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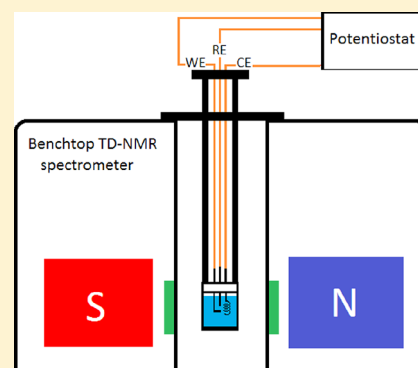
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ABSTRACT: The use of a low-cost benchtop time-domain NMR (TD-NMR) spectrometer to monitor copper electrodeposition in situ is presented. The measurements are based on the strong linear correlation between the concentration of paramagnetic ions and the transverse relaxation rates (R_2) of the solvent protons. Two electrochemical NMR (EC-NMR) cells were constructed and applied to monitor the Cu^{2+} concentration during the electrodeposition reaction. The results show that TD-NMR relaxometry using the Carr-Purcell-Meiboom-Gill pulse sequence can be a very fast, simple, and efficient technique to monitor, in real time, the variation in the Cu^{2+} concentration during an electrodeposition reaction. This methodology can also be applied to monitor the electrodeposition of other paramagnetic ions, such as Ni^{2+} and Cr^{3+} , which are commonly used in electroplating.



The development of spectroelectrochemistry techniques to study electrochemical reactions in real time is of crucial importance.^{1–4} Among all spectroscopic techniques, nuclear magnetic resonance (NMR) has gained importance in recent years because it is the most effective technique for determining the chemical structure of molecules.⁵ However, when coupling electrochemical and NMR techniques, the electrodes inside the NMR coil strongly interfere with the weak NMR signal and thus reduce the overall spectral sensitivity and resolution.⁶ As a result, research has focused on constructing electrochemical-NMR (EC-NMR) cells, with minimal interference, to monitor electrochemical reactions by NMR in situ.^{2–4,7,8} Most EC-NMR experiments have been performed on solutions,⁹ catalyst surfaces,¹⁰ or lithium ion batteries¹¹ that generally use expensive high-resolution spectrometers, which are normally based on superconducting magnets.

In this study, a low-cost benchtop time-domain NMR (TD-NMR) spectrometer for use in monitoring copper electrodeposition in situ is presented. The measurements are based on the strong linear correlation between the concentration of paramagnetic ions and the transverse relaxation rates (R_2) of the solvent protons. The results show that TD-NMR relaxometry can be a very fast, simple, and efficient technique to monitor variation in the Cu^{2+} concentration in real time during the electrodeposition reaction.

EXPERIMENTAL SECTION

Reagents. The analytical grade salts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and KCl were supplied by Quemis and Synth (São Paulo, Brazil), respectively. CuSO_4 solutions between 1×10^{-4} and 0.2 mol L^{-1} were prepared in an aqueous KCl solution (1.0 mol L^{-1}).

The water was purified by a Milli-Q (Millipore) purification system.

Apparatus. Electrochemical measurements were performed using an EmStat2 potentiostat from Palm Instruments BV (Netherlands). The NMR measurements were performed with a Spinlock benchtop time-domain NMR spectrometer, model SLK-100 (Cordoba, Argentina). This instrument has a permanent magnetic field of 0.23 T (9 MHz for ^1H). A 32 mm probe head was used in the experiments.

Design of the TD-NMR-Electrochemical Cells. Figure 1 shows diagrams of the electrochemical cells used in the NMR electrodeposition studies. Figure 1A shows cell-A with larger electrodes inside the NMR coil, and Figure 1B shows cell-B with the small electrodes inserted in the probe above the NMR coil.

Cell-A (Figure 1A) was built in a cylindrical acrylic flask with a height of 19 mm, an outside diameter of 20 mm, an inside diameter of 16 mm and a bottom thickness of 0.8 mm. The total volume of the cell was 2.8 mL. The working electrode (WE) was a platinum plaque ($A = 110 \text{ mm}^2$), the counter electrode (CE) a platinum coil (1 mm wire), and the reference electrode (RE) was a silver wire (1 mm diameter). Cell-A was fixed inside the NMR probe with a Teflon holder, and the cell was placed in the center of the rf coil.

The cell-B reservoir (Figure 1B) was a glass tube of dimensions 7 cm \times 0.8 cm filled with 5 mL of solution. The electrodes were placed inside the solution but above the NMR

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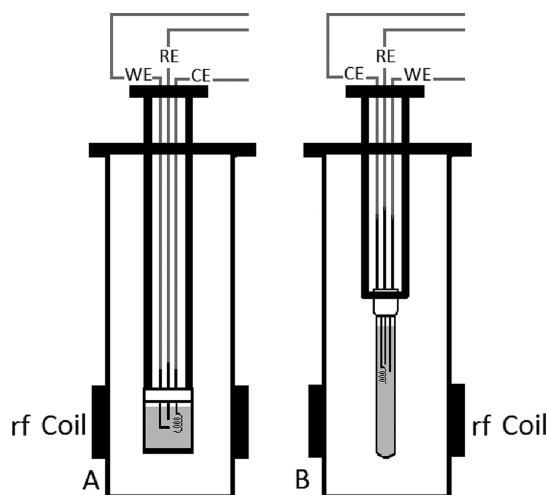


Figure 1. Diagrams of the electrochemical NMR cells (EC-NMR) used in in situ copper electrodeposition measurements. (A) The electrodes of cell-A were as follows: WE and CE, platinum; RE, silver. (B) The electrodes of cell-B were as follows: WE, gold; CE, platinum; RE, Hg/HgO/NaOH.

coil to reduce the mutual inference between the NMR spectrometer and the potentiostat. The CE was a coil of platinum wire 0.5 mm in diameter and 2 cm long; the WE was a gold disk with a surface area of 0.8 mm². The RE was a Hg/HgO/NaOH electrode (1.0 mol L⁻¹ NaOH).

In Situ TD-NMR-Electrochemical Measurements. The copper electrodeposition reaction was monitored using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence.¹² The CPMG parameters for cell-A were as follows: a $\pi/2$ flip angle (5.3 μ s), an echo time (τ) equal to 1000 μ s, acquisition of 1500 even echoes 500 μ s after the π pulses (10.6 μ s), and a recycle delay of 1 and 32 scans. The CPMG parameters used in the analysis of the reaction in cell-B were as follows: a $\pi/2$ flip angle (6 μ s), an echo time (τ) equal to 300 μ s, acquisition of 1000 even echoes 150 μ s after the π pulses (12 μ s), and a recycle delay of 0.5 and 128 scans. The T_2 were determined by monoexponential curve fitting. The CPMG data were collected every 10 min during the 3 h of the electrodeposition reaction, and the reaction was held at a constant potential. The copper reduction potential using cell-A, measured via cyclic voltammetry, was approximately -0.3 V. Therefore, a potential of -0.5 V was used for copper electrodeposition. The copper reduction potential in cell-B, measured by cyclic voltammetry, was -0.6 V. Therefore, the in situ copper electrodeposition was performed at -0.7 V to guarantee complete deposition. The NMR and electrochemical parameters were different in both analyses due to cell-A and cell-B presenting different designs.

RESULTS AND DISCUSSION

The effect of the electrodes of cell-A and cell-B on the homogeneity of the magnetic field was evaluated by monitoring the variation of the time constant (T_2^*) of the free induction decay NMR signal. The T_2^* values of 0.02 mol L⁻¹ CuSO₄ aqueous solution in the presence and in the absence of the electrodes were similar, approximately 2 ms, for both cells. Therefore, the distortion of the homogeneity caused by the electrodes was not critical, unlike that for high-resolution NMR, because of the inherently low homogeneity of TD-NMR magnets.¹³

Conversely, the electrodes strongly reduce the signal-to-noise ratio (SNR) in both cells. Figure 2A shows the CPMG decays

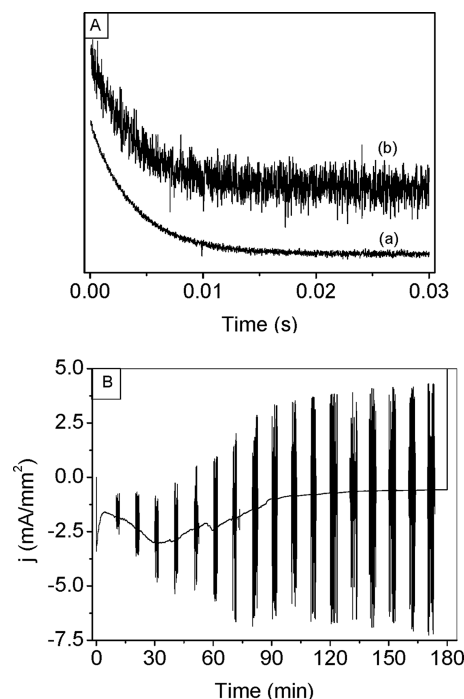


Figure 2. (A) Decay of the CPMG signal of a 0.02 mol L⁻¹ CuSO₄ solution, containing 0.1 mol L⁻¹ KCl in an electrochemical cell-A without (a) and with electrodes (b). (B) Variation in the current density as function of electrolysis time, at constant potential $E = -0.5$ V.

of a 0.02 mol L⁻¹ CuSO₄ aqueous solution in cell-A, in the presence of the electrodes (a) and in the absence of the electrodes (b). The SNR of the CPMG decay decreased by more than a factor of 3 from 6 to 1.6, as the electrodes were introduced. The large metallic electrodes inside the NMR coil attenuate the radio frequency (rf) signals, resulting in a reduction of the amplitude of the oscillating magnetic field (B_1) used to excite the NMR transitions; thus, the weak NMR signal is attenuated.⁴ Consequently, these interferences increase the noise and reduce the NMR signal, degrading the SNR. Nevertheless, this result shows that despite the reduction in SNR, the EC-NMR experiment, using the CPMG sequence, can be performed in less than 3 min in a benchtop TD-NMR spectrometer. In cell-B, the electrodes reduce the SNR by approximately 2-fold because the electrodes are small and above the NMR coil.

Figure 2B shows the interference of the CPMG pulses, the oscillation that occurs every 10 min, in the chronoamperogram. Although the interference of the rf pulses in the chronoamperogram was very strong, it did not cause any disturbance in the electrodeposition, as the reactions with and without rf pulses show a similar extent of copper deposition.

To measure the Cu²⁺ concentration in the solution during electrodeposition, it used the positive and linear correlation between the transverse relaxation rate ($R_2 = 1/T_2$) and the concentration of paramagnetic (Cu²⁺) ions in the solution.^{14,15} The R_2 values were calculated from the time constant (T_2) of decay of the CPMG pulse sequence.¹² Figure 3A shows the calibration curve ($r = 0.999$) between R_2 (s⁻¹) and Cu²⁺ solutions with the concentration varying between 3×10^{-2} to

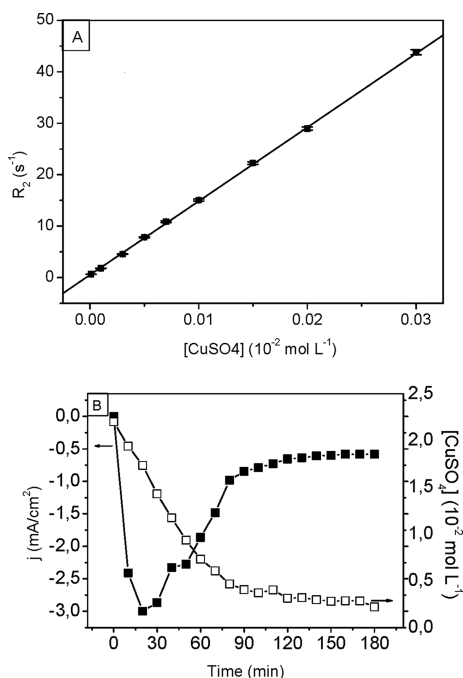


Figure 3. (A) Calibration curve correlating the transverse relaxation rate R_2 (s⁻¹) and the Cu^{2+} concentration in aqueous solution. (B) Variation of the Cu^{2+} concentration (□) and the potentiostat current (■) during the electrodeposition reaction, using cell-A.

1×10^{-4} mol L⁻¹ that was used to calculate the Cu^{2+} concentration during electrodeposition. The limit of quantification of the relaxometry (LOQ = 2.3×10^{-5} mol L⁻¹) was measured using the residual standard deviation of the response of three curves (10σ) divided by the slope of the calibration curve (S) of Figure 3A. This result shows that LOQ of relaxation measurements for Cu^{2+} in aqueous solution is approximately 2 orders of magnitude lower than the one obtained by UV–visible measurements (LOQ = 1.1×10^{-3} mol L⁻¹).

Figure 3B shows the reduction of the Cu^{2+} concentration, measured by NMR (□) and the potentiostat current (■), at 10 min intervals during the 3 h electrodeposition reaction. This figure shows a rapid decrease in the Cu^{2+} concentration during the first 100 min, followed by a slower decrease. At the same time, the potentiostat current increased rapidly in the first few minutes, reaching a maximum at approximately 20 min, followed by a decrease in current to reach a steady-state value at approximately 110 min. Therefore, as expected, there is a strong correlation between the copper electrodeposition and the potentiostat current. After reacting for 3 h, the Cu^{2+} concentration in the solution was 2×10^{-3} mol L⁻¹, corresponding to 10% of the initial Cu^{2+} concentration. This efficient reduction in the Cu^{2+} concentration was possible due the larger surface area (110 mm²) of WE electrode and a smaller cell reservoir (2.8 mL) of cell-A.

When using the cell-B, which uses a WE with surface area of 0.8 mm², no significant variation in T_2 was observed after running the electrodeposition reaction for 1 h. However, the cell-B was efficient and reduces the Cu^{2+} concentration using dilute solutions (10^{-4} mol L⁻¹) as shown in Figure 4. The ■ in this figure are R_2 values and the □ the Cu^{2+} concentration during the in situ electrodeposition reaction, obtained from the calibration curve (Figure 3A). In this cell, the Cu^{2+} concentration varied from 5.36×10^{-4} to 3.00×10^{-4} mol

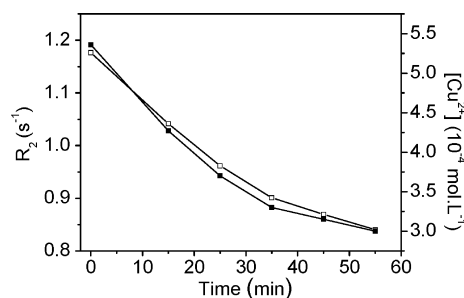


Figure 4. Decay of R_2 (s⁻¹) values (■) and Cu^{2+} concentration (□) during the electrodeposition reaction using cell-B.

L⁻¹ during the hour-long reaction, which is equivalent to the deposition of 44% of the Cu^{2+} initially present in the solution.

CONCLUSIONS

Given the results, we can conclude that both cell-A and cell-B can be used to monitor the electrodeposition reaction of paramagnetic ions with TD-NMR. TD-NMR relaxometry can be a feasible, simple, and efficient analytical technique to monitor the electrochemical reaction by the CPMG sequence in real time. The analysis can be performed with different electrode materials, cell configurations, and differences in the initial Cu^{2+} concentration spanning 2 orders of magnitude, as demonstrated. Furthermore, TD-NMR relaxometry can also be applied in future studies of others paramagnetic ions that are commonly used in electroplating, such as Ni^{2+} and Cr^{3+} ,^{16,17} and in analysis the effect of magnetic fields in the electrodeposition reaction.¹⁸

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Notes

The authors declare no competing financial interest.

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