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Minimization of Energy Wastage in the Electrochemical Recovery of Copper from Its EDTA Complexes in Wastewaters

Philip Chi-Wah Cheung[1, *], Daryl Robert Williams[1], Donald Wilfrid Kirk[2], James Barker[3]

[1]Department of Chemical Engineering, Imperial College, London, United Kingdom
[2]Department of Chemical Engineering, University of Toronto, Toronto, Canada
[3]Department of Chemical and Pharmaceutical Sciences, Kingston University, Kingston-on-Thames, United Kingdom

Email address

philip.cheung@imperial.ac.uk (P. Chi-Wah C.)
[*]Corresponding author

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Abstract: For the first time, the recovery of copper from Cu(II)-EDTA complexes in waste streams, which originated from electroless plating of printed circuit boards (PCB), is optimized with respect to the consumption of electrical energy required for the separation process. To narrate the sequence of arguments which result in this minimization of energy expenditure, an electrochemical reactor is set up so that the ways in which electric potential and pH influence the rate of electrodeposition of copper, and therefore power usage, can be followed closely. The initial concentrations of the components of this simulated wastewater are 0.04 mol dm^{-3} of Cu^{2+} ions and 0.13 mol dm^{-3} of EDTA, typical of this type of liquid waste. By applying an electric potential of -1.0V for 4 hours, recovery of copper by electrodeposition at pH = 10.7 in the electrolysis cell equipped with a cation exchange membrane is evinced, successfully removing 31% of Cu^{2+} ions from aqueous solution. This is carried out for demonstrative purposes, with full recovery expected to be achieved in 12 hours. Studying the rate-controlling mechanisms for the electrodeposition of copper by utilizing a rotating disc electrode reveals that the deposition process is both kinetically and mass transport controlled, down to potentials of -1.5V relative to a Standard Calomel Electrode (SCE). Favored mass transfer mode of operation therefore exists at potentials considerably more negative than -1.5 V, in a potential region where hydrogen production is significant and therefore not viable for electrodeposition. This is the electric potential of sole interest to this work because it is to be avoided. Visual confirmation of copper deposits on the cathode confirmed feasibility of this clean technology for metal recycling. Moreover, a threshold potential of -1.0 V against which engineers can benchmark during preliminary reactor design has been identified in this pioneer work. The authors wish to emphasize that the present work focuses on the theme of "energy efficiency" for a proposed electrolytic process, and in this short space, does not seek to include elucidation of the modes of film deposition and nucleation on surfaces of electrodes by instrumental methods such as scanning electron microscopy (SEM), x-ray diffraction (XRD) or energy dispersive x-ray analysis (EDX). This will be in the domain of future work. (46 references from 1923 – 2018).

Keywords: Minimization of Energy Loss, Printed Circuit Boards, Electroless Copper Plating, Wastewater, Copper Recycling

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1. Introduction

1.1. Symbols

Appraisals of the overall performances of electrochemical reactors systems engineered for the deposition of copper in the presence of EDTA or other chelating agents focuses on three parameters usually symbolized by R_{Cu} (% recovery of copper within a specified time period), η_{Cu} (current efficiency, also expressed as a percentage), with the corresponding recovery of

EDTA written as R_{EDTA}. These symbols are often encountered in literature and are now defined precisely in order to facilitate discussion throughout this article:

R_{Cu} = (Actual amount of Cu deposited onto the cathode / Initial amount of Cu present in the catholyte) x 100%.

η_{Cu} = (Actual amount of Cu deposited onto the cathode / Amount of Cu deposited based on Faradays 2nd law of electrolysis) x 100%.

R_{EDTA} = (Amount of EDTA recovered / amount of EDTA in untreated wastewater) x 100%.

1.2. Minimizing Energy Loss in a Recycling Task

One of the core ideas underpinning the progress towards a sustainable industrial economy is called "Zero Waste". It is a visionary ideal which requires the design and management of processes and products to mitigate and eliminate the amount and toxicity of wastes, and to recover as many useful materials as possible. Incineration, landfilling and indefinite storage (with no plans to reprocess the stored materials) are to be avoided by careful planning. The authors' philosophy for resource management is in complete harmony with that propounded on World Water Day (22nd March, 2017), an annual event instituted by the United Nations General Assembly. The main theme of the 2017 convention is the acknowledgment that wastewater is an "untapped resource" (UNESCO, 2017). In the associated document, Payne (2017) argued cogently that many valuable components present in wastewaters can be extracted for reuse [1]. So it is with the recovery of copper in this work. Alternatively, Su *et al.* (2016) chose to produce H_2 (*g*) as a fuel by photocatalytic oxidation of EDTA in wastewaters [2], liquids very similar to the one in this work. Their approach of waste-to-fuel is valuable if H_2 can be fed directly into a fuel cell to produce electricity, or else provisions must be made for hydrogen storage, a most pressing technological challenge.

The fabrication of Printed Circuit Boards (PCB) in the electronics industry involves the electroless plating of copper onto a non-conducting substrate, typically fiberglass with epoxy resin. At the end of the bath life the resulting alkaline wastewater contains copper-EDTA complexes, unbound EDTA anions, organic compounds such as formaldehyde and formate ions, and additives. Recycling requires the reduction of Cu^{II} (*aq*) to Cu^{0} (*s*), then to re-melt and purify the copper in an ore smelter. While it is not necessary to produce a smooth, bright and reflective surface as required of aesthetic ornaments, the key to the success of this separation process is the design and construction of electrochemical reactors capable of extracting Cu^{II} ions from its chelated complexes of which multidentate EDTA moieties are the ligands. In this sense, a sustainable recycling process is also one in which energy is used efficiently, with minimum energy loss, and this demand is the main theme of this work.

1.3. An Electrochemical Separation Process

In recovering the chelating agent EDTA from aqueous solutions which also contained Cu^{2+} ions, the proposed separation techniques were such that electrolysis resulted in metallic copper being plated onto the cathode (*e.g.*, a copper sheet), leaving unbound EDTA in solution [3, 4]. To prevent EDTA from being anodically oxidized (*i.e.*, fragmented), the electrolysis cell is divided into two compartments with a cation exchange membrane. While the cathodic chamber contained the copper-EDTA solution to be treated, the anodic chamber housed Na_2CO_3 or $NaNO_3$ (*aq*). The recovered yield of EDTA was reported to be 94%. Later work confirmed that EDTA which had not been quarantined in this fashion decomposed to smaller molecules [5, 6].

The choice of electrolysis over lime-precipitation has also been proposed [7]. A case of very high materials recovery (R_{Cu} = 97.7%, R_{EDTA} = 99.3%) but very low current efficiency with η_{Cu} = 3.2% was reported by Peters [8]. He cited an interpretation of similar results offered by Allen & Chen [9], who noted that "as the current density increased the current efficiency decreased. The current efficiency was greater for the free metal than for the metal-EDTA complexes. To achieve high current efficiency, it becomes necessary to have low current density to minimize side reactions and to use an electrolysis cell having a high efficiency." Juang & Lin [10] encountered a similar situation. They showed the recovery of copper and EDTA under various combinations of current densities, treatment times, solution pH values and $NaNO_3$ concentrations in the anolyte. The lowest recovery rate was 37.5% (Cu) and 39.2% (EDTA) with 18.5 A m^{-2}, resulting in η_{Cu} = 62.4%. The highest was 98.6% (Cu) and 98.5% (EDTA) with 139.0 A m^{-2}, resulting in η_{Cu} = 18.7%. In the separation of Cu^{2+} ions from its EDTA ligand, the "economically acceptable" condition of $\eta_{Cu} > 60\%$ must be held [10] and that for separation of Cu^{2+} ions from a citrate ligand, a requirement of $\eta_{Cu} > 50\%$ was essential [11].

Etzel & Tseng [12] used a two-chamber reactor to extract Cu^{2+}, Zn^{2+} and Ni^{2+} ions from EDTA. Plating of Cu and Zn, but not of Ni, was achieved. This technology was used to re-extract EDTA from wash-water of soil contaminated by Pb, recovering > 95% of EDTA [9]. Juang & Wang [13] managed to recover Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} ions from soil wash-water in the presence of EDTA, no doubt basing this work on their earlier success of treating a simpler aqueous system containing Cu^{2+} and Pb^{2+} only [14]. This approach was extended in parallel work [10, 11] to include NTA (nitroloacetic acid) as a ligand [15], while Oztekin & Yazicigil [16] found that it was possible to separate Co^{2+}, Ni^{2+} and Cu^{2+} ions from their EDTA, NTA and citrate ligands (nine different metal-ligand pairs in total) using different kinds of membranes, therefore improving upon on the earlier studies on nickel [12]. All of these workers have contributed much to the understanding of the two-chamber process.

Scientists who deploy cation-exchange membranes for separating out metallic ions have reported with vividness the extraordinary depreciation in effectiveness of adsorption caused by the presence of EDTA in wastewaters. The uptake of Co^{2+} and Cu^{2+} by a sulfonate membrane called "Nafion" ($R\text{-}SO_2\text{-}O^-H^+$) was hampered by EDTA which formed anionic complexes with these metals [17]. Fortunately, this is not the reason why an ion-exchange membrane is installed for this work. Reversely, EDTA and other powerful chelants are excellent sequestration agents when grafted onto solid resin matrixes for the removal of free (hydrated) metallic ions, a current topic of intense research [18, 19].

1.4. Significant Effects of Analyte pH

In a two-chamber process, Juang & Lin [15] used 0.1 mol dm^{-3} of $NaNO_3$ as the anolyte. The catholyte was an alkaline solution of the Cu(II)-EDTA complex, with copper content in the range 0.01 - 0.08 mol dm^{-3}. The cathode current density was varied up to 140 A m^{-2}, and this upper limit was found to be optimal for copper recovery R_{cu}. Both R_{cu} and η_{cu} attained maximum values at pH = 2.2, and remained constant up to pH = 9, demonstrating that recovery was not a strong function of pH. From the perspective of a wastewater engineer, this is welcome since substantial pH adjustments and the resulting liquid cooling are not required, as these will no doubt add to the materials, time and energy costs for metal recovery. In addition, Juang & Lin [15] observed that although the catholyte pH may increase due to reactions expressed by equations (1) and (2), alkalinity actually remained constant at pH = 12.3, providing that the initial pH of the solution is above a value of 2.2.

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \quad E^o = +\,0.401\text{ V} \tag{1}$$

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \quad E^o = -\,0.828\text{ V} \tag{2}$$

Since the migration current is dependent on the ionic strength of the solution, it is not too surprising that these workers also found that an increase in the concentration of the chemically inert supporting electrolyte $Na^+NO_3^-$ (in the anolyte) also led to increases in recovery R_{cu} and efficiency η_{cu}. Coupled with the observations of Etzel & Tseng [12], these results converge to explain why the type and concentration of anolyte affects the pH of the catholyte. Etzel & Tseng [12] discovered that when an acid is the anolyte, it reduces the pH of the catholyte and precipitates the electrically neutral EDTA molecule on the membrane surface, since hydroxonium ions H_3O^+ replace Na^+ as charge-carriers across the membrane, followed by protonation of the negatively-charged conjugate bases of EDTA.

1.5. Status Quo of the Technology in Literature

The literature presented so far in this introduction belongs to the proof-of-concept genre. Most of these articles are documentations of success stories of the recovery of copper and other metallic ions from EDTA, and they provide useful guidance in this field of research. Only a handful of papers alluded casually and discussed parsimoniously on the impact of applied voltage on overall performance, and almost none with respect to the efficiency with which electrical energy is consumed. It is only appropriate to discuss their relevance, with full reference, in the Results & Discussion section in juxtaposition with the findings of this work, which the authors present with the intention of filling this gap of knowledge.

2. Developments in Theory and Applications

2.1. Diffusional Mass Transfer

The kinetics and the mass transfer characteristics of electrolyzing copper–EDTA solutions have been reported for cases where the presence of chelating agents in alkaline solutions elevated the reduction potential [20, 21]. Various diffusion coefficients of metal complexes in solutions were determined; those most relevant are listed in Table 1. The kinematic viscosity for a Cu-complexed solution was quoted as 0.01148 $cm^2\ s^{-1}$, at 25°C. Note that Y is the electrically neutral EDTA molecule ($C_{10}H_{16}N_2O_8$), and Y_{-4H} and Y_{-3H} are the quadruply and triply de-protonated EDTA moieties, carrying negative charges of -4 and -3 respectively.

Table 1. *Diffusion coefficients of copper-EDTA complexes in solution [20, 21].*

Chemical species	Diffusion Coefficient, D (x 10^{-6} $cm^2\ s^{-1}$)	Comments on conditions
$[Cu(H_2O)_6]^{2+}$	5.30	Independent of pH.
$[CuY_{-4H}]^{2-}$	2.26	pH range 5 to 12; 0.01 M for both Cu(II) and EDTA.
$[CuY_{-3H}]^{-}$	2.85	pH range 5 to 12; 0.01 M for both Cu(II) and EDTA.

2.2. Recent Wastewater Management Practices

The need for satisfactory treatment of wastewaters which contain metal chelates, including effluents arising from manufacture of printed circuit boards, is an ongoing challenge. Ju & Hu [22] deployed a method called the "interior micro-electrolysis" whereby Fe^0 (scrap iron) is oxidized to generate Fe^{2+} and Fe^{3+} to displace Cu^{2+} ions already complexed by EDTA, with air as the oxidant. The R_{cu} index was reported to be 98% and R_{EDTA} was 32% at pH = 3.0 [23, 24]. The interest in recycling and reusing EDTA from wash-waters of contaminated soils has been aroused for almost a decade [25 to 29]. The choice of chitosan as an absorbent for metals and dyes was reviewed by Ngah *et al.* [30] who emphasized the need to regenerate the absorbent in order to make the separation process economically viable. To illustrate the roles that mass transfer play in influencing the rate of chemical sequestration of metallic contaminants, soil scientists have taken a mathematical modelling approach used by chemical engineers by including intraparticle diffusivity and the fluid mechanics of water through packed beds of soil, with useful results [31].

In a review paper, Cheung & Williams [32] examines critically the efficacy of eighteen methodologies for the treatment of hazardous wastes of which metal complexes (*e.g*, Cu-EDTA) are major constituents. The techniques include (and not limited to) electrodeposition, simultaneous electrodeposition of metals and ligand destruction, electro-membrane separation and electrodialysis, all viable options for extracting metals for reuse.

3. A Pourbaix Diagram for Copper Recovery

The cathode substrate and aqueous chemistry of a metal-ligand system has a significant bearing on the overall efficiency in the recovery of a metal. The potential required for an electrode reaction to proceed at a rate in order to achieve a desired result depends predominantly on speciation. Equilibria of the Cu-H_2O-EDTA system are presented as a Pourbaix (pH-E_h) Diagram, Figure 1. The composition of the solution is 0.04 mol dm^{-3} of Cu^{2+} and 0.13 mol dm^{-3} of EDTA activities, at 25°C. The equations for the construction of the diagram were adapted from Aksu & Doyle [33], with minor additions and modifications.

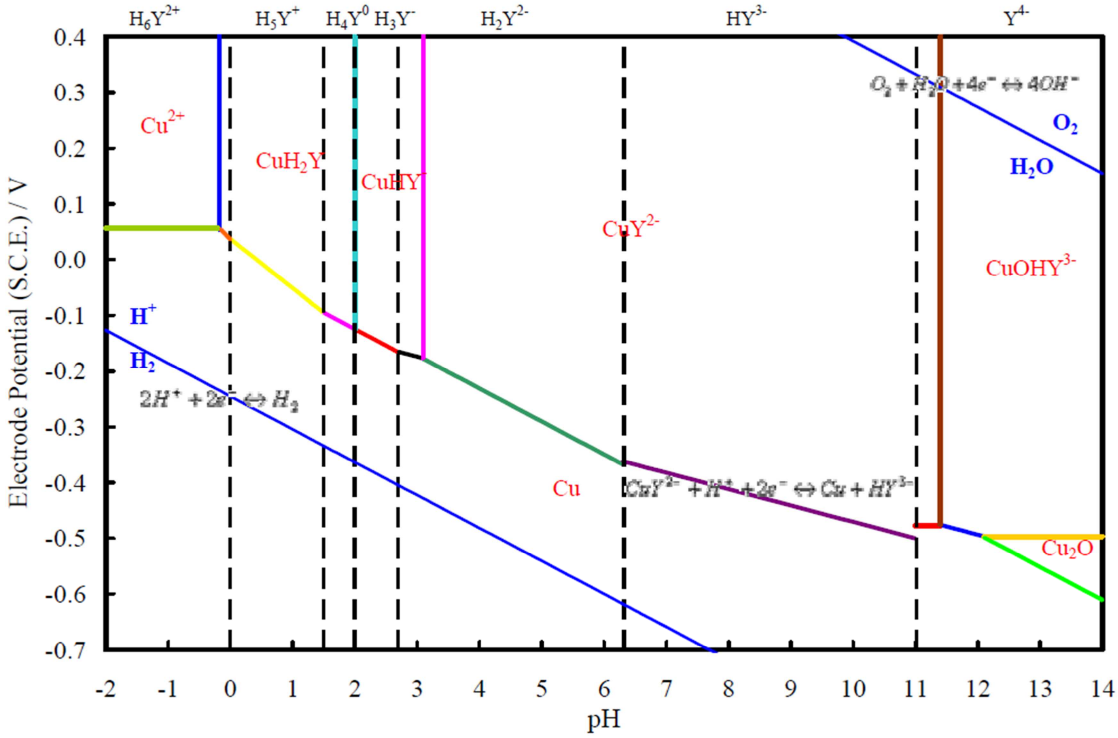


Figure 1. *Pourbaix diagram for Copper-EDTA-Water at 25°C.*

The area of interest is the region pH ≥ 10 which covers the electroplating bath's operating range. The dashed lines indicate a change in EDTA species. At pH=10 and 0 volt, the chelated complex $[Cu(Y_{-4H})]^{2-}$ coexists with the free ligand Y^{3-}. However, at pH=11 and 0 volt, the same complex coexists with Y^{4-} in solution. The diagram is used to predict the dominant species for any combination of E_h and pH. On applying a potential of -0.3 V to a solution at pH=10 containing $[Cu(Y_{-4H})]^{2-}$ and Y^{3-}, the following reaction is thermodynamically favorable in the reverse direction, *i.e.*, Cu^{II} ions remain in solution and are not plated out since they are still protected by EDTA despite in alkaline medium:

$$[CuY_{-4H}]^{2-} + H^+ + 2\,e^- \rightleftharpoons Cu^0 + Y^{3-} \tag{3}$$

The same set of condition also favors equation (1) chemistry, but if a potential of -0.5V is applied, equation (3) is favored to proceed in the forward direction and copper is deposited. This is likely to be a predominantly kinetically controlled reaction, but if a more negative potential is applied, such as -1.0V, the reaction will fall under the control of transport phenomena increasingly. Additionally, undesirable hydrogen evolution is likely to take place:

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2\,(g) \uparrow \tag{4}$$

It is important to note that at -0.5V and pH ≥ 12, formation of the electrical insulator $(Cu^I)_2O$ (red cuprous oxide) is thermodynamically favoured and may hinder desirable electrochemical activity such as plating. For instance, if a potential of -0.55 V is applied to a highly alkaline solution at pH = 13 containing $[Cu^{II}(OH)(Y_{-4H})]^{3-}$ and Y^{4-}, then the thermodynamic possibility exists that a film of this cuprous oxide will form before copper is plated. Deposition would slow to the point of cessation, depending on the magnitude of the potential applied.

4. Methods and Materials

Investigative research to discover the magnitude of applied voltage for the optimum performance of the electrolysis system consists of two parts:

a. Kinetics of electrodeposition of copper
b. Reactor development for the separation process

4.1. Kinetics of Electrodeposition of Copper

Electrolysis is a Lewis redox reaction and is a non-equilibrium thermodynamic process. Designers of reactors will aim for an operation controlled by the mass transport regime. This is important to reactor performances because:

a. High current densities (present in mass transport controlled regimes) enhance R_{Cu} values, space velocities s, mass transfer coefficients k_L, and ultimately, the "space-time yield ρ_{ST}" which is directly proportional to s and k_L. The mathematical relationship $\rho_{ST} = \rho(s, k_L)$ has been rigorously derived by Fletcher & Walsh [34] with the same symbols presented here. The "space-time yield" is one of the most valuable indicators of electrochemical reactor performance. It is defined as the mass of desired product obtained per unit time, per unit cell volume. A larger yield implies less capital cost required for the same type and amount of material to be treated.
b. The current density is uniform over the electrode surface and minimizes unwanted reactions, therefore maintaining higher current efficiencies, higher material yields, and most importantly from the point of review of recycling and reuse, that of selectivity.

The Rotating Disc Electrode (RDE) in laminar flow is a well-known analytical instrument for examining the mass transport characteristics of an electrochemical reaction under steady state conditions. It can locate the mass transport regime and determine its relationship to the system. The technique is based on the knowledge that a stagnant boundary layer comprised of the solution liquid rests on the surface of the electrode, even while the bulk of the solution is stirred vigorously by the rotating electrode. The relative velocity of the layer to the electrode is zero, *i.e.*, the layer appears to be motionless with respect to the electrode. Rotational momentum drags species onto the electrode where redox reactions can take place. Providing rotation speeds are kept within limits so that laminar flow is maintained, the mass transport equation will be given by the Levich Equation, which is usually presented in c.g.s. units:

$$|j_L| = 0.620 \text{ x } \{\text{n. F. A}_e.\ \nu^{-1/6}.\ \omega^{1/2}.\ \text{D}^{2/3}.\ \text{C}_{\text{analyte}}\} \quad (5)$$

where: $|j_L|$ = absolute current density, units: A cm^{-2}; n = number of electrons transferred in the half reaction; F = Faraday's Constant, units: 9.64 x 10^4 C mol^{-1}; A_e = electrode surface area, units: cm^2; ν = solution kinematic viscosity, units: cm^2 s^{-1}; ω = angular velocity of RDE, units: rad s^{-1}; D = Fick's diffusion coefficient, units: cm^2 s^{-1}; $C_{analyte}$= molar concentration of the analyte, units: mol cm^{-3}. The Levich Equation is a conceptual tool used in this exercise provided kinematic viscosities and diffusion coefficients are known (see Table 1). Plotting experimental current densities for particular rotation velocities allows comparisons of kinetic modes. For example, when non-linear experimental data, or discrepancies between data and predictions made by equation (5) appear, it is an indication that the system is not operating in the totally mass transfer controlled region.

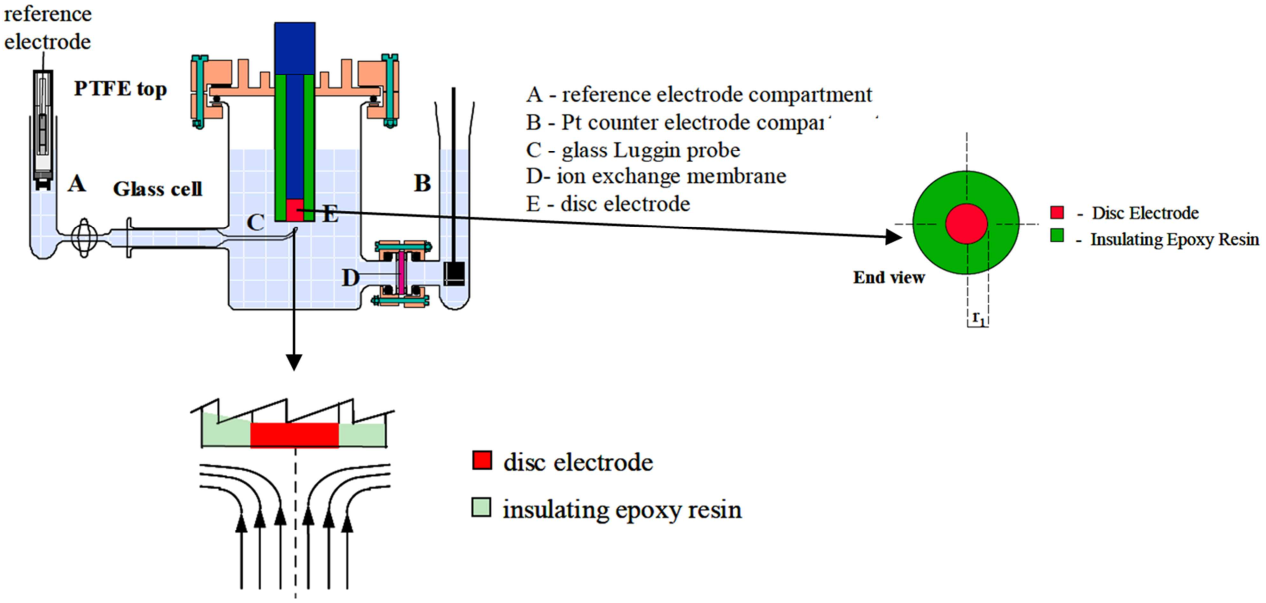


Figure 2. *Rotating disc electrode and liquid flow field details [36].*

The kinetics of the Cu(II)–EDTA system was studied with a rotating disc electrode (Pine Research, Durham, North Carolina, USA, see Figure 2) connected to an Autolab potentiostat ("Metrohn") *via* a computer controlled by GPES software [35]. A cylindrical rod of electrode material is embedded in an insulating cylindrical sheath which has significantly larger diameter than the electrode. The sheath and RDE surfaces are polished flat. The electrode is vertically rotated on its axis and acts as a pump; electrolyte is pulled vertically upwards towards the center of the disc and then helically thrown outwards towards the circumference. As rotation speed increases, the “diffusion layer”, or the layer that ions can diffuse from the surface before being removed by convection, decreases. Therefore, the higher the rotation frequencies, the greater the material fluxes to the electrode. The steady state for the system is one in which the current becomes mass transport limited. The Levich Equation, *i.e.*, equation (5), can then be used to analyze the relationship between rotation speed and current.

The electrode used was a metal disk of area 0.229 cm^2 that could rotate at speeds up to 3000 rpm for which the flow profile remains laminar. All potentials were referenced to a Standard Calomel Electrode (SCE). The experiments were performed at room temperature 298 ± 3 K.

All chemicals used were of analytical grade from Sigma-Aldrich and dissolved in deionized water. The stock solution was composed of 0.04 mol dm^{-3} of $CuSO_4$ and 0.13 mol dm^{-3} of Na_2EDTA, the composition of a simulated wastewater which has not been modified to any substantial extent since its patenting [37], without the complication of contributions to electroactivities from formaldehyde or other proprietary additives.

Typical spent plating solutions are in the range pH = 12 to 14, and the solution was initially adjusted to pH = 14 using NaOH. However, it was discovered that copper could not be plated in these extreme alkaline environments, even when potentials as low as -1.5 V were applied. This was due to the presence of a “passive” layer of cuprous oxide which forms at pH = 12 to 14 (Figure 1).

The pH of the test solutions was then reduced to pH = 10.7 when copper was deposited successfully. Trial experiments identified that copper could be plated relatively easily onto platinum, and so Pt electrodes were used. These experiments also showed that plating a precursor thin film of Cu onto the Pt electrode prior to the main experiment achieved higher success. This preparative procedure was accomplished using -1.5 V for 24 hours.

A cationic exchange membrane “Neosepta CM-1” (Tokuyama Soda Co. Ltd.) was used which stops unbound, negatively charged EDTA ligands from diffusing to the anode and being oxidized; see [13 to 15]. This is important if EDTA is also a target material for recovery. The membrane of 0.15 mm thickness was washed with 0.1 mol dm^{-3} NaOH and HCl, followed by three rinses with deionized water, and finally immersed overnight in 0.1 mol dm^{-3} $NaNO_3$ before use in the electrolysis bath.

Single voltammagram scans were obtained at a scan rate of 0.002 V s^{-1} and a step potential of 0.079 V. Specifying the starting potential and the 1st and 2nd vertex potentials was the final step. The starting potential and second potential were always set to be the same so that the end point of the return sweep would coincide with the starting point and the cycle could be easily repeated. Various combinations of starting potentials and first vertex potentials are reported below. Faraday’s 1st Law states that $Q = n \times F \times N$, where Q is the number of coulombs used in transforming N moles of material electrically, and n is the number of moles of electrons transferred in the process; F is the Faraday constant. The current *i* can be expressed as:

$$i = dQ/dt = (n \times F) \times dN/dt \quad (6)$$

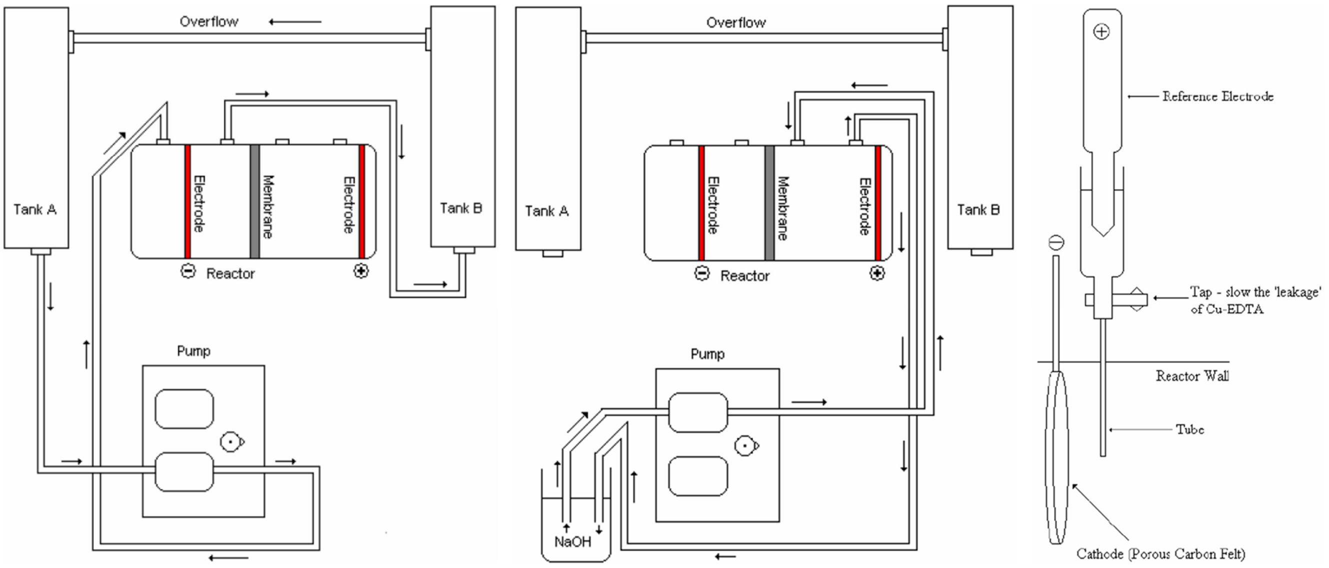
Therefore, the value of *i* also represents the rate of material conversion. The analytical method called “amperometry” is a technique which investigates the relationship between *i* and disc rotation frequency, at potentials relevant to the mass transport controlled region. The only input needed for this method was the potential to be applied, which varied for each set of results generated. Graphical plots of current versus time were obtained for -0.7 V, -1.0 V and -1.5 V, whilst varying the rotation rate: 240, 540, 960, 1500, 2160 and 2940 rpm.

4.2. Reactor Development for the Separation Process

The reactor volume was 60 cm^3 for the cathodic chamber and 80 cm^3 for the anodic chamber with 50 cm^3 of a simulated waste solution was used as the catholyte. The anolyte was a highly concentrated solution of NaOH at pH = 13.8; see [13]. In the reactor layout below, Figure 3(a) represents the catholyte flow loop and Figure 3(b) describes the anolyte flow loop. The catholyte flows from Tank A through a diaphragm pump and then into the reactor. It passed through a porous carbon felt cathode and then to Tank B. The process was continuous due to the “overflow” from Tank B returning treated catholyte to Tank A. A large volume of NaOH solution was stored, providing both the fresh anolyte entering the reactor and receives the electrolysed anolyte leaving the reactor. A second diaphragm pump controlled the flow rate around the loop. Separate pumps were used to control both the anolyte and catholyte flowrates at 1 dm^3 per minute. The voltage applied across the cathode and anode *via* a potentiometer is not equivalent to the electrode potential. To determine the electrode potential, and therefore control the amount of voltage/current supplied to the system, the potential difference between the cathode and the copper-EDTA solution immediately in contact with the porous carbon felt was measured. This was accomplished by connecting a multi-meter between the cathode (-) and the reference electrode (+). A current was supplied to the pilot reactor electrodes through the potentiometer such that the voltage across the cathode and SCE was -1.0V.

$$\text{The time required for plating (in seconds)} = [(n \times F) / i_{total})] \times (m_{dep} / 63.5) \quad (7)$$

where i_{total} is the total current passing through the system, m_{dep} = mass of Cu depleted from solution; the atomic mass of copper is 63.5.



(a) (b) (c)

Figure 3. *Diagram of the (a) reactor catholyte flow loop, (b) reactor anolyte flow loop and (c) reactor reference electrode.*

It was estimated that 2 to 4 hours are needed to lower (deplete) the catholyte solution from its initial concentration of 3 grams of Cu^{2+}/dm^3, to between 2 and 1 gram/dm^3. The reactor operated for 3 hours and the solution was regularly sampled. At the end of the experiment, the reactor was disassembled to inspect whether copper had been plated onto the cathode.

5. Results and Discussions

5.1. Kinetics of Electrodeposition of Copper

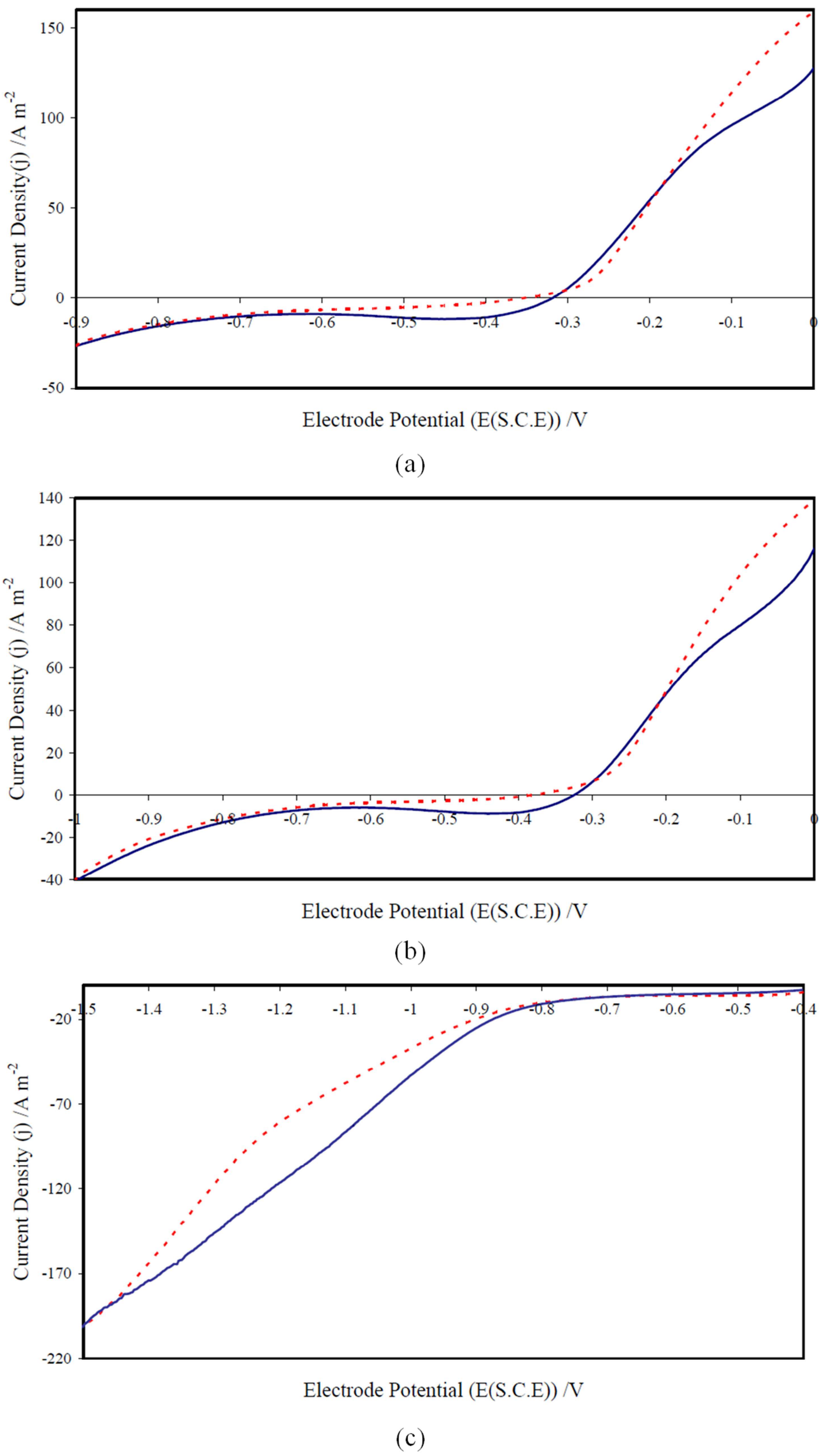
Referring to Figure 4, the current for a reduction in electrode potential (represented by the solid line), followed by an increase in potential (represented by the dashed line), were measured, generating voltammagrams. Each graph shows a different electrode rotation rate (1700, 500 and 1000 rpm), as well as potential range. The cycle in Figure 4(a) had a starting potential of zero volt (0 V), reached down to a first vertex potential of -0.9 V and finished on the second potential of 0 V. As noted, the solid line represents the 'forward-sweep' from 0 to -0.9 V and the dashed line represents the 'reverse-sweep' from -0.9 to 0 V. It is clear from Figure 4(a) that the path of the 'reverse-sweep' curve is not equivalent to that of the path of the 'forward-sweep' curve; the dashed line, on average, always shows more positive current densities. The same phenomenon appears in Figures 4(b) and 4(c), and can be attributed to differences in surface areas between forward and reverse sweeps, owing to plating. In Figure 4(b), between potentials of 0 V and -0.32 V to -0.35 V (depending on the sweep direction), the net current densities are positive. This signifies that oxidation was the main reaction. The only oxidation reaction that could be occurring within the system is the reverse of the reaction represented by equation (3), *i.e.*,

$$Cu^0 + [HY_{-3H}]^{3-} \rightarrow [CuY_{-4H}]^{2-} + H^+ + 2e^- \qquad (8)$$

This means that the copper that had already been present on the platinum electrode, as a result of intense plating prior to the experiment, was being oxidized and entering into solution. The current densities for the reaction represented by equation (8), would normally be slightly higher for each potential than those indicated on the plot. The net current was slightly less due to a simultaneous reaction, namely, the reduction of oxygen.

The interpretation of Figure 4(a) can be complemented by the Pourbaix diagram (Figure 1). At pH = 10.7, and in the vicinity of -0.32/-0.35V and above, oxidation of any Cu in the system to $[Cu(Y_{-4H})]^{2-}$ is thermodynamically favourable. The diagram also indicates that the reduction of oxygen is also favourable. Oxygen reduction had little effect on the net current density in comparison to the oxidation of copper since very low concentrations were involved. (The solubility of O_2 in water at 25°C is about 8 ppm).

However, another region on the Pourbaix diagram (Figure 1) is important. Formation of $[Cu^{II}(OH)(Y_{4-})]^{3-}$ at pH ≥ 11 is noteworthy. In a separate speciation exercise using the software MINEQL+ (Environmental Research Software, Hallowell, Maine 044347, USA) it was found that at pH = 11, the mole ratio of $[Cu^{II}(Y_{-4H})]^{2-}$ to $[Cu^{II}(OH)(Y_{4-})]^{3-}$ is very close to 1:1, which means that two (and not just one) copper complexes are being electrolyzed. This two-species scenario has to be taken into account in future interpretation of data,



(a)

(b)

(c)

Figure 4. *(a) Cycle 1: 0 V to -0.9 V and reversed: pH = 10.7, 1700 rpm, (b) Cycle 2: 0 V to -1 V and reversed, at pH = 10.7 and 500 rpm (8 Hz) (c) Cycle 3: -0.4 V to -1.5 V and reversed at pH = 10.7 at 1000 rpm.*

Referring to Figure 4(a), close to -0.32/-0.35 V, the net current density becomes negative, implying that reduction was the most influential reaction occurring in the system at that point. The net current densities up to the vicinity of the potential -0.70 V are only slightly negative in comparison to those observed from -0.70 V onwards. Perhaps the reduction process has not begun in earnest even though oxidation of copper ceased. This may mean that the current density is mainly a result of the oxygen reduction reaction. At -0.7 V, the current density begins to tail off implying that the start of a significant reduction process is occurring, *i.e.* the electrodeposition of copper.

The Pourbaix diagram (Figure 1) confirms this analysis. It shows that at pH = 10.7 and -0.70 V, it is thermodynamically favourable for copper to be removed from solution by electroplating. Note carefully that EDTA is protecting Cu^{2+} ions from precipitating as $Cu(OH)_2$ in alkaline solution right up to the juncture of electrodeposition [38].

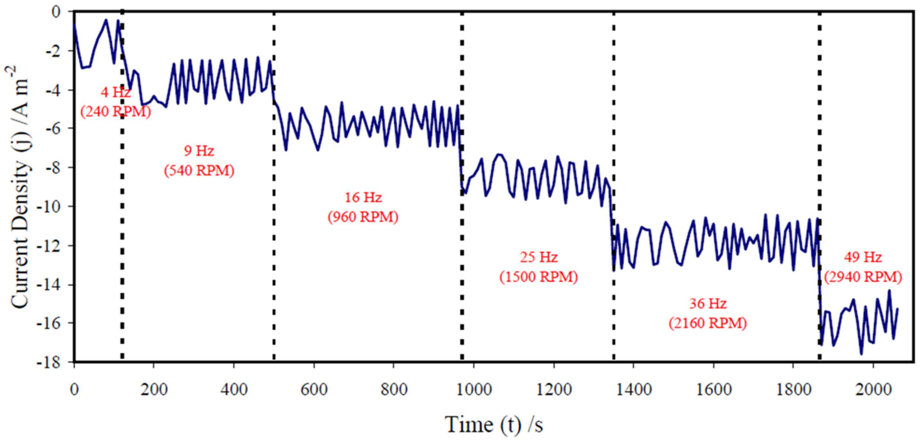
The Pourbaix diagram (Figure 1) indicates that the copper reduction process should begin at a potential around -0.47 V. This is different from the situation that Figure 4(a) implies, as reduction is not expected to commence until the potential -0.70 V has been reached. This does not, however, depreciate the verisimilitude of utilizing a Pourbaix diagram for the interpretation of voltammetry findings, since it is possible that the advent of the kinetic controlled region in Figure 4(a) happened earlier than first anticipated. To demonstrate that Figure 4(a) displays data typical of the process, additional voltammetry curves were plotted, at different rotation rates.

Figures 4(b) and 4(c) show the voltammetry curves for rotation rates of 500 rpm and 1000 rpm respectively. The cyclic voltammagram Figure 4(c) follows the same pattern as that in Figure 4(b), in the sense that the reduction of Cu^{II} did not initiate until approximately -0.70 V. Therefore, even with a change of rotation rate, the end of the oxidation process and the advent of the reduction process remained the same. However, on this occasion, the ‘first vertex’ has been extended to -1.00 V, an attempt to distinguish between the total kinetic and total mass transport controlled regions for the reduction of Cu^{II} ions ($Cu^{II} \rightarrow Cu^{I} \rightarrow Cu^{0}$), which began at approximately -0.70 V, as already discussed. The behavior exhibited at -0.7 V onwards, portrayed in Figure 4(b), did not indicate clearly any definitive mass transport controlled region, but a region of mixed control modes. To pursue this further, another cyclic voltammetry plot was generated, this time with a first vertex potential of -1.50 V (and 1000 rpm). As with Figure 4(b), no plateau characterizing the existence of mass transport control is present between -0.70 V and -1.50 V, which is compelling evidence that the process is controlled by both redox kinetics at the electrode, and by ion transport phenomena in the bulk of the solution, even down to potentials of -1.50 V. In this work, it is of cardinal importance to have discovered that, at approximately -0.90 V and onwards, a further reduction process takes place, that of the evolution of hydrogen:

$$E_{H+/hydrogen\ gas} = -0.059\ pH - 0.245 = -0.88\ V\ (SCE,\ at\ pH = 10.7) \qquad (9)$$

The implication is that operating in the totally mass transport controlled region favoured for reactor operation will generate considerable hydrogen and increase operating costs. As already discussed, a potential of -0.70 V signifies the onset of copper reduction, beyond which cyclic amperometry was unable to distinguish between the kinetic and mass transport controlled regimes. To resolve this, three amperometry plots (Figure 5) were generated for potentials which are beyond -0.70 V to discover the potential at which the process becomes mass transport controlled, and the results compared to Levich predictions, at pH = 10.7 and at various rotation rates.

An amperometry plot at a potential of -1.0 V was generated, Figure 5(b), though at this potential in order to achieve total mass transport control, the evolution of hydrogen is encouraged. Although there is less noise in the results compared to Figure 5(a), the presence of an element of kinetic control is still implied. The process appears to operate in a total mass transport region only when -1.50 V is reached, a potential which causes significant hydrogen production, Figure 5(c). Definitive and relatively smooth step changes occur as a result of changes in rotation rate. However, only when the results are compared to the predicted results from the Levich Equation will there be certainty that the process is operating in a totally mass transport controlled environment. Progression from Figures 5(a) to 5(c) provides evidence of the drive towards total transport-control mode as the potentials increased. To evaluate the extent to which, at each potential, that mass transport control exists, the results were plotted against those predicted from the Levich equation as already shown.



(a)

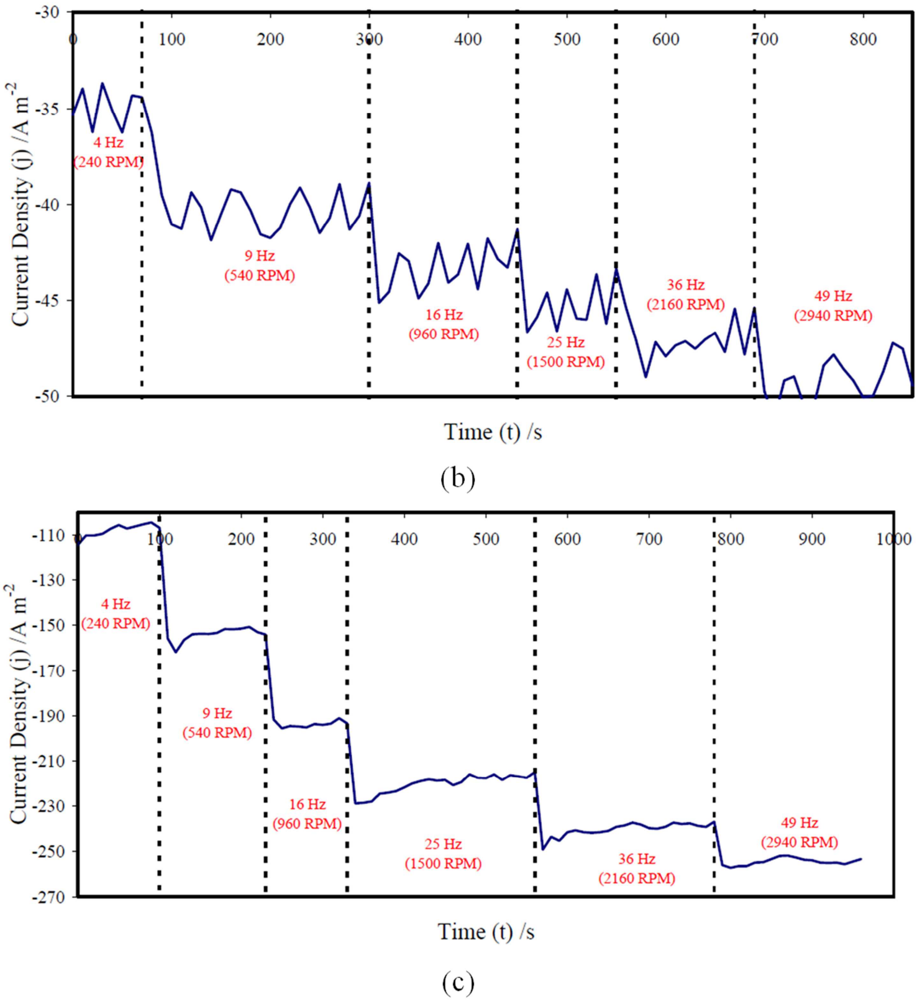


Figure 5. *Current density vs. time: (a) -0.7V (b) -1V (c) -1.5V.*

The average stationary current density values for each of the six rotation rates were recorded for the potentials: 0.70 V, -1.00 V and -1.50 V and plotted against the square root of the rotation frequency (*f/Hz*). The predicted current densities for various rotation rates *via* the Levich equation, *i.e.*, equation (5), were also plotted. The current densities for the O_2 to OH^-, and of the $[Cu(Y_{-4H})]^{2-}$ to Cu^0 equilibria, were calculated and then summed to give the total theoretical current density for the system. Data used in the Levich calculation is tabulated in Table 2.

Table 2. *Numerical values in S.I. units for parameters for the Levich calculation.*

Variables	**O_2 evolution**	**Cu deposition**
n	4	2
A_e (m^2)	2.29 x 10^{-5}	2.29 x 10^{-5}
D (m^2 s^{-1})	1.7 x 10^{-9}	5.3 x 10^{-10}
v (m^2 s^{-1})	1.3 x 10^{-6}	1.15 x 10^{-6}
$C_{anolyte}$ (mol m^{-3})	0.2	47.2

Figure 6 shows the experimental current densities *vs.* square root rotation rate at different electrode potentials, and the Levich based predictions. The most significant observation is that the current densities are far lower than the values predicted by the Levich equation, a direct indication that the process is predominantly kinetically controlled. As the gradient of the result's line increases towards that of Levich's predicted line, mass transport control becomes more predominant. As expected, the gap is reduced as the potential becomes more negative, since the process is obviously moving closer towards total mass transport control. From Figure 6 the non-linear relationships indicate that kinetic controlled mechanisms outweigh mass transport in the mixed controlled system.

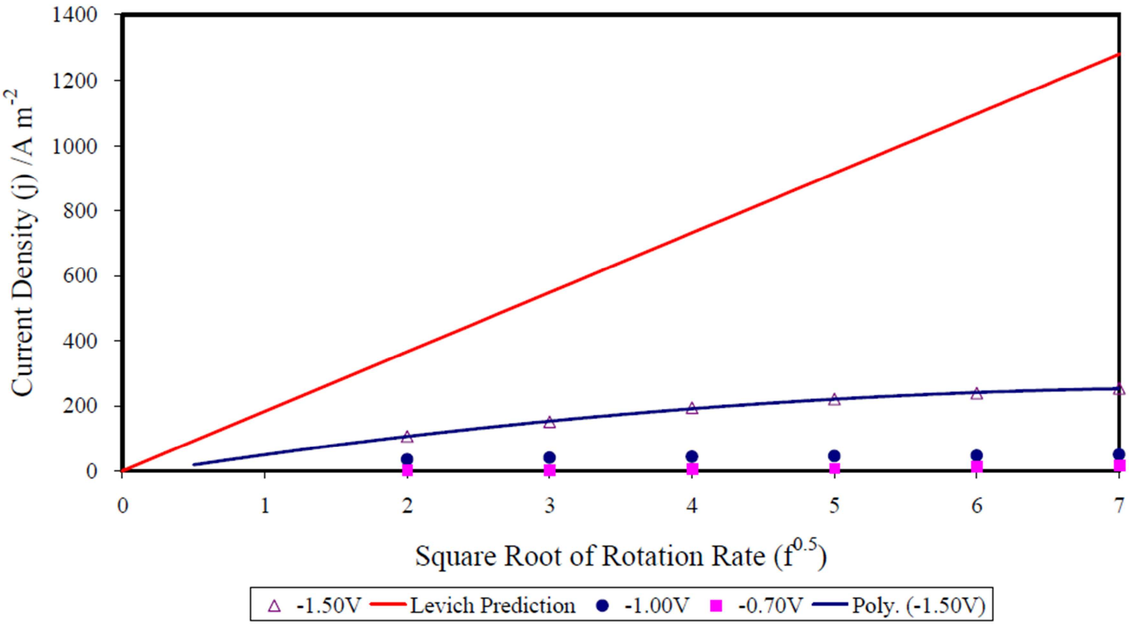


Figure 6. *Experimental current densities versus prediction using the Levich Equation.*

Even at an electrode potential as negative as -1.50 V, initially considered to be in a primarily mass transport controlled region, the data is curved as highlighted by the trend line. However, the first three values (1st three points) of the square roots of frequency, $(f)^{0.5}$ = 2, 3 and 4 respectively, appear to exist in a linear relationship indicating a degree of mass transport control. However, the curvature at the end of the line hints at kinetic influence, and that the overall plating process is still controlled in a mixed fashion. Even at -2.0 V, it was discovered that total mass transport was not attained. At this juncture of events, the voltage is so negative with respect to the nominal value of -1.0 V for hydrogen production that no further significant information is expected to be gained by delving into more negative regions. Lastly, it can be argued that mass transfer across the boundary layer is enhanced by bubble release. Conversely, entrapment of a bubble on the surface creates a region where electrodeposition is difficult. In practice, hydrogen bubbling enhances plating kinetics, unfortunately accompanied by substantial wastage of electrical energy.

The works of Allen & Chen [9] and of Juang & Wang [13], which contributed much to the understanding of copper recovery from EDTA solutions, have been mentioned earlier. The publications from these two groups (and others) belong to a genre of literature which focuses on proof of technological feasibility, carried out at a voltage that will not induce H_2 evolution, although the determination of the optimal voltage was not their immediate concern. This is not a deficiency in theory or understanding, only that the emphasis of the laboratory exercise is different to the one here. Nonetheless, literature pinpointing to the idea of an optimized voltage which can be readily applied to an electrochemical reactor for the purpose of wastewater treatment is extremely rare. In any case, the conditions for electrodeposition of copper carried out by the former group are vastly different to those encountered in this work. For example, the pH value at the commencement of plating using a copper cathode was 3.2, increasing to the final value of 12.7 over a time span of 221 minutes, and the voltammetric half-wave reduction potentials (SCE) were -0.20 V for the metallic ion in the presence of EDTA (in the acidic region where Cu^{2+} ions are not fully sequestrated) and -0.59 V for single protonation of the copper-EDTA complex itself [9]. At these potentials H_2 production is not likely to occur. The latter group of workers did recognize that "increasing the current density results in an increase of metal recovery, but a decrease of current efficiency owing to a greater extent of side (*i.e.*, competitive) reaction such as the evolution of H_2" [13]. They posited that "there is an optimal current density with respect to two such factors at a specific condition, including the electrolysis time and the environments of catholyte such as pH and complex concentration". They did, however, propose a two-step process, *i.e.*, de-chelation followed by plating: $[ML]^{2-} \rightarrow M^{2+} + L^{4-}$, then $M^{2+} + 2e^{-} \rightarrow M$ (*s*). The standard reduction potential for the plating step (Cu^{2+}/Cu) *vs*. Standard Hydrogen Electrode (SHE) is -0.126 V. The comment about H_2 evolution was the closest ever to the fundamental concept of this work.

The results presented in this present work have shown that knowledge and insight in this area can be augmented, and the best types are the ones linked to the economics of operational performance directly. Indeed, the cost implications of these results are as follows. It is plausible that highly negative potentials are needed for the system to enter into a state of total mass transport control instead of mixed mode control due to the chemical nature of the chelated complexes themselves. One can tentatively hypothesize that de-chelation of the complexes is the rate determining step, rather than the diffusion of complexes through the boundary layer. This may explain why the potentials must be so negative before the mass transfer mode can be recognized within the results.

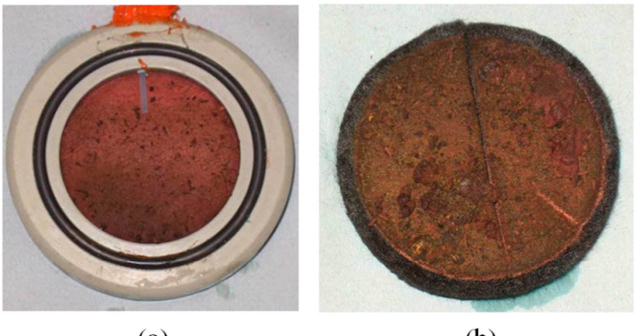
The technological implication is that, on supplying a huge increment in electrical energy the copper can be removed rapidly and the separation of copper ions from EDTA no longer limits the rate of the process as much as the passing through the diffusion layer.

This investigation reveals that an electrochemical reactor for the treatment of wastes containing metal-EDTA complexes in alkaline solution is compelled to operate in a predominantly kinetic controlled mode, which ensures that the potential is not too negative, thereby reducing the amount of hydrogen produced. Although this process reduces the overall plating rate, for which larger reactor volumes can compensate, an increase in capital costs ensues. The reduction in hydrogen production signals a reduction in operational costs which account for the bulk of the costs associated with the process over its lifetime. In summation, operating in a predominantly kinetic controlled zone appears to be the more economically attractive option.

For equipment design engineers, the other important economic issue is the choice of the type of power source for the electrolysis cell. The supply of electricity by transformer-rectifiers is considerably cheaper than that of potentiostats, which offer the option of the control of electrode potential. Typically, the cost differential can be up to ten-fold. However, if a continuous electrochemical reactor is to be constructed, then the use of the potentiostat can hardly be justified. Except for the starting-up and shutting-down operations, a continuous reactor functions in the steady-state, and the cheaper constant voltage source will suffice. To be ensured is that the distributions in electrode potential and current density are acceptable.

5.2. Electrodeposition Copper Products and Copper Recovery Kinetics

Products produced by the reactor's operation are presented here in pictorial form. The first indication that copper has been plated appears when the reactor is disassembled, the anolyte section of the reactor removed, and the cathode of diameter = 54 mm is exposed for visual inspection, Figures 7(a) and 7(b).



(a) (b)

|------- 54 mm -------|

Figure 7. *Images of copper deposits on cathodes of 54 cm diameter, (a) and (b).*

In the reactor system, copper is present *either* in the aqueous *or* solid phase. The Law of Conservation of Mass demands that the total number of Cu atoms within the system remains constant, *i.e.*, a decrease in the aqueous phase concentration with time (see Table 3) means a concomitant deposition of Cu^{2+} (*aq*) ions to become a solid film of Cu^0. The presence of copper could be confirmed by scanning electron microscopy (SEM) and the associated technique of energy dispersive x-ray spectroscopy (EDX), but their use is unnecessary on this occasion since there is no other metal in the solution that could be deposited.

Definitions for R_{Cu}, η_{Cu} and R_{EDTA} have already been given at the beginning of this paper and use is now made of them to address copper recovery. The "concentration of Cu^{II} ions *vs.* time" behavior in the waste solution was determined as electroplating proceeds using Optical Emission Spectrometer (Perkin-Elmer Instruments, Optima 2000 DV). The mass balance for copper atoms is such that the amount reduced in solution is equals the amount deposited, so that at any time t > 0 the cumulative recovery R_{Cu} can be simply calculated as:

$$R_{Cu} = 1 - ([Cu^{II}]_{t=t} / ([Cu^{II}]_{t=0}) \qquad (10)$$

In Table 3 is listed the results with the reactor's operational time period at which each sample was taken. The parameter $(R_{Cu})_{t=t}$ is then plotted against time. After 226 minutes, the recovery was 30.9%. This is equivalent to an average of 8.2% recovery per hour. Therefore, complete recovery is estimated to take about 12 hours, by linear proportion.

The results from Parts (A) and (B) of this set of experiments complete the quest for an optimal potential for this electrochemical separation process. Technical feasibility of electrodeposition under prevailing conditions together with a detailed and an informative inquiry into overall kinetics are shown.

Table 3. *Cumulative recovery $(R_{Cu})_{t=t}$ as a function of electrolysis time (t).*

Time, *t* (min.)	$[Cu^{II}]_{t=t}$ (mass conc., g dm^{-3})	Cumulative R_{Cu}
0	3.10	0%
60	2.99	3.5%
132	2.57	17.0%
217	2.23	28.0%
226	2.14	30.9%

5.3. Extended Discussion of Electroplating

Discourses on electrodeposition phenomenology in the manufacturing industries deserve attention since there are relevant concepts which need emphasis. The total mass of metal deposited on a particular surface of finite area depends primarily on the magnitude of the applied electric current, the amount of time allocated for plating, and the efficiency with which electrons are transferred from cathode to metallic ion, all linked up by the simple expression: $m_{total} = i \times t \times \eta_{cathode}$. The current is determined by the applied voltage and the electrical conductivity of the aqueous solution. For an object of irregular shape, the actual thickness of the deposited material on an infinitesimal area depends heavily on the current density (units of A m^{-2}) at that localized point. The current density at a point, in turn, depends on how current is partitioned over the entire surface, but this is influenced by the shape of the object itself. Except for "small" (relative to the dimension of the opposite electrode) flat sheets to be plated, 3-dimensional objects (such as machinery parts) have protrusions that are in closer propinquity to the anode than the recessed or "hidden" areas, a coating of even thickness over the entire target object is not easy to achieve. The current density is larger at prominences due to the shorter distance between cathode and anode, implying a lower overall resistance to current flow, which is just another name for the transport of charged species. The prominent protruding points therefore enjoy a thicker coating. Owing to the fact that 3D geometry exerts the greatest influence on localized current densities, current apportionment is synonymous with spatial distribution of depository abundance.

Besides geometric factors, metal distribution is affected by cathode polarization, the relationship between current density and cathode efficiency, and the electrical conductivity of the solution. Polarization potential develops because of the electron-transfer reactions and other interfacial processes occurring on an electrode, and depends on the rates of these reactions, *i.e.*, the current density (A m^{-2}). The complex relationship between these combined factors which govern current distribution and hence metal distribution is called "throwing power". A method for the measurement and mathematical expression of "throwing power" is the Haring Cell test [39].

An electroplating system with good "throwing power" can deposit metal with uniform thickness over the entire object, and such is the case with alkaline copper cyanide baths, which enjoys high cathode polarization and a favorable relationship between current density and cathode efficiency (cathode efficiency is low at higher current densities). The opposite is true for acidic copper sulfate baths, where the "throwing power" is poor because cathode polarization is low and efficiency is extremely high. In general, a plating solution that exhibits a decrease in cathode efficiency as current density increases exhibits better "throwing power", *i.e.*, more even plate thickness distribution, than other solutions. A rule-of-thumb amongst practioners in the art of electroplating is such that the solutions having positive "throwing power" are those that contain some complexing/chelating agent for the metallic ion being deposited. Chelants are used intentionally to impede the transfer and reduction of the metal ion in the cathode film, promoting concentration polarization. Mizumoto *et al.* [40] reported excellent throwing power on a mini-scale in the electroplating of copper, from Cu-EDTA, in the manufacture of Printed Wire Boards (PWB). The recipe of the plating solution includes KCl, glycine and formaldehyde. Albery [41] commented upon a noticeable delay in the reduction step ($Cu^I \rightarrow Cu^0$) in a $CuCl_2$ bath (in the absence of CN^- and EDTA) and attributed this to the stabilization of Cu^+ by Cl^-. The possibility of formation of the inorganic diatomic intermediate $[Cu\text{-}Cl]^0$ has not been discarded. Incidentally, no such delay was observed in a sulfate bath, it was reported [41].

It is worthwhile to note that cathodic concentration polarization has great propensity to cause the evolution of hydrogen as a competing and therefore energy-consuming reaction. As pH of the cathode film edges towards the alkaline region, insoluble metal hydroxides may form (when the solubility product is reached or exceeded) and be occluded in the fabric of this film. The inclusion of hydrogen may cause brittleness of the deposit and, by migration into the substrate, also results in its embrittlement. Hydrogen overvoltage, *i.e.*, the polarization for the specific reaction discharging hydrogen at a specified electrode, is a two steps process, production of hydrogen atoms which are adsorbed on the electrode surface, followed by formation of gaseous hydrogen and its evolution. The latter step is rate-determining, and a higher potential is probably needed to expel the gas.

For a while, industrial technologists found themselves in the interesting if not paradoxical situation whereby the use of complexants is *sine quo non* to the workability of the technology and in quality control, and yet the presence of thermodynamically stable metal chelates offer them one of the most difficult problems in wastewater treatment to be solved.

5.4. Scrutiny of Contemporary Research Tendencies Linking Mechanism Elucidation to Instrumental Methods of Surface Analysis

Etymology of the word "mechanism" reveals that it originated from the Greek "mecha", meaning "contrivance". The Oxford Dictionary defines contrivance as "a thing which is created skillfully and inventively to serve a particular purpose". Currently, "mechanism" has two meanings. The first one is philosophical in nature. It is the notion that all processes within the physical world conform to the laws of physics and chemistry. The second meaning is that a particular process can be envisaged as if it is composed of components which fit together to predict all the essential observations from first principles as a direct and inescapable consequence of the components of the mechanism. Put simply, it implies that any physical and chemical phenomena conforms to the Newtonian idea of the clockwork universe and the mechanism as described needs merely to be activated (the metaphor is to wind up the clockwork) to predict the physico-chemical aspects, behaviors and outcomes of the system.

Therefore, for a hypothesis or a model of metal deposition, *e.g.*, nucleation which, incidentally, is not the theme of this work because it need not be, to be properly described as a mechanism, it must be able to predict all the key associated phenomena. Paramount among these is the identity-specific nature of many species in aqueous solution. In general, the species conditions in the aqueous phase are adequately described by Pourbaix diagrams such as the one introduced in this work, but in much of surface science there is simply no universally accepted pathways which explain or predict the species-specific nature of these phenomena. At the liquid-solid interface, complex intra-molecular electronic rearrangements happen. Being able to characterize the mere appearance of the deposited film and taking snapshots of the shape it adopts when it grows (*e.g.*, by high-resolution microscopic examination), together with tests for adherence, texture and resistance to mechanical wear and chemical attack of a film does inform one of the electrochemical reaction pathway in the aqueous phase, or "why" and "how" a deposit has assumed such properties. The propwerties are only there to be tested.

Moreover, as an extra example to illustrate the point, and on the same argumentative parlance as above, there are similar difficulties in understanding the surface phenomena of corrosion which needs elucidation. Prevention of corrosion is the order of the day in industry albeit much remains unknown, but this does not stop deep-sea drilling for oil and crude petroleum processing. The reasons why stainless steels are pitted by chloride and bromide ions but not fluoride, but commercial aluminium is pitted by all three ions, requires investigative research. Another mystery is the thermal oxidation of metallic uranium occurring at low temperatures even though the "protective" surface oxide layer adopts a close-packed configuration.

In these cases, all that can be done is that a mechanism is constructed (apply again the meaning of "mechanism" to mean contrivance) and then allowed to act on a description of the system to predict the observable phenomena without imposing any constraints arising from individual measurements. Application of the mechanism to the real system should produce a self-consistent prediction of a set of observable and testable phenomena, the majority of which are well established in the literature as characteristic of that particular type of material deposition on a surface, and of corrosion. A particular mechanism is validated by its ability to predict most or all of these observations. It is therefore at odds with the assertions by advocates of certain instrumental techniques, which allege to have "proven" a particular "mechanism" by providing "crucial evidence". A true mechanism simply does not rely on one technique alone for validation. The Scientific Method demands that it should not.

Scientists cannot stipulate advocating a particular instrumental method of analysis to "prove" a mechanism of electrodeposition, unless they can demonstrate beyond reasonable doubt as to why that technique is essential, in which case they need to justify the emphatic assertion being made. If they cannot, then it could be implied that their interest is in the study of a particular instrumental technique for its own sake and not to elucidate the underlying mechanism. In the authors' view, "mechanisms" arising solely from a wish to deploy certain techniques are not really mechanisms.

The authors utilize SEM, XRD and EDX regularly for research but this is not the occasion for this set of methods to be deployed. The present work is built on clear objectives, which in turn circumscribes it within the focus on a single-parameter optimization in order to benefit process design, a core activity in chemical engineering.

6. Future Work

Firstly, the authors wish to scale up the electrolytic process to become a pilot plant facility and operate it with the voltage identified in this work, treating real-life wastewaters from the printed circuit board industry and recovering copper. A parallel project aims at recovering EDTA for reuse is being considered.

Secondly, much enthusiasm is being shown by colleagues in applying adsorption techniques for the treatment of effluents which contain copper ions, EDTA or chelated complexes thereof. Here are a few examples. Zou *et al.* synthesized nanoparticles of $CoFe_2O_4$ with EDTA attached, allowing the organic ligand to sequester Cu^{2+} ions, a contaminant [42]. Adewuyi & Peirera also "functionalized" Adansonia digitata seeds from Nigeria with EDTA to do the same task [43]. Fan *et al.* synthesized nano-composites of Fe^0 and graphene oxide (in reduced form) for removing Cu^{2+} ions [44]. Jilal & Barkany had entertained the idea of grafting EDTA onto hydroxyethyl cellulose for the removal of Cu^{2+} and Pb^{2+} ions [45]. Larsson *et al.* employed diatomaceous earth particles modified by glutaraldehyde-polyethyleneimine to remove dissolved copper in acid mine drainage [46]. All these materials are effective adsorbents which can be packed into columns designed by chemical engineers for continuous separation processes aimed to remove the vestigial remnants of the metallic ion populace which was freed from ligand bondage.

The questions are the ones about determining the break-through curves, estimating the necessary frequency of regeneration and maintenance of the packed bed, and what the management options will be for the backwash water which will now contain desorbed hydrated Cu^{2+} ions. Both the technical feasibility and economics of such sorption systems have to be examined holistically, and will be part of the mainstay of future work.

7. Conclusions

The optimal operating voltage for the electrochemical recovery of copper from a simulated wastewater containing 0.001 mol dm^{-3} of Cu^{2+} ions, and excess EDTA, has been identified. The rate of recovery is 31% within 4 hours, under the conditions of pH = 10.7, and an electric potential of -1.0V. The reactor was operated at this potential in order to minimize hydrogen evolution while maintaining an acceptable rate of copper plating. For practitioners of copper recovery, this potential is recommended for testing in the conceptual design stage of an electrochemical reactor. A Pourbaix diagram for the Copper-Water-EDTA system was constructed and its predictions were in general agreement with the observed behaviour of the system. The mode of rate-control of plating is mixed, but is predominantly under the influence of kinetic control rather than mass transport control, even at electric potentials as low as -1.5V. Future work has been recommended.

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