In Situ Study of the Magnetoelectrolysis Phenomenon during Copper Electrodeposition Using Time Domain NMR Relaxometry

Bruna Ferreira Gomes,[†] Luiza Maria Silva Nunes,[†] Carlos Manuel Silva Lobo,[†] Luís Fernando Cabeça,[‡] and Luiz Alberto Colnago*,[§]

[†]Instituto de Química de São Carlos, Universidade de São Paulo, Avenida Trabalhador São-Carlense 400, São Carlos, SP CEP 13560-070, Brasil

[‡]Universidade Tecnológica Federal do Paraná—UTFPR, Londrina, PR, Brasil

[§]Embrapa Instrumentação, Rua XV de Novembro 1452, São Carlos, SP 13560-970, Brasil

ABSTRACT: Although the effect of magnetic field (**B**) on electrochemical reactions (magnetoelectrolysis phenomenon) has been long known, it has not been considered in electrochemical reactions analyzed *in situ* by magnetic resonance methods, such as nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and magnetic resonance imaging (MRI), which are intrinsically performed in the presence of **B**. In this report, the effect of **B** on the copper electrodeposition reaction, measured by a low-field (0.23 T) NMR spectrometer, was demonstrated. As expected, an enhancement in the reaction rate in comparison to the *ex situ* electrodeposition reaction was observed. Such enhancement was not dependent on electrodes/magnetic field orientations. Parallel and perpendicular orientations showed similar electrodeposition rates, which is explained by the cyclotron flows generated by distortions in electric and magnetic field lines near the electrode and the electrode edge. Therefore, NMR spectroscopy is not a passive analytical method, as assumed in preceding *in situ* spectroelectrochemical studies. Although the magnetoelectrolysis phenomenon demonstrated in this report used a paramagnetic ion, it can also be observed for diamagnetic species, since the magnetoelectrolysis phenomenon is independent of the nature of the species. Consequently, similar convection effects may occur in other electrochemical nuclear magnetic resonance (EC-NMR) experiments, such as the electrochemical reaction of organic molecules, as well as in electrocatalysis/fuel cells, lithium-ion batteries, and experiments that use electrochemical electron paramagnetic resonance (EC-EPR) and electrochemical magnetic resonance imaging (EC-MRI).
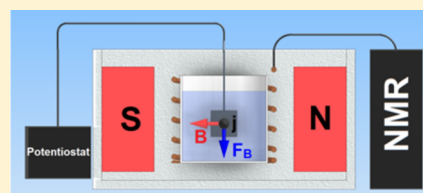
The number of studies that use magnetic resonance (MR) methods, such as nuclear magnetic resonance (NMR) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and magnetic resonance imaging (MRI), to monitor electrochemical reactions *in situ* has substantially increased over the past decade.[1−11] Such electrochemical magnetic resonance (EC-MR) methods have been used to obtain structural, dynamic, and spatial information in real-time electrochemical reactions, such as electroplating[1,12−15] and reduction of organic molecules.[2−4] They have also been used in electrocatalysis/fuel cells[5,6] and lithium-ion batteries.[7−9]

Although EC-MR experiments are intrinsically performed in the presence of a magnetic field (**B**), neither *in situ* NMR and EPR spectroscopy nor *in situ* MRI studies have considered the effect of **B** on the electrochemical reaction (known as magnetoelectrolysis).[1−11]

It is well-known that when a conductive solution is submitted to an electric and magnetic field, as in EC-MR, the fluid is subject to forces known as magnetoconvection forces.[16−20] The magnetic force (**F**$_B$), or magnetohydrodynamic force (MHD), is the most effective force[16,17] during an electrolysis performed in a magnetic field. **F**$_B$ is the magnetohydrodynamic force (integral force density that acts on all species in solution) that is the cross product between the current density (**j**) and the magnetic induction (**B**), which produces a force perpendicular to

both vectors (**F**$_B$ = **j** × **B**). Therefore, the resultant force generates a flow in the solution, increasing mass transport.[16,17,21]

The magnetoelectrolysis phenomenon has been widely studied in copper electrodeposition reactions,[14,16,17,20,22,23] because of its numerous technological applications.[24,25] Consequently, there has been a growing interest in magnetoelectrolysis, because of the possibility of controlling the deposit morphology,[13,26,27] mass transport of the reactive component toward the electrode, and the reaction rate at the electrode/electrolyte interface.[16] In this report, the effect of **B** on copper electrodeposition reaction monitored *in situ* by low-field (0.23 T) NMR spectrometer, was demonstrated. As expected, an enhancement in the reaction rate, caused by magnetoconvection forces, was observed in comparison to the *ex situ* electrodeposition reaction.

■ EXPERIMENTAL SECTION

Apparatus. EC-NMR experiments were performed on a 0.23 T, TD-NMR spectrometer (Spinlock, Córdoba Argentine) and EmStat2 potentiostat (Utrecht, The Netherlands), as described elsewhere.[1]

Reagents. The electrolyte solution was prepared with Milli-Q water, 0.01 mol L^{-1} CuSO$_4$·5H$_2$O (QHEMIS) and 0.1 mol L^{-1} Na$_2$SO$_4$ (ISOFAR).

Electrochemical Cells. Two different electrochemical cells were used. Cell-A consisted of a rectangular platinum working electrode (WE) of 5 mm × 10 mm × 0.3 mm dimensions and a useful area of 100 mm^2. Platinized platinum was used as a counter electrode (CE) of same dimensions as the WE and the reference electrode (RE) was a Ag/AgCl (3 mol L^{-1} KCl) electrode. Both sides of the platinum plaques were useful. The separation distance between the WE and CE was 5 mm and the cell could hold up to 2 mL of solution.

Cell-B also contained a Ag/AgCl (3 mol L^{-1} KCl) electrode as RE. The WE and CE were circular platinum plaques of 5 mm diameter and 0.3 mm thickness and had only one useful side of 19 mm^2; the other side was covered by glass. The surfaces of the WE and CE were parallel to each other; the separation distance between WE and CE was 5 mm, and the volume of the cell was 4 mL.

The first step in the cleaning of the working electrode was to hold it at +2.0 V vs Ag/AgCl for 2 min. It was then cycled between −0.222 and +1.10 V vs Ag/AgCl at 100 mV/s, stopping after 10 cycles at the positive limit (+1.10 V).

Magnetoelectrolysis Phenomenon Study. The magnetoelectrolysis phenomenon was studied by cyclic voltammetry and chronoamperometry using *ex situ* and *in situ* configurations. For *in situ* configuration, all measurements were performed with the surface of the electrodes parallel and perpendicular to the NMR magnetic field (**B**). The real-time NMR measurements of copper ion concentration were performed *in situ*. All measurements were performed in triplicate at a temperature of 23 °C.

Cyclic Voltammetry Parameters. Cycling (10 cycles) were performed between −0.8 V and +0.4 V vs Ag/AgCl (3 mol L^{-1} KCl) at 40 mV s^{-1}. The measurements were made for *ex situ* and *in situ* configurations. The values of current density, **j**, were taken from the cyclic voltammetry at −0.4 V to estimate the resultant |**F$_B$**|.

***In Situ* Chronoamperometry: NMR Measurements.** Copper was electrodeposited with the surface of the electrodes parallel and perpendicular to the NMR magnetic field (**B**) and a constant potential of −0.4 V vs Ag/AgCl (3 mol L^{-1} KCl) was applied for 3 h. The variation of Cu^{2+} concentration during the reaction was determined by a calibration curve of the transverse relaxation rate ($R_2 = 1/T_2$), measured by a Carr−Purcell−Meiboom−Gill (CPMG) pulse sequence. Measurements of the Cu^{2+} concentration were collected every 20 min simultaneously with the electrodeposition reaction.[1]

***Ex situ* Chronoamperometry: NMR Measurements.** The same reaction was performed in the absence of **B** in Cell-A and Cell-B, for 30 min, 1 h, 2 h, and 3 h. The NMR technique was used to measure the Cu^{2+} concentration before and after the reactions.

CPMG Parameters. A $\pi/2$ flip angle (6.2 μs), an echo time (τ) equal to 2000 μs, 500−20000 echoes optimized for each sample, π pulses (12.4 μs), and a recycle delay of 1.5 and 8 scans. The maximum time for each experiment was 1.5 min.

■ RESULTS AND DISCUSSION

The effect of the oscillating magnetic field, B_1, was not considered in the magnetoelectrolysis studies because of its small intensity in comparison to static field, **B**. Furthermore, B_1

does not present a preferential direction due to its oscillatory nature, therefore its effect is negligible.

In most magnetoelectrolysis experiments, the effect of the relative orientation between **j** and **B** (parallel or perpendicular) on the mass transfer has been measured by cyclic voltammetry, in which the current density, **j**, is proportional to the reaction rate.[22,24,26,28] The cathodic branch in the cyclic voltammogram for the Cell-B is shown in Figure 1. Similar results were
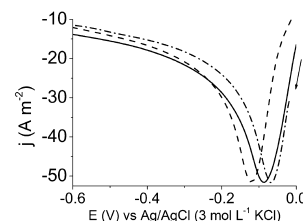

Figure 1. Cyclic voltammograms of 0.01 mol L^{-1} CuSO$_4$ in 0.1 mol L^{-1} Na$_2$SO$_4$ on the platinum electrode in Cell-B recorded at 40 mV s^{-1} and at 23 °C under different configurations: **B** = 0 (dash-dotted line), **B**∥**j** (dashed line), and **B**⊥**j** (solid line).

obtained for the other cell. When cyclic voltammetry was realized in the presence of **B**, there was a shift of the cathodic branch to more negative potentials. This effect can be explained by the interaction between copper and the magnetic field, since copper is paramagnetic. Therefore, this interaction can affect the Fermi levels and move the cathodic branch to more-negative potential values.[13]

In Cell-B, for example, **j** = (18.40 ± 0.40) A m^{-2} for **B**⊥**j**, **j** = (18.60 ± 0.30) A m^{-2} for **B**∥**j** and **j** = (15.20 ± 0.45) A m^{-2} in the absence of **B**, at E = −0.4 V vs Ag/AgCl (3 mol L^{-1} KCl). It was calculated that the product |**jB**| is close to 4.6 N m^{-3}, for both cases when **B** ≠ 0. This value is in agreement with the literature.[22] In this case there is a higher current density for the *in situ* experiments and there is no significant difference between **B**⊥**j** and **B**∥**j**, as initially expected. Hinds et al.,[22] Cierpka et al.,[14] and Tschulik et al.[29] found similar results and explained that there are edge effects and distortions of the magnetic field caused by the introduction of metallic electrodes; thus, there is always a resultant, **F$_B$**, acting on the ions in solution. As a result, independently of the electrodes' orientation in relation to the magnetic field, there will always be a resulting **F$_B$**, which increases mass transport.

To evaluate the magnetoelectrolysis phenomenon on copper electrodeposition rate chronoamperometric measurements were performed *in situ* for determination, in real time, of the copper ion concentration by CPMG sequence pulse. Prior to electrolysis, it was necessary to investigate the influence of copper ion concentration on the transverse relaxation rate. The linear relationship between R_2 and Cu^{2+} concentrations was obtained for concentrations ranging between 2.5 × 10^{-4} and 0.1 mol L^{-1} with a correlation coefficient of r = 0.9999. The values of Cu^{2+} concentration in the electrolyte solutions were obtained by a CPMG calibration curve that is described by eq 1:

$$[Cu^{2+}] \, (mol \, L^{-1}) = \frac{R_2 - (0.21 \pm 0.07)}{(1460 \pm 4)} \qquad (1)$$

Figure 2A shows the decay of the Cu^{2+} concentration in the presence (**B**⊥**j** and **B**∥**j**) and absence of **B**, in Cell-A. The results show an enhanced reaction rate in the presence of **B**, and no significant difference between the reaction rates when **B**⊥**j** and **B**∥**j**. After 3 h of electrolysis for both configurations,
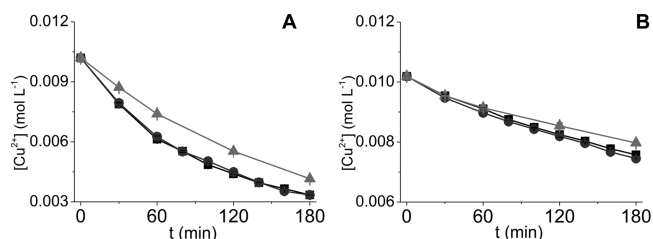
Figure 2. Variation of Cu^{2+} concentration as a function of electrolysis time performed in (A) Cell-A and (B) Cell-B recorded at 23 °C under different configurations: (■) **B**⊥**j**, (●) **B**∥**j**, and (▲) **B** = 0. Solution: 0.1 mol L^{-1} Na$_2$SO$_4$ electrolyte containing 0.01 mol L^{-1} CuSO$_4$. Conditions: $E_{applied}$ = −0.4 V vs. Ag/AgCl (3 mol L^{-1} KCl). The Cu^{2+} concentration data were determined by CPMG pulse sequence, as indicated on the Experimental Section. The standard error is represented by the error bars (n = 3).

the Cu^{2+} concentration was (3.350 ± 0.006) × 10^{-3} mol L^{-1}. In the absence of **B**, the final Cu^{2+} concentration was (4.150 ± 0.002) × 10^{-3} mol L^{-1}. The largest difference in the consumption of copper ions occurs for electrodepositions lasting 1h, in which the absence of **B** leads to a 27.00% ± 0.02% consumption and the presence of **B** shows a 39.5% ± 1.3% consumption.

The same experiments were performed in Cell-B, which differs from Cell-A by the smaller WE area, leading to reduced edge effects. Figure 2B shows the results obtained with Cell-B and it can be noted that they are similar to those obtained on Cell-A. The copper deposition rate is the same in both orientations, after 3 h of electrolysis the Cu^{2+} concentration was (7.57 ± 0.05) × 10^{-3} mol L^{-1}. The difference in size between the WE of both cells lead to a larger consumption of copper ions in Cell-A; this justifies the different curve shapes seen in Figure 2. Therefore, in both cells, **B** enhances the reaction rate and there is no statistically significant difference between the reaction rates for **B**⊥**j** and **B**∥**j**.

CONCLUSIONS

Low-field nuclear magnetic resonance (NMR) spectroscopy is not a passive analytical method for *in situ* electrochemical NMR (EC-NMR) studies. The NMR magnetic field enhances the electroplating reaction rate in *in situ* reactions, in comparison to the reaction rates of *ex situ* experiments. The **B**⊥**j** and **B**∥**j** orientations show a similar enhancement caused by distortions in electric and magnetic field lines near the electrode and the electrode edge. Although the magnetoelectrolysis phenomenon was demonstrated in this report with a paramagnetic ion, it can also be observed for diamagnetic species, since the magnetoelectrolysis phenomenon is independent of the nature of the species, as long as the species is immersed in a conductive solution.[30] Consequently, similar convection effects may occur in high-resolution EC-NMR experiments, such as the electrochemical reaction of organic molecules, electrocatalysis/fuel cells and lithium-ion batteries and also in experiments that use EC-EPR and EC-MRI.

AUTHOR INFORMATION

Corresponding Author
*Fax: +55-1621072902. E-mail: luiz.colnago@embrapa.br.
Notes
The authors declare no competing financial interest.

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