mVs^{-1}, in order to decrease the influence of double layer capacitance charge on measured current and occurring electrocapillary forces on quartz resonance.

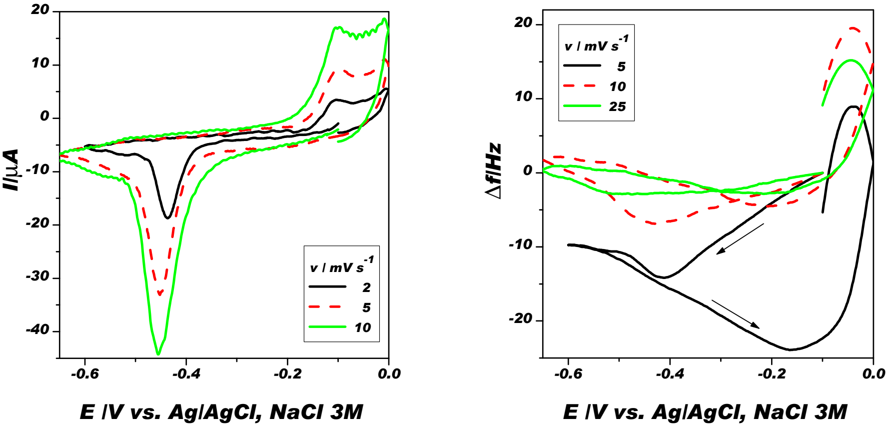
As can be seen in Fig. 1, for pH=10.51, the voltammograms present a single cathodic peak, at potentials between -0.5 and -0.55V, and two consecutive anodic peaks at approx. -0.15 and -0.025V, respectively. Only the last anodic peak exhibits an approx. proportionality between the peak current and square root of the scan rate, which is an indication of involvement of diffusion of reactants. On the contrary, for the other two peaks the slopes of I_p *vs* v plots in logarithmic coordinates are bigger that 1/2 as expected for processes involving diffusion of electroactive species, but less than one as expected for processes involving adsorbed electroactive species; this suggest that the formation of the first two peaks is the result of some complex charge transfer processes involving both soluble and adsorbed (or at least immobilized on the electrode) reactants.

Conversely, the frequency shift of quartz crystal resonator has a more complicated behavior. During the initial reduction scan there is a frequency decrease even in the potential range when a noticeable current peak is not present. As indicated by the Sauerbrey equation, the decrease of the frequency denotes an increase of the mass of the electrode. Further, on the potential range where the first voltammetric cathodic peak is present, there is an important mass loss. During the initial stages of oxidation scan a small mass increase is noticeable in a potential domain in which any voltammetric peak is absent, but the first anodic peak takes place with a more important mass increase, while the second anodic peak takes place with a very important mass loss, process that continues during the initial stages of the final reductive scan. Similar behaviour can be noticed at all the investigated pH values, see Fig. 2.



(a) (b)

Figure 1. Influence of scan rate on current intensity (a) and resonance frequency shift (b) for pH=10.51.

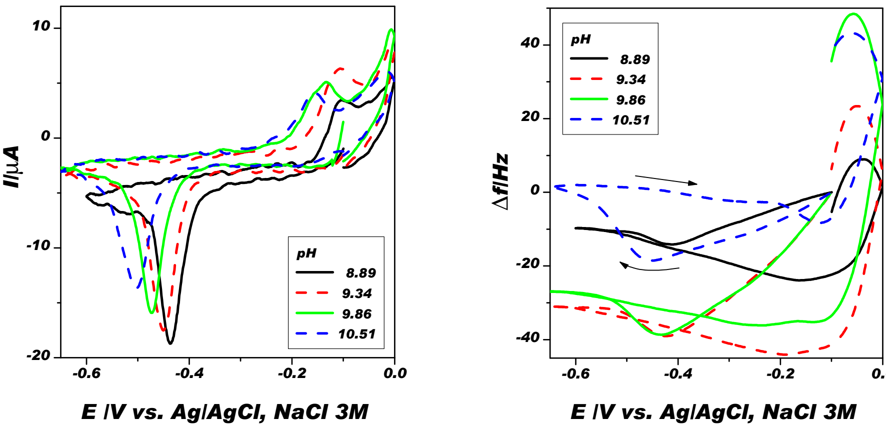


(a) (b)

Figure 2. Influence of scan rate on current intensity (a) and resonance frequency shift (b) for pH=8.89.

Qualitative analysis is further completed by describing the influence of pH of the solution on measurements, as indicated by Fig. 3. As evidenced in Fig. 3a, the increase of pH reduces the cathodic current peak and shifts the potential peak towards more negative values. This indicates that the reaction responsible for this voltammetric peak has at least one of the reactants with the concentration influenced by the pH; it can be a species with decreasing concentration upon alkalinification – like H^+, HCO_3^- or CO_2 – and exclude as reactants the species of those concentration increases upon alkanification, like OH^- or carbonate ions. In addition, it is also possible the involvement of an electroactive species in large excess to those of which the decrease of interfacial concentration causes the formation of the voltammetric peak; in this case, H^+ could be a reactant or OH^-, a product. The involvement of an electroactive species in large excess causes a peak potential shift without influencing the peak current.

The influence of pH on the first anodic peak is more complex without a clear dependence, while the second anodic peak is not always present. These suggest that the peaks are not correlated, namely are evidence of some chemically irreversible charge transfer processes.



(a)

(b)

Figure 3. Influence of pH on current intensity (a) and resonance frequency shift (b) for 2mV s^{-1} scan rate.

The influence of pH on the mass changes of the electrode is more complex as the mass changes at intermediate pH values are larger than those at extreme pH values. However, there are correlations between the mass decreases and mass increases on every pH values.

In order to attempt a quantitative evaluation, the scanned potential range was divided in several potential windows in which a possible individual process takes place. These potential windows are presented in Tab. 1 alongside the charge calculated by integration of voltammograms in the given potential window, the mass changes, and the calculated parameter ΔM/n.

Table 1. Electrogravimetric parametres for pH=8.89 and v=2mV s^{-1} scan rate.

Zone	Potential window / V	ΔQ / μC	Δm / μg	ΔM/n / g mol^{-1}
C1	-0.1 to -0.3	-340	9.73	2.7
Cp	-0.42 to -0.5	-438	-3.72	-0.8
C3	-0.6 to -0.16	-767	14.9	1.9
Ap1	-0.16 to -0.06	81.9	-4.09	-4.8
Ap2	-0.06 to 0 to -0.04	34.4	-22.70	-62.8
C0	-0.04 to -0.1	-28.7	15.09	50.7

The zone **C1**, in which the charge is transferred without formation of an voltammetric peak, could easily be confused with a capacitive zone. But the important mass increase is a strong indication that a faradaic process occurs. More likely is the underpotential hydrogen formation, a process in which the hydrogen obtained remains adsorbed as a monolayer on the interface:

$$2H^{+} + 2e^{-} \rightarrow H_{2(ads)} \quad \Delta M / n = 1\ g\ mol^{-1} \tag{3}$$

Common hydrogen evolution, where the hydrogen is desorbed and released as bubbles, is not thermodynamically possible in this potential range, and would have ΔM/n = 0 g mol^{-1}; this process was reported only at potentials more negative than about -0.9V [13]. It is possible that a parallel reduction, with higher ΔM/n, is the cause for the discrepancy between the experimental and theoretical values.

The zone **Cp** includes the cathodic peak and takes place with a very modest mass decrease. Due to the difficult kinetics, it is unlikely that hydrogen evolution would take place at potentials larger than -0.5V. More reasonable is to assume the oxygen reduction:

$$2H^{+} + O_2 + 2e^{-} \rightarrow H_2O \qquad \Delta M / n = 0\ g\ mol^{-1} \tag{4}$$

or oxygen reduction with some involvement of adsorbed hydrogen obtained in zone **C1**, like:

$$H^{+} + O_2 + 1/2 H_{2(ads)} + e^{-} \rightarrow H_2O \qquad \Delta M / n = -1\ g\ mol^{-1} \tag{5}$$

Only these two reactions predict correctly the influence of pH on the cathodic peak parameters.

The zone **C3** does not contain a voltammetric peak but the mass increase is yet important. The reaction (3), compensating the vacancies from the hydrogen monolayer generated by reaction (5), can be responsible only partial for the behavior as the charge involved in **C3** is more than twice that of **C1**. More likely another reduction process with higher ΔM/n is also involved, but the obtained experimental data make difficult a complete identification.

The zone **Ap1** includes the first anodic peak and takes place with significant mass decrease. Even more important mass decrease takes place in zone **Ap2**, zone that includes the second anodic peak.

Such important anodic mass decreases can be only asserted taking into consideration copper oxidation as:

$$Cu - 2e^- \rightarrow Cu^{2+} \qquad \Delta M/n = -64\ g\ mol^{-1} \tag{6}$$

or oxidation with formation of a soluble copper complex, like

$$Cu + 2CO_3^{2-} - 2e^- \rightarrow \left[Cu\left(CO_3\right)_2\right]^{2-} \quad \Delta M/n = -64\ g\ mol^{-1} \tag{7}$$

Regardless the nature of the formed soluble copper products, these reactions could explain the behaviour in zone **Ap2**.

The lower value of ΔM/n in zone **Ap1** as compared to this of **Ap2** suggests additional processes. The oxidation of adsorbed hydrogen:

$$H_{2(ads)} \rightarrow 2H^+ + 2e^- \quad \Delta M/n = -1\ g\ mol^{-1} \tag{8}$$

and copper oxidation leading to insoluble products, like:

$$Cu + CO_3^{2-} - 2e^- \rightarrow CuCO_{3(s)} \ \Delta M/n = +60\ g\ mol^{-1} \tag{9}$$

could contribute to the lowering of founded value of ΔM/n as compared with theoretical ones of reactions (6) and (7).

Finally, the last cathodic zone, **C0**, takes place with important mass increase. Combination of following reductions could be assigned:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad \Delta M/n = 64\ g\ mol^{-1} \tag{10}$$

$$\left[Cu\left(CO_3\right)_2\right]^{2-} + 2e^- \rightarrow Cu + 2CO_3^{2-} \ \Delta M/n = 64\ g\ mol^{-1} \tag{11}$$

$$CuCO_{3(s)} - 2e^- \rightarrow Cu + CO_3^{2-} \ \Delta M/n = -60\ g\ mol^{-1} \tag{12}$$

$$2CuCO_{3(s)} - 2e^- \rightarrow Cu_2CO_{3(s)} + CO_3^{2-} \ \Delta M/n = -30\ g\ mol^{-1} \tag{13}$$

in which reactions (10) or (11) have the most important contribution.

CONCLUSIONS

The present study attempted the investigation of the phenomena occurring during reduction on copper of a carbonate solution. The evidence for the blocking of the electrode with insoluble or adsorbed species and the evidence of CO_2 reduction would have provide some insights about this important process.

Unfortunatelly, no direct evidence for CO_2 reduction was observed in the investigated potential window. The only potential window in which this process could have been present is that of the investigated more negative values. As already mentioned, in zone **C3** a process with $\Delta M/n$ higher to those evidenced in **C1** and **Cp** could be related also to some kind of CO_2 reduction. In this potential window, and also at more negative potentials, further studies should be carried out.

It is favourable to mention that between a large number of potentially solid state copper compounds, which could caused passivation towards CO_2 reduction by covering the copper electrode, neither was has significant contribution to the electrochemical behaviour of the system. The only species found to cover significantly the copper electrode is a monolayer of hydrogen which, due to its reactive state, could even participate as a mediator in homogenous reduction reactions.

EXPERIMENTAL

The measurements were carried out using a computer controlled potentiostat (PARStat 2273, Princeton Applied Research, USA) and a quartz crystal microbalance (QCM922, Princeton Applied Research, USA). The resonator allowing the monitoring of mass changes was a 9 MHz quartz crystal (QA-A9M-AU), inserted into a well cell resonator holder (QA-CL4, Princeton Applied Research, USA).

The measurements were performed in a conventional single compartment cell, equipped with three electrodes: the working electrode (WE) consisted of the exposed face of the resonator (A=0.196 cm^2); the auxiliary electrode was a Pt wire; and Ag/AgCl, $NaCl_{\mathbf{sat}}$ was used as reference electrode.

The working electrode was obtained by the electrodeposition of a thin film of Cu from an Oettlel solution ($CuSO_4$ 125 g L^{-1}, C_2H_5OH 50 g L^{-1}, H_2SO_4 50 g L^{-1}, all Reactivul, Bucharest, Romania) onto one of the gold faces of the quartz crystal. The electrodeposition was performed galvanostatically by appling a current density of 20 mA cm^{-2} for 20 s, conditions allowing the obtaining of a 150 nm thick copper film.

The four investigated electrolyte solutions contained Na_2CO_3 (0.01, 0.03, 0.06 and 0.09M), $NaHCO_3$ (0.09, 0.07, 0.04 and 0.01M, respectively) and 0.5M Na_2SO_4 as supporting electrolyte. The measured pH values were 8.89, 9.34, 9.86 and 10.51, respectively.

Prior to any measurement, the electrode was conditioned at -0.1V for 30s. The scans use a four potential scheme, when a initial reduction scan, from -0.1 to -0.65V, is followed by an oxidation scan, to 0V, and the cycle is completed by a reduction scan to the initial -0.1V value.

Electrolyte solution were prepared by dissolving Na_2CO_3 (Reactivul, Bucharest, Romania), $NaHCO_3$ (Chimopar, Bucharest, Romania) and Na_2SO_4 (Reactivul, Bucharest, Romania) in distilled water. All measurements were performed at room temperature (23 ± 1 ^{o}C).

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