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A novel method of current efficiency determination

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A simple and rapid method, based on the open-circuit decay of potential, is described for the determination of the current efficiency with which metals are electrodeposited. The advantages and disadvantages of the method are discussed.

1. Introduction

Conventional methods of current efficiency determination are either directly based on chemical analysis or weight gain or indirectly on the measurement of the amount of the product of a parallel reaction, e.g., the amount of hydrogen evolved. In the case of thin electrodeposits, these conventional methods either permit only a limited accuracy or are difficult to implement, e.g., the measurement of minute amounts of evolved hydrogen. In such circumstances, it is often possible to adopt the novel method of current efficiency determination described below.

2. Principle of the Method

The basic procedure consists of switching off the deposition current, immediately placing the plated electrode in contact with a non-passivating electrolyte in which the deposit corrodes uniformly, and observing the open-circuit decay of the electrode potential as a function of time. It will be observed that this potential, which is virtually stable as long as the deposit covers the substrate, undergoes a marked change once the substrate surface becomes exposed. The time interval, t_c on the potential-decay curve between the beginning of corrosion and the marked change of potential can be related through Faraday's laws to the weight, W, of metal deposit:

$$W = \frac{I_c t_c M}{nF} \quad (1)$$

where I_c is the corrosion current and (M/n) the equivalent weight of the metal. But, W is also related to the time of deposition, t_d:

$$W = \frac{I_M t_d \mathrm{M}}{nF} \quad (2)$$

where I_M is the partial current for metal deposition. It follows therefore that the current efficiency, *CE*, for metal deposition is given by

$$CE = I_M/I_T = \frac{I_c t_c}{I_T t_d} \quad (3)$$

where I_T is the total electrodeposition current. Since all the terms on the right hand side except I_c are known and since I_c can easily be obtained from a separate experiment (e.g., by weight loss measurements), the current efficiency can be determined with the aid of Equation 3.

3. Experimental verification

In the case of deposition from a bath in which the metal deposit tends to corrode unless cathodically protected by the plating current, the method described above becomes even more straightforward because the commencement of corrosion corresponds to the cessation (by switching-off) of the deposition current. In short, the transfer of the plated electrode to a corrosive solution becomes unnecessary.

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Such conditions are satisfied by the electrodeposition of manganese from a 0·2 M $MnSO_4$–1·0 M $(NH_4)_2SO_4$ bath (pH7), and therefore this plating process was used to verify the method suggested.

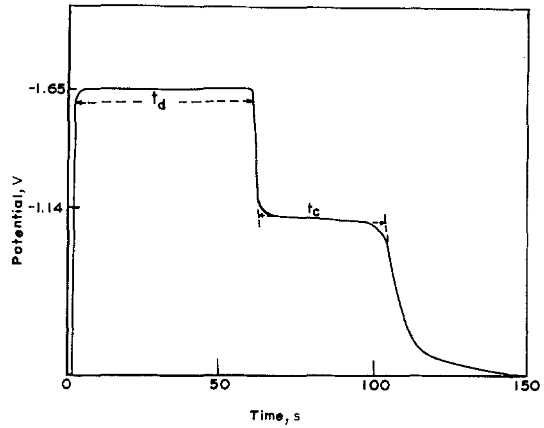

Fig. 1. Open-circuit potential decay transient for Mn deposition at current density 100 mA cm^{-2}.

A typical potential-time transient obtained on a strip-chart recorder is shown in Fig. 1. It can be seen that both t_d and t_c can be determined from the same transient. The corrosion current I_c was obtained by measurements of the weight loss of electrolytic manganese in the same solution. Precautions were taken to expose a smooth and clean surface of manganese to the solution and to keep the exposed area of the electrode the same as in the open-circuit potential-decay experiment.

A comparison of the current efficiencies obtained by conventional weight gain measurements with those obtained by the potential-decay method is given in Fig. 2. It can be seen that there is reasonable agreement between the two sets of values and there is less scatter with the potential-decay method.

4. Discussion

The chief merits of the proposed method are the ease of experimentation and its applicability to thin metallic deposits for which current efficiency determinations are otherwise difficult to carry out. The method can be employed even for metals which tend to passivate in their plating baths, but in such cases one has to carry out the potential-decay experiments after transferring the plated electrode to a solution that corrodes the metal uniformly, for example, sodium hydroxide solution for chromium deposits and potassium cyanide solution for gold deposits.

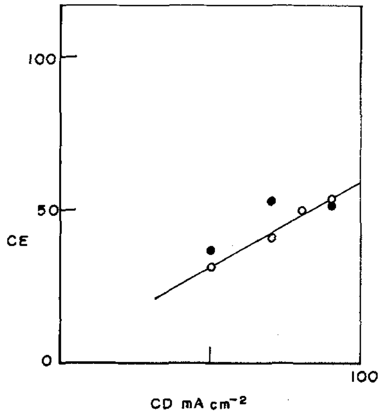

Fig. 2. Plot of current efficiency versus current density.
●, Weight-gain method;
○, Potential-decay method.

The main limitations of the method appear to be as follows: (1) in the case of relatively *thick* metallic coatings, the corrosion current may not remain constant over the entire duration of dissolution, thus introducing difficulties in the determination of t_c from the potential-decay curve and (2) the potential-decay curve can be obtained only in solutions that attack the metal uniformly without pitting or inter-granular corrosion.

The method of current efficiency determination developed here may have practical applications in industrial processes such as the electrowinning of manganese. The simplicity and rapidity of the measurement permits its use as a control check on the catholyte either in the industrial cell itself or in the tanks in which the catholyte is prepared. If the method is to be used in the industrial cell, then an assembly consisting of a substrate piece (with a defined area of exposure to the electrolyte) and a compact reference electrode is required. The assembly must be capable of being hooked on to the industrial cathodes with a switch either to make electrical contact with the cathode and thus carry out manganese deposition, or to break the electrical contact and initiate the open-circuit decay and corrosion. The quantity t_c could be found with the aid of an electrical timer (of the type used in electrodeposit thickness testers) which can be switched *on* by the cessation of the deposition current and switched off by the marked change of potential associated with the dissolution of all the deposit. If the method is used outside the industrial cell, then it must incorporate a power supply to deposit the manganese.

One important precondition for the industrial use of the method is a detailed knowledge of the corrosion currents in the baths used for electrodeposition. In the case of manganese electrowinning, however, it has been shown [1,2] that the corrosion current is virtually independent of pH, and varies about 8% for a change in selenious acid concentration from 0.05 gl to 0.2 gl. Hence, even without a detailed study of corrosion current as a function of pH, the current efficiencies can be quickly determined to within about 10%.

References

[1] P. Radhakrishnamurthy, Ph.D. Thesis (1972)
[2] P. Radhakrishnamurthy and A. K. N. Reddy, *Journal of Applied Electrochemistry,* 4 (1974) 317–321.