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Rates of Metal Electrodeposition from Aqueous Solutions in the Presence of Chelating Agents

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ABSTRACT

The rates of Cu deposition from aqueous solutions containing chelating agents, such as citric acid, nitrilotriacetic acid (NTA), and ethylenediaminetetraacetic acid (EDTA), in an electrochemical membrane cell were measured. An equimolar solution of chelating agents and metals was examined. The iridium oxide and Pt coated on titanium electrodes were used as the anode and cathode, respectively. The cation-exchange membrane Neosepta CM-1 was used to separate the cathode and anode chambers. All experiments were carried out as a function of current density (18.5–139 A/m^2), initial catholyte pH (1–9), and metal concentration (10–80 mol/m^3). It was shown that the initial rates of Cu electrodeposition decreased in the order citrate $>$ NTA $>$ EDTA, which was not wholly related to the complexing ability of metals and the chelating agents.

Key Words. Initial rates; Electrodeposition; Cu(II); Chelating agents; Cation-exchange membrane

INTRODUCTION

Strong chelating agents including EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), and citric acid are used in such applications as metal plating (e.g., electroless copper plating for printed circuit boards), wa-

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ter softening, photography, textile and paper processing, and industrial cleaning (1, 2). They are often applied to remediation washing of metal-contaminated soils (3–5). These agents complicate the treatment of industrial polluted effluents by reducing the efficiency of metal removal using traditional chemical precipitation (e.g., OH^-, S^{2-}), ion exchange, and other processes (6). Also, the migration behavior of metals and radionuclides in subsurface and aqueous environments is significantly altered by complexation. Particularly, EDTA does not biodegrade rapidly and concerns about its effects are magnified by its persistence (1, 2). These problems have led to a search for effective treatment processes.

The treatment methods depend greatly on the particular chelating agent and metals and on their concentrations. For diluted solutions, resin ion exchange (7–9), adsorption onto activated carbon (10, 11), inorganic materials (12), and functional polymers (13) have been tried. Regardless of which concentration/removal method is being used, the chelated metal cannot be destroyed and the possible process used to recover metals should be aided via electrolysis such as by electrowinning (14, 15). However, Johnson et al. (16) indicated that EDTA was oxidized into many compounds, including CO_2, formaldehyde, and ethylendiamine, during metal deposition on a Pt anode in acidic sulfate solutions. Thus, simultaneous recovery of metals and chelating agents is not possible using common electrolytic methods.

A two-chamber electrolysis cell separated by a cation-exchange membrane to prevent oxidation of EDTA at the anode was used to recover EDTA and metals such as Cu(II), Zn(II), and Pb(II) from complexed solutions (3, 17–19). The chelates were destroyed, so that metal was deposited on the cathode and EDTA was regenerated. Although such an electrochemical membrane process has been shown to be feasible based on the overall recovery and current efficiency only, little attention has been paid to examining the rates of metal deposition. The work reported here was conducted to give better knowledge about these rates. These data would be useful and critical because the amount of metal deposition generally shows an abrupt increase during the initial stage of electrolysis. All experiments were carried out with an equimolar solution of metals and chelating agent, and as a function of current density, initial catholyte pH, and metal concentration.

EXPERIMENTAL

Apparatus, Membrane, and Solutions

The cell for electrolysis experiments is illustrated in Fig. 1. It was made of Pyrex glass. Two chambers were attached by inserting six screws on their flanges with a cation-exchange membrane in between. The membrane was cut as a circle with a diameter of 34 mm and glued into the inner mounting wall

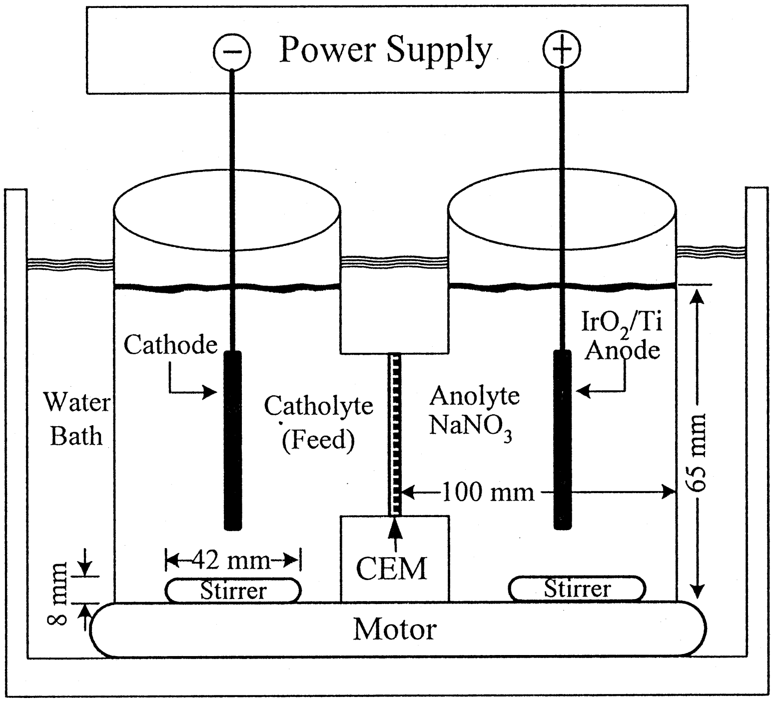

FIG. 1 Schematic of the electrochemical membrane cell.

of the two chambers with silicone rubber sealant to prevent leakage between the chambers. The electrodes were totally immersed in solutions and were symmetrically separated about 65 mm from the membrane surface.

Iridium oxide (Ti/IrO$_2$) and platinum (Ti/Pt) coated on titanium electrodes were used as the anode and cathode, respectively, both with dimensions of 52 × 52 × 1.5 mm. The power supply used in the electrolysis experiments was capable of supplying a potential up to 200 V and a DC up to 3 A. The cation-exchange membrane Neosepta CM-1 was from Tokuyama Soda Co., Ltd. It is a homogeneous film comprised of a crosslinked sulfonated copolymer of vinyl compounds on a synthetic reinforcing fabric. Table 1 lists its properties. It was washed with 100 mol/m^3 NaOH and HCl to remove inorganic impurities, and then with deionized water (Millipore Milli-Q) three times. Prior to use, the membrane was immersed in 100 mol/m^3 NaNO$_3$.

Analytical reagent-grade citric acid, NTA, EDTA, and other inorganic salts were from Merck Co. The catholyte was prepared by dissolving equimolar amounts of CuSO$_4$ and chelating agents in deionized water, and the original pH was within 2.08–2.2, depending on the types of chelating agents. When the effect of the initial catholyte pH was being studied, it was adjusted by adding a small amount of HNO$_3$ or NaOH. The anolyte was 100 mol/m^3 NaNO$_3$, and the initial pH was adjusted to be 3.0. The initial concentration of Cu(II) ranged

TABLE 1
Properties of the Cation Exchange Membranes Used in This Study

Property	Neosepta CM-1	Neosepta CM-2
Type	Strongly acidic, cation-selective	Strongly acidic, cation-selective
Characteristics	Low electric resistance (Na-form)	Low diffusion (Na-form)
Ion-exchange groups	Sulfonate	Sulfonate
Thickness, mm	0.13–0.16	0.13–0.16
Electrical resistance,[a] Ω-cm^2	0.8–2.0	2.0–3.5
Burst strength,[b] kgf/cm^2	1.5–3.0	1.5–3.0

[a] Measured by equilibrating with a 500 mol/m^3 NaCl solution at 298 K.
[b] Measured by a Mullen Brust Strength Device.

from 10 to 80 mol/m^3, and the concentration of chelating agent was about one order of magnitude larger than the level of most industrial effluents (2).

Experimental Procedures and Chemical Analysis

Equal volumes (250 cm^3) of the anolyte and catholyte were poured into each chamber after the cell was assembled. The voltage was adjusted so that the electrolysis experiments were carried out at constant current. When the metal concentration decreased in the cathode chamber, the cell voltage required to maintain a given current was decreased to a minimum. The pH values in the catholyte and anolyte were measured with a Horiba pH meter (Model F-23).

As expected, vigorous mixing reduced the thickness of the double layer adjacent to the electrodes, thereby enhancing mass transfer of the chelates toward the cathode. A stirring speed of 700 rpm was selected to prevent the formation of a serious vortex in the electrolytic cell. Samples were taken at preset time intervals from the cathode chamber. The concentration of Cu(II) was analyzed using an atomic absorption spectrophotometer (GBC Model 932). The temperature was held at 298 K by immersing the whole cell in a water bath. Each experiment was duplicated under identical conditions.

RESULTS AND DISCUSSION

Reactions Involved in the Electrolysis Cell

Citric acid, NTA, and EDTA are all polyprotic acids (H_xL) which can exist in many protonated forms in aqueous solutions. They form stable chelates with most divalent metals in a 1:1 molar ratio over a rather wide pH range. Essentially, the distribution of species at different pH values is obtained from a set of mass-balance equations by considering the overall formation constants (20). For an equimolar diluted solution of Cu(II) and EDTA (10 mol/m^3), for example, it was found that the divalent chelated anions CuL^{2-} absolutely dominates at pH 3–12 and the univalent chelated anions $CuHL^-$ at pH < 3 (9). In the case of Cu(II) and NTA, the univalent chelated anions CuL^- dominate at pH 1.5–11 (21).

As indicated above, the cell voltage was adjusted so that electrolysis was carried out at a constant current. The catholyte pH increased during electrolysis due to the production of OH^- at the cathode. In addition, H^+ is generated at the anode. Hence, when a current is applied, the following reactions may occur at the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E° = -1.229\ \text{V} \tag{1}$$

$$H_2O \rightarrow H^+ + OH^- \qquad E = -0.828\ \text{V} \tag{2}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad E° = -0.401\ \text{V} \tag{3}$$

$$2OH^- \rightarrow H_2O_2 + 2e^- \qquad E° = -0.547\ \text{V} \tag{4}$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad E° = -0.682\ \text{V} \tag{5}$$

whereas at the cathode:

$$CuL^{2-x} + 2e^- \rightarrow Cu(s) + L^{x-} \tag{6}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E° = 0.401\ \text{V} \tag{7}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E° = 0\ \text{V} \tag{8}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E° = -0.828\ \text{V} \tag{9}$$

Evidently the evolutions of O_2 and H_2 gases are the main side reactions at the anode and cathode, respectively, which would reduce the current efficiency.

Effect of Current Density on Electrolysis

The effect of current density on Cu recovery, R_{Cu}, from aqueous EDTA solutions at different electrolysis times is shown in Fig. 2. Here R_{Cu} is defined as

$$R_{Cu}\ (\%) = 100 \times \frac{\text{actual amount of Cu deposited onto the cathode}}{\text{initial amount of Cu(II) in the catholyte}} \tag{10}$$

It was found that R_{Cu} increases with increasing both electrolysis time and current density. In this work the recovery of both Cu and the chelating agent is almost consistent (not shown), indicating that the membrane Neosepta CM-1 is absolutely cation-selective (3).

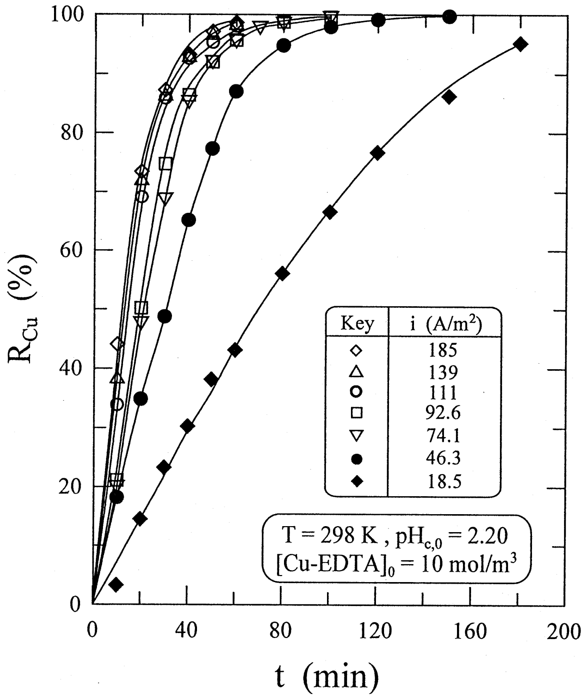

FIG. 2 Typical effect of electrolysis time on Cu recovery from EDTA solutions at different current densities.

Because the time profiles of R_{Cu} strongly depend on current density, catholyte pH, and the chelate concentration, a pseudofirst-order kinetic model was applied to quantify the phenomena of the system (22, 23). In practice, a linear trend of the logarithm of the amount of metal deposition as a function of parameter τ was verified according to Eq. (11) (Fig. 3), at least at the beginning of electrolysis (within 20–40 minutes):

$$\ln(n_{Cu,t}/n_{Cu,0}) = \ln(1 - R_{Cu}) = -k_{app}\tau \qquad (11)$$

where k_{app} is the pseudofirst-order rate constant and n_{Cu} is the amount of metal present in the catholyte. The parameter τ equals tS/V, where t is electrolysis time, S is the geometric area of the cathode (54 cm^2), and V is the volume of catholyte (250 cm^3). Basically, this is an initial-rate concept.

Figure 4 shows the effect of current density on the apparent rate constant k_{app}. It appears that k_{app} increases with increasing current density and eventually reaches a plateau. When a current is applied to the cell, the anolyte provides Na^+ to carry the current through the membrane into the cathode chamber and to regenerate the chelating agents to its Na form. To maintain electroneutrality in the anolyte, the loss of Na^+ must be accompanied by the generation of other cations, i.e., H^+ via oxidation of water (Eqs. 1, 2, and 5). At a higher current density, a larger amount of Na^+ is transferred and thus a

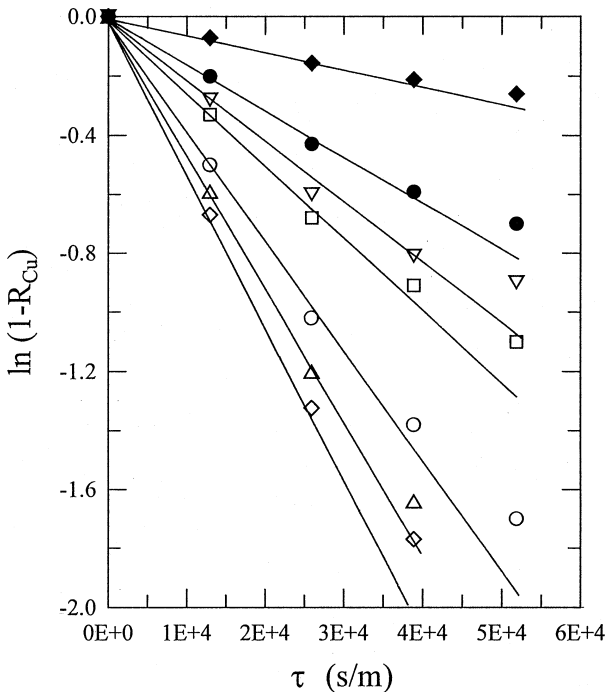

FIG. 3 Pseudofirst-order kinetic fit of Cu deposition from EDTA solutions at different current densities.

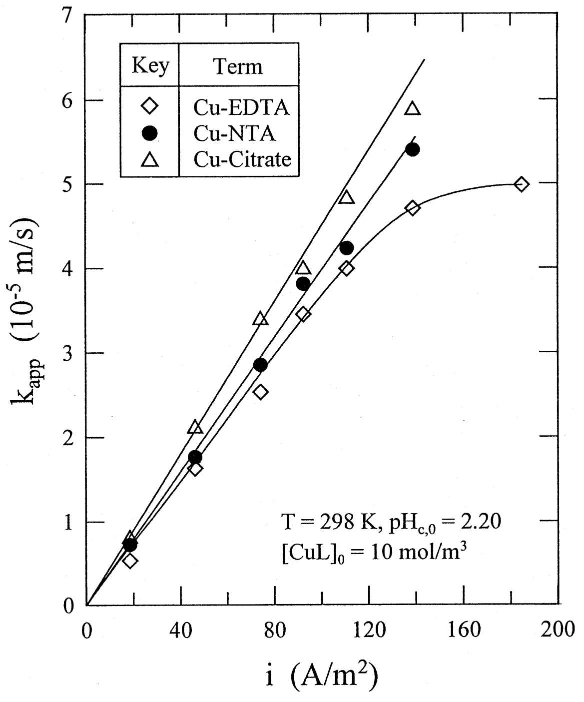

FIG. 4 Effect of current density on apparent rate constant.

larger amount of H^+ is required, which renders the current less effective for Cu deposition and hence k_{app} is unable to increase continuously.

In addition, k_{app} decreases under comparable conditions in the following order for different types of chelated Cu(II): citrate $>$ NTA $>$ EDTA. This order is exactly opposite to that of the overall formation constant (K_f) of the most stable 1:1 complex CuL^{2-x}. For example, the values of log K_f (in molar unit) are 7.2 for citrate, 14.2 for NTA, and 20.5 for EDTA at 298 K and zero ionic strength (20). It is seen that the differences of k_{app} among the three types of the chelates are insignificant, although the K_f values differ by 6–7 orders of magnitude. This may imply that only a small amount of electric energy is needed to break the binding of Cu(II) chelates. Most is consumed to facilitate side reactions, migrate the chelated Cu(II) anions toward the cathode, or transfer Na^+ across the membrane.

A similar kinetic model has been applied to treat the rate data of COD removal during electrochemical oxidation of landfill leachates containing high concentrations of chlorides and ammonium nitrogen (22), and those of TOC removal for industrial effluents (23). Using a Ti/PbO_2 cathode, k_{app} was found to be 5×10^{-6} and 1.2×10^{-5} m/s at current densities of 50 and 150 A/m^2, respectively (22). However, the present value of k_{app} is comparatively larger when using the similar cathode material Ti/IrO_2: they are about 2×10^{-5} and 5×10^{-5} m/s at current densities of 50 and 150 A/m^2, respectively (Fig. 4).

No membrane separator was used in the previous studies (22, 23). This probably means that the role of membrane resistance to the overall process is negligible and that the catholyte has an extremely low conductivity. In fact, a second membrane, Neosepta CM-2, was also tested here. It has the same thickness and polymeric matrix as CM-1 but has twice the electrical resistance (2.0–3.5 Ω-cm^2) of CM-1 (Table 1). However, there was no detectable difference in k_{app} between using CM-1 and CM-2 (not shown).

Effect of Initial Catholyte pH

Figure 5 shows the effect of initial catholyte pH on k_{app}. It was found that k_{app} exhibits a maximum at an initial pH of 2.0–2.2, which is exactly the original pH without any adjustment. The relatively low k_{app} at pH < 2 is probably related to the greater amount of H^+ ions discharged at the cathode and thereby producing H_2 gas bubbles (24, 25).

When the initial catholyte pH is greater than 2.2, a larger amount of Na^+ is present in the catholyte. This is due to the extra addition of NaOH for pH adjustment or its migration from the anolyte through the membrane, resulting from a larger amount of Cu deposition on the cathode. Hence, a certain amount of current is more easily consumed to preferentially reduce water (Eq. 9), rather than Na^+, at the cathode. This is experimentally supported because the catholyte pH quickly increases after electrolysis; e.g., it becomes nearly

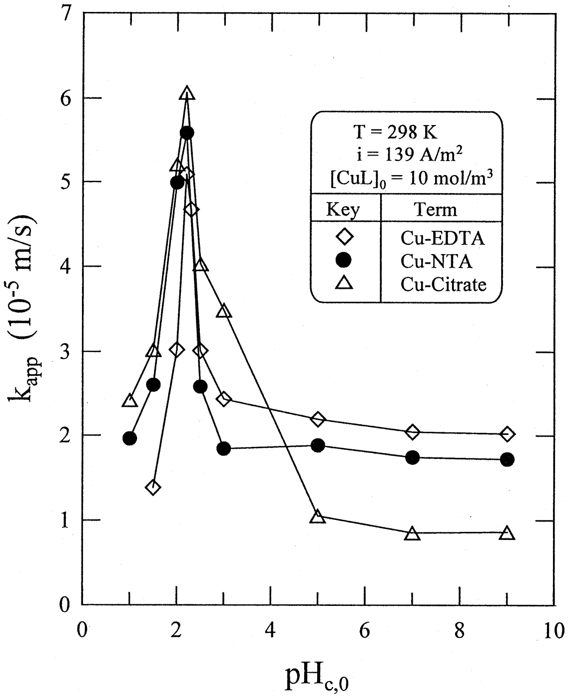

FIG. 5 Effect of initial catholyte pH on apparent rate constant.

constant at pH 12.3 (EDTA solutions) after 40 minutes if the initial pH is not less than 2.2. This can account for the drop of k_{app} at pH > 2.2.

At a sufficiently high initial catholyte pH (>5), on the other hand, k_{app} decreases in a different order (EDTA $>$ NTA $>$ citrate) than at low pH (Fig. 5). This may be due to the fact that the effect of OH^- ions produced from side reaction Eq. (9) on catholyte pH in EDTA medium is less than in NTA and citrate media (2).

Effect of Initial Chelate Concentration in the Catholyte

Figure 6 illustrates the effect of the initial chelated Cu(II) concentration on k_{app}. It is seen that k_{app} decreases with an increase of the initial chelate concentration. If the deposition of metals in the present electrochemical membrane process follows first-order kinetics, the rate constant will not depend on the initial chelate concentration. This appears to be the case only under sufficiently high chelate concentrations. The is probably because the cathode chamber is an “open” system in which Na^+ or H^+ is transferred from the cathode chamber to maintain electroneutrality; in addition, the amount of transference depends on the chelate concentration.

In a word, the apparent rate constant k_{app} is located within the 10^{-5} m/s order under the experimental conditions studied. The rate of Cu electrodeposi-

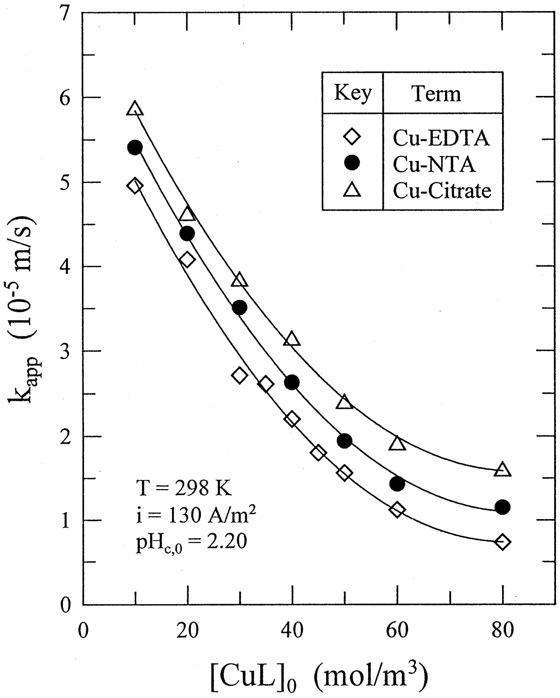

FIG. 6 Effect of initial Cu(II) concentration on apparent rate constant.

tion on the cathode mostly decreases in the following order for chelated Cu(II): citrate $>$ NTA $>$ EDTA, except when the initial catholyte pH is high enough (e.g., pH > 5, at a current density of 139 A/m^2 and an initial chelate concentration of 10 mol/m^3).

CONCLUSIONS

A pseudofirst-order kinetic model was applied to describe the rates of Cu deposition from solutions containing EDTA, NTA, or citrate in an electrochemical membrane cell. The following results were obtained.

1. A pseudofirst-order kinetic model (Eq. 11) was verified to describe the metal deposition process, at least at the beginning of electrolysis (within 20–40 minutes). The apparent rate constant k_{app} is located within the 10^{-5} m/s order under the ranges studied.
2. It seems that k_{app} increases with increasing current density and reaches a plateau. The plateau of k_{app} at a higher current density is due to a larger amount of Na$^+$ being transferred, and thus the larger amount of H$^+$ is required, which renders the current less effective for Cu deposition.
3. At an initial catholyte pH within 2.0–2.2, k_{app} has a maximum. The low k_{app} at pH < 2 is likely due to the larger amount of H$^+$ discharged at the

cathode and the production of H_2 bubbles. The drop of k_{app} at pH > 2.2 is due to the larger amount of Na^+ present in the catholyte which has migrated from the anolyte or which was added for pH adjustment.

4. Under comparable conditions, k_{app} decreases in the following order for chelated Cu(II): citrate $>$ NTA $>$ EDTA, except when the initial catholyte pH is high enough. Such an order cannot be wholly related to the complexing ability of Cu(II) and the chelating agents.

NOTATION

$E°$	standard reduction or oxidation potential (V)
H_xL	chelating agent
i	current density (A/m^2)
k_{app}	apparent rate constant (m/s)
K_f	overall formation constant of the aqueous complexes (molar unit)
n_{Cu}	amount of Cu(II) present in the catholyte (mol)
R_{Cu}	Cu recovery (%)
T	absolute temperature (K)
S	geometric area of the cathode (m^2)
t	electrolysis time (min)
V	volume of the catholyte (m^3)
[ ]	molar concentration of species in the brackets (mol/m^3)

Greek Letter

τ	parameter defined in Eq. (11) (s/m)

Subscripts

a	anolyte
c	catholyte
f	final
t	time t
0	initial

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