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CURRENT EFFICIENCY AND ELECTROCHEMICAL EQUIVALENT IN AN ELECTROLYTIC PROCESS

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ABSTRACT

Calculations of current efficiency of an electrolytic reaction and of electrochemical equivalent of the metal involved are discussed. A formula for the electrochemical equivalent of a ternary alloy is also given.

The current efficiency of an electrolytic process is that percentage of total quantity of electricity consumed, which is effectively utilised for the desired electrolytic reaction. In metal deposition, for example, the conditions of bath operation, like temperature and current density are so chosen that the current efficiency is high without the desirable properties of the deposit being deleteriously affected. A high current efficiency is desirable for any cathodic or anodic process for, only then can one be sure of the reaction concerned, proceeding unimpeded.

In cases where only a single metal is involved, the current efficiency can be determined from relevant data with a simple formula as below :

$$\text{Current efficiency (per cent)} = \frac{\text{Mass of metal deposited or dissolved} \times 100}{\text{ampere seconds (coulombs) of electricity consumed} \times \text{electrochemical equivalent of the metal}}$$

An extension of this formula to electrolytic alloy deposition or dissolution leads one to conclude that summing up of the individual current efficiencies is necessary. The formula for current efficiency of alloy deposition is given by

$$\frac{P_1 M_a}{e_1 I T} + \frac{P_2 M_a}{e_2 I T}$$

where P_1 and P_2 are the percentages by mass M_a of the alloy deposit, e_1 and e_2 the respective electrochemical equivalents and I, the current passed for a duration of T seconds, is of great help in determination of the current efficiency of a binary alloy [1].

It is well known that the electrochemical equivalent should be taken into account for calculation of the current efficiency. The formula for electrochemical equivalent

$$e_a = \frac{e_1 e_2}{e_1 f_2 + e_2 f_1}$$

where e_1 and e_2 are the individual electrochemical equivalents of binary alloy constituents and f_1 and f_2 are fractions by mass, was reported to be applicable to binary alloy deposition with 100 per cent current efficiency [2]. A close examination of the factors involved shows, however, that the electrochemical equivalent of an alloy is not connected with the current efficiency though it should be useful for determination of the latter. How can one calculate the electrochemical equivalent of a binary or even a ternary alloy and hence the overall current efficiency for its electrolytic deposition or dissolution is shown in the following paragraphs.

Let M_a be the mass of the binary alloy deposited under certain conditions. If it is assumed that e_a is the electrochemical equivalent of the alloy, e_1 and e_2 those of the constituent metals, and M_1 and M_2 their masses making up the deposit,

$$e_a = \frac{M_a}{\text{current in coulombs of electricity effectively consumed in alloy deposition}}$$

$$= \left[\frac{M_a}{\frac{M_1}{e_1} + \frac{M_2}{e_2}}\right] \qquad (\because M_a = M_1 + M_2)$$

Dividing both the numerator and denominator on the right hand side by M_a,

$$e_a = \left[\frac{1}{\frac{1}{M_a}\left(\frac{M_1}{e_1} + \frac{M_2}{e_2}\right)}\right]$$

$$= \left[\frac{1}{\frac{1}{e_1}\cdot\frac{M_1}{M_a} + \frac{1}{e_2}\cdot\frac{M_2}{M_a}}\right]$$

$$= \left[\frac{1}{\frac{f_1}{e_1} + \frac{f_2}{e_2}}\right] \qquad (f_1 \text{ and } f_2\text{, fractions by mass})$$

$$= \frac{e_1 \quad e_2}{f_1 e_2 \quad + \quad f_2 e_1}$$

Now only a simple calculation is required for determining the current efficiency of binary alloy deposition.

$$\text{Current efficiency (\%)} = \frac{M_a \times 100}{e_a \times \text{coulombs of electricity passed}}$$

$$= \frac{M_a \times 100}{\left[\dfrac{M_a \times Q}{\dfrac{M_1}{e_1} + \dfrac{M_2}{e_2}}\right]}$$

$$= \frac{M_a \left(\dfrac{M_1}{e_1} + \dfrac{M_2}{e_2}\right) \times 100}{M_a \cdot Q}$$

$$= \frac{100\,(Q_1 + Q_2)}{Q}$$

$$= 100 \left(\frac{Q_1}{Q} + \frac{Q_2}{Q}\right)$$

If P_1 and P_2 are percentages by mass of each alloy constituent and Q is taken as IT,

$$\text{current efficiency (\%)} = \left[\frac{P_1 M_a}{e_1 \cdot IT} + \frac{P_2 M_a}{e_2 \cdot IT}\right]$$

which is the same as referred to earlier.

The formula for the electrochemical equivalent of a ternary alloy can also be derived. If M_1, M_2 and M_3 are the masses of the alloy constituents and e_1, e_2 and e_3 their electrochemical equivalents respectively,

$$e_a = \frac{M_a}{\dfrac{M_1}{e_1} + \dfrac{M_2}{e_2} + \dfrac{M_3}{e_3}}$$

$$= \frac{1}{\dfrac{1}{M_a}\left(\dfrac{M_1}{e_1} + \dfrac{M_2}{e_2} + \dfrac{M_3}{e_3}\right)}$$

$$= \frac{1}{\left(\dfrac{M_1}{M_a} \cdot \dfrac{1}{e_1}\right) + \left(\dfrac{M_2}{M_a} \cdot \dfrac{1}{e_2}\right) + \left(\dfrac{M_3}{M_a} \cdot \dfrac{1}{e_3}\right)}$$

$$= \frac{1}{\dfrac{f_1}{e_1} + \dfrac{f_2}{e_2} + \dfrac{f_3}{e_3}}$$

$$= \frac{e_1 \cdot e_2 \cdot e_3}{f_1 e_2 e_3 + f_2 e_3 e_1 + f_3 e_1 e_2}$$

$$\text{Current efficiency (\%)} = \frac{M_a \times 100}{e_a \times \text{coulombs of electricity passed}}$$

$$= \frac{M_a \times 100}{\left(\dfrac{M_a \times Q}{\dfrac{M_1}{e_1} + \dfrac{M_2}{e_2} + \dfrac{M_3}{e_3}}\right)}$$

$$= \frac{M_a \left(\dfrac{M_1}{e_1} + \dfrac{M_2}{e_2} + \dfrac{M_3}{e_3}\right) \times 100}{M_a \cdot Q}$$

$$= \frac{100\,(Q_1 + Q_2 + Q_3)}{Q} \quad (Q_1, Q_2, Q_3 \text{ coulombs of electricity consumed})$$

$$= 100 \left(\frac{Q_1}{Q} + \frac{Q_2}{Q} + \frac{Q_3}{Q}\right)$$

If P_1, P_2 and P_3 are the percentages by mass of each alloy constituent, and Q is taken as IT,

$$\text{Current efficiency (\%)} = \left[\frac{P_1 M_a}{e_1 IT} + \frac{P_2 M_a}{e_2 IT} + \frac{P_3 M_a}{e_3 IT}\right]$$

$$= \left[\frac{M_1}{e_1 IT} + \frac{M_2}{e_2 IT} + \frac{M_3}{e_3 IT}\right]$$

The current efficiency is thus equal to the sum of the individual current efficiencies.

REFERENCES

1. A. Brenner, *'Electrodeposition of Alloys'*, Vol. I, New York, Academic Press (1963), p.149
2. F.A. Lowenheim (Ed), *'Modern Electroplating'*, New York, Third Edition, John Wiley & Sons, Inc. (1974), p.502.