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Concentrating, refining and purification by means of rotating bipolar electrode cell

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The use of a 'rotating bipolar electrode' (RBE) cell to achieve a transfer of a substance (copper) from solutions of low concentration to high concentration is described. The RBE cell employed consists of a central, rotating, cylindrical electrode, surrounded by axial wiper blades which form three compartments through which the electrode surface passes during rotation. An outer electrode in each compartment governs the potential of the rotating electrode, and copper is deposited on the electrode surface in two of the compartments, and stripped in the other. Stripping can be achieved by either electrochemical or chemical means. Very high compartment concentration ratios (> 250) can be achieved and sustained by using cells with more than two compartments. The process can be operated with conditions thermodynamically more advantageous than possible with conventional cells. Typical costs for a RBE cell process are given.

1. Introduction

We have recently carried out a study [1] of a novel type of electrochemical cell employing a 'rotating bipolar electrode' (denoted by 'RBE'). Cells of this type can offer many unique advantages including the ability to effect a 'continuous activation' of the electrode surface to control the current efficiency and selectivity of some electrode reactions, and to transfer a substance from a solution of low concentration to one of high concentration. We report here on the latter ability of a RBE cell. Such a transfer of substance is a central and necessary part of many concentrating, refining and purification processes.

The RBE cell used in this study consisted of a central, cylindrical rotating electrode surrounded by three axially located wiper blades. These wiper blades serve to form three electrically isolated compartments through which the electrode surface passes during rotation. An outer electrode in each compartment governs the potential of the rotating electrode, and in this fashion the rotating electrode can be made monopolar, bipolar or tripolar, and conditions similar to potential and current pulsing can be obtained using steady-state potentials and currents. A detailed description of the construction of the cell and an overview of the study has been given elsewhere [1, 2]; a sketch of the cell showing the configuration and important dimensions is presented in Fig. 1. One other cell employing the rotating bipolar electrode principle has been described in the literature [3], however, no additional information regarding this cell is available to the authors at this time.

For the purposes of illustration the (Pt)Cu/Cu^{++}, $H_2SO_4(O_2)$ system has been selected. With this system the transfer process involves copper, and takes place by adsorption of copper on the rotating electrode in one compartment followed by stripping in another. The processes taking place at the inner rotating electrode are shown in Fig. 1. The central rotating electrode was platinum, the electrolyte was 0·05 mol dm^{-3} H_2SO_4 and contained varying amounts of Cu^{++} ($10^{-5} - 10^{-2}$ mol dm^{-3}), and oxygen was bubbled through the electrolyte (4·6 cm^3 s^{-1} per compartment). The electrode rotation rate was relatively slow, and varied from 0·22–1·51 rad s^{-1} (1 revolution per 32 s to 1 revolution per 0·42 s). Unless otherwise stated, potentials are given with respect to the RBE, and current densities (cds) with respect to the real surface area

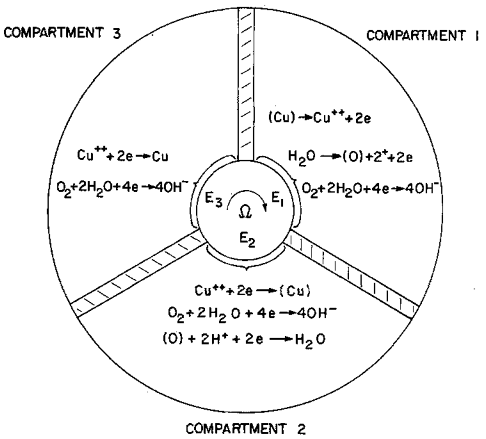

Fig. 1. Sketch of the rotating bipolar electrode cell (top view). Dimensions: radius of rotating electrode = 1·858 cm, radius of outer electrode = 10 cm, width of wiper blades = 1·38 cm, height of inner electrode = 12·5 cm, total geometric area of rotating electrode = 145·8 cm^2, geometric area of outer electrodes = 114 cm^2 (per compartment). Reactions taking place at inner electrode during transfer of Cu^{++} from compartments 2 and 3 to compartment 1 are shown.

exposed in each compartment. Determination of Cu^{++} in solution was carried out by atomic absorption spectrophotometry with a Perkin Elmer 303 spectrophotometer.

The important features of this system can be summarized as follows. The standard electrochemical potential for the reaction

$$Cu^{++} + 2e \rightleftharpoons Cu \qquad (1)$$

is 0·3 V NHE [4]. The reversible potential (E_{rev}) is dependent on the concentration of Cu^{++} and for dilute solutions will normally lie in the range 0·2–0·3 V NHE. Deposition of appreciable amounts of Cu (more than one monolayer) will take place at potentials somewhat less (i.e. cathodic) than these. However, submonolayers of Cu [denoted here by (Cu)] are deposited at 'underpotential' [5–11], that is, at potentials more *anodic* than the reversible potential, in the potential region $E_{rev} < E < 0{\cdot}8$ V. This apparent violation of thermodynamics has been discussed by Byrnes and Rogers [12] who show that such deposition is energetically feasible if Cu atoms adsorbed on an inert surface are more stable than Cu atoms in the Cu lattice. Usually it is found that deposition is under kinetic control [7, 13] if the bulk Cu^{++} concentration (c_b) is greater than 10^{-3} mol dm^{-3}, and is under diffusion control [6, 9, 11] if $c_b/r_f < 10^{-4}$ mol dm^{-3} (where r_f = roughness factor of the electrode surface). Cu dissolution or stripping takes place rapidly in the region $E_{rev} < E < 0{\cdot}8$ V, and is independent of the Cu^{++} concentration. Stripping is essentially complete at 0·8 V [8]. Stripping of Cu can also take place by dissolved oxygen in solution (i.e. [14]) via a catalytic chemical reaction, and can be thought of in terms of two electrochemical reactions: oxidation of Cu via Reaction 1 above, and reduction of oxygen via the reaction:

$$O_2 + 4e + 4H^+ \rightleftharpoons 2H_2O. \qquad (2)$$

Such chemical stripping takes place at open circuit, and the electrode assumes a potential governed by the relative rate of the electrode Reactions 1 and 2. If the electrode is maintained at a relatively cathodic potential ($E < 0{\cdot}75$ V), oxygen is rapidly reduced (Reaction 2) under diffusion limiting conditions. In this situation the concentration of oxygen at the electrode surface is effectively zero, and presumably does not affect the deposition of Cu (little work appears to be published regarding the latter point).

1.1. *Description of the transfer process*

In the rotating bipolar electrode cell, the various processes involved in the transfer of copper from one compartment to another are summarized in Fig. 1. In compartments 2 and 3 the electrode potential is relatively cathodic ($< 0{\cdot}75$ V, in this work it was maintained at 0·1–0·2 V), and copper is deposited on the rotating electrode surface. In compartment 3 the electrode is anodic (in this work 0·8–1·2 V) and the copper is stripped from the electrode surface. At the latter potentials an oxide film is also formed on the electrode surface; this is reduced in compartment 2 at cathodic potentials ($< 0{\cdot}45$ V). This process, together with the charging of the double layer, serves to augment the currents in compartments 1 and 2 and lower the efficiency of the overall process.

It can be seen that the transfer process described here relies only on maintaining the differing potentials in the compartments. Oxygen is not necessary for the process, although it does serve to agitate the solution and increase the rate of deposition of Cu. However, an alternative mode of operation is to maintain a cathodic potential in compartments 2 and 3 as above, and to simply short-circuit the electrodes of compartment 1 or operate the compartment at open-circuit. In this situation stripping is achieved by a chemical or combined chemical-electrochemical process. This has the advantage of requiring only one power supply for the cell for compartments 2 and 3.

2. Experimental results

To illustrate the transfer process the results of two sets of experiments will now be described. In the first set the initial concentration of Cu^{++} in all compartments was approximately 10^{-5} mol dm^{-3}, the outer electrodes of compartments 2 and 3 were connected together, and the potential of the rotating electrode in compartments 3 and 1 was maintained at 0·1 and 1·2 V, respectively. The electrode was rotated at 0·94 rad s^{-1} (1 revolution per 7 s) and with time Cu^{++} is transferred from compartments 2 and 3 into compartment 1. A typical result is shown in Fig. 2: after about 3·2 hours the concentration of the copper in compartments 1, 2 and 3 was $4{\cdot}3 \times 10^{-5}$, 3×10^{-6} and 7×10^{-7} mol dm^{-3}, respectively.

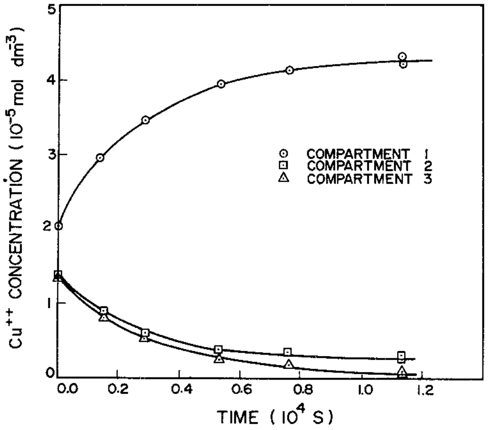

Fig. 2. Concentration of Cu^{++} in the compartments versus time. (Experiment 1).

In the second set the initial copper concentration was approximately 10^{-3} mol dm^{-3}, the rotation rate 0·78 rad s^{-1}, and the electrode potential in compartments 2 and 3 was maintained at 0·2 V. Rather than controlling the potential in compartment 1 however, the rotating electrode and the outer electrode were simply connected via a 5 Ω resistor. The compartment was thus effectively short-circuited, and stripping took place by a combined chemical-electrochemical process. Copper transfer took place in a similar way to the first experiment, and in a typical run after approximately 6 h the concentration of Cu^{++} in compartments 1, 2 and 3 was $2{\cdot}15 \times 10^{-3}$, $1{\cdot}1 \times 10^{-4}$ and $8{\cdot}5 \times 10^{-6}$ mol dm^{-3}, respectively, as shown in Fig. 3.

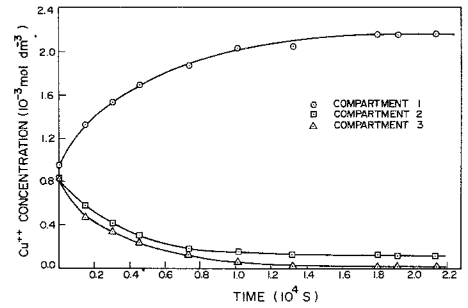

Fig. 3. Concentration of Cu^{++} in the compartments versus time. (Experiment 2).

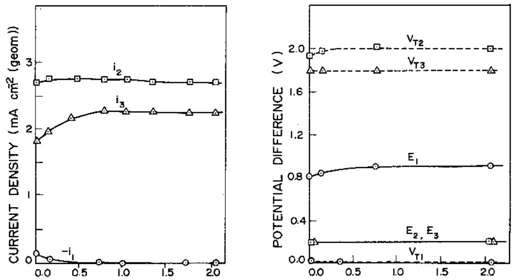

Fig. 4. Compartment terminal voltages (V_T), rotating electrode potential (E, V RHE), and current densities (i) versus time. (Experiment 2).

These experiments clearly illustrate the transfer of copper from solutions of low concentration to solutions of high concentration by the RBE cell, and in addition, the ability of effecting the stripping step by a chemical-electrochemical process. We have obtained concentration ratios as high as 30 for adjacent compartments (with the electrode travelling from the more concentrated to the less concentrated), while ratios of 250 were observed for compartments separated by a third. In fact, in obtaining the latter ratio a full equilibrium was not attained, and even higher concentration ratios could be achieved. It can be said that a multi-compartmental cell is much superior than a simple two-compartment cell in its ability to achieve and sustain high compartment concentration ratios.

The variation of the cell currents, voltages and electrode potentials associated with the second set of experiments is shown in Fig. 4. Initially the currents and voltages vary slightly with time; this happens because the concentration and deposition rate of copper in compartments 2 and 3 are relatively high, and the rate of oxygen reduction taking place in these compartments is somewhat inhibited. At longer times less copper is deposited, and the rate of oxygen reduction increases. The current density in compartment 1 (measured via the 5 Ω resistor) decreases with time and represents the amount of copper being stripped, with minor contributions from oxide formation and double layer charging. The potential of the rotating electrode in compartment 1 stabilizes at approximately 0·9 V.

A simple experiment was carried out to determine the rate of stripping of Cu by oxygen under short-circuit conditions, and at open-circuit. A known amount of Cu was deposited first on the electrode surface (by treatment at 1·2 V for 30 s, followed by 0·3 V for 60 s), and then the coverage of the electrode was measured at varying times in an open-circuit and short-circuit configuration. Since it is difficult to determine the extent of copper coverage directly by conventional galvanostatic or potential-sweep techniques in the presence of a large background oxygen reduction current, the inhibition of the oxygen reduction rate $(i_0 - i_t)/i_t$ was taken as a measure of the copper coverage. Here i_0 and i_t represent the uninhibited and inhibited rate of oxygen reduction, respectively. Complementary potential sweep measurements were carried out and although approximate in nature they qualitatively confirm that the inhibition is directly dependent on the copper coverage. The variation of inhibition (or copper coverage) with time at open-circuit and short-circuit is shown in Fig. 5. For comparison, the inhibition associated with copper deposition at 0·3 V is also shown. As expected, inhibition decreases quite rapidly with time at open circuit, and even more rapidly at short-circuit. It can be seen that about 90% of the deposited copper is stripped off in about 5 s. The measurements, together with the results of the second set of experiments, confirm that chemical stripping is quite rapid and does present a valid alternative to an electrochemical stripping process. Of course in the RBE cell, the effectiveness of a chemical stripping process depends on several factors besides the stripping time, such as the amount of the substance deposited, and the rate at which the chemical reaches the electrode surface.

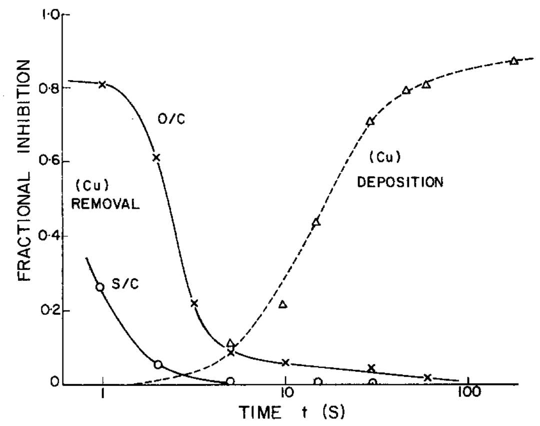

Fig. 5. Stripping of deposited copper (as measured by the inhibition of the oxygen reduction reaction) at open-circuit and short-circuit by dissolved oxygen. 10^{-4} mol dm^{-3} Cu^{++} + 0·05 mol dm^{-3} H_2SO_4; electrode stationary, oxygen rate = 4·6 cm^3 s^{-1} per compartment. Details of curves: inhibition shown results from an anodic pretreatment at 1·2 V RHE for 30 s followed by (○) 60 s at 0·3 V RHE, t s as short-circuit; (×) 60 s at 0·3 V RHE, t s at open-circuit; (△) t s at 0·3 V RHE.

3. Analysis of the transfer process

The transfer from compartment to compartment can be better understood by carrying out a mass balance on the ith compartment of a multicompartment RBE cell:

rate of removal = rate of deposition +

rate of leakage (via electrode-wiper gap) (3)

$$-\frac{dc_i}{dt} = \frac{r_0}{c_0}c_i + \frac{L_e R \Omega g}{2V_{\text{compt}}}(c_i - c_{i-1}). \quad (4)$$

In this equation, c_i = bulk copper concentration at time t in the ith compartment (mol dm^{-3}); c_0 = initial bulk copper concentration (mol dm^{-3}); r_0 = rate of deposition when $c_i = c_0$ (mol dm^{-3} s^{-1}); L_e = depth of the electrolyte in the compartment; V_{compt} = volume of the electrolyte in the compartment; g = effective gap between the inner rotating electrode and the stationary wiper blade; R = radius of the rotating electrode, and Ω = angular rotation rate of the electrode (rad s^{-1}). If all the compartments are initially at the same concentration and the effective gap size is small, then the rate of leakage will also be small. In this case the initial rate of mass transfer from compartment to compartment will depend only on the rate of deposition:

$$-\frac{dc_i}{dt} = r_0. \qquad (5)$$

In turn, the rate of deposition is dependent largely on the electrode potential, when under conditions of kinetic control, and on the electrode rotation rate, agitation of the electrolyte, and concentration, when under conditions of mass transfer control. It was found in this work that deposition was under mass transfer control when the copper concentration was less than 10^{-2} mol dm^{-3}. (In this last regard, the mass transfer process at a wiped, rotating cylindrical electrode is the subject of a paper now in preparation.)

After long periods of operation the compartment concentrations reach a steady-state, the rate of deposition equals the rate of leakage, and the steady-state (maximum) ratio of compartment concentrations is given by:

$$\frac{c_{i-1}}{c_i} = 1 + \frac{2(r_0/c_0)V_{\text{compt}}}{L_e R \Omega g} \qquad (6)$$

$$\simeq 1 + 4\pi\left(\frac{r_0/c_0}{w\Omega}\right)\left(\frac{G}{g}\right). \qquad (7)$$

In these equations, w represents the number of wiper blades (symmetrically located), and G the annular gap between the inner and outer electrodes. It can be seen that the maximum attainable ratios can be increased by decreasing the volume of the cell compartment (or more precisely, the ratio G/g). Of course, the greatest concentration ratios can be obtained by using cells with more than one compartment for deposition. By rearranging Equation 6, an expression for the effective electrode-wiper blade gap can be obtained:

$$g = \frac{2(r_0/c_0)}{L_e R \Omega}\left(\frac{c_i}{c_{i-1} - c_i}\right). \qquad (8)$$

The effective gap size for the RBE cell used in this work was calculated by this expression, using the ratio of the concentrations in compartments 1 and 2. In experiments of several hours' length it was usually found that equilibrium was obtained between compartments 1 and 2, whereas equilibrium between compartments 2 and 3 took much longer to achieve and usually was not reached. The estimated effective gap size varied from 0·4–0·9 × 10^{-3} cm for rotation rates in the range $0{\cdot}5 < \Omega < 1{\cdot}5$ rad s^{-1}, and increased approximately linearly with rotation rate. This linear dependence is expected from standard bearing theory [15].

Table 1. *Cost of substance recovery via a RBE cell*
Assumes: Two compartment RBE cell of cost 1100 \$ m^{-2} total rotating electrode area (this cost is appropriate for conventional nickel-clad construction without labour-saving mass production techniques), deposition of substance is mass transfer controlled, and electrode is rotating at a rate which minimizes the substance recovery cost; aqueous solution of high conductivity (0·25 S cm^{-1}); July 1973 prices.

Cost per mol of substance transferred (\$ mol^{-1})	*Cell exit concentration (mol dm^{-3})*
3300	10^{-6}
3·3	10^{-3}
0·33	0·01
0·034	0·1
0·0073	1·0

Finally, it should be noted that when the electrode is rotating, often less than one monolayer of copper will be deposited; this can be expected to be the case when the copper concentration is less than 10^{-3} mol dm^{-3}. In this situation deposition can take place at 'underpotential', and it follows that from a thermodynamic viewpoint the process can be more efficient than a conventional electrochemical process involving the deposition of bulk copper. A theoretical analysis of the deposition and stripping of submonolayer copper films in the RBE cell was carried out in the principal reference [1].

4. Economics of the RBE cell

A cost study of a cylindrical RBE system in various applications [1] has been also performed and a brief summary of relevant costs is given in Table 1. For applications involving the transfer of a substance from compartment to compartment the cost (\$ mol^{-1} transferred) depends mainly on the RBE cell capital cost and the concentration of the substance. The cost is virtually independent of the fraction of the substance recovered per passage of the solution through the cell compartment. Noting, for example, that the price of copper is about 0·12 \$ mol^{-1}, it is apparent from Table 1 that the recovery of substances from solution will only be economic for relatively expensive materials at fairly high concentration (c.f. the economic exit concentration of 10^{-6} mol dm^{-3} for gold,* which has a cost of approximately 4500 \$ mol^{-1}). Generally, other electrochemical processes [i.e. 17–18] involving large surface area electrodes would appear to be more suitable for low concentration solutions.

We are at present investigating a rotating bipolar disc electrode system which promises to provide a considerably cheaper means of carrying out the substance transfer.

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* In seawater, the concentration of gold is of the order of 2–4 × 10^{-5} mol dm^{-3} [16].