

CURRENT EFFICIENCY OF ALLOY PLATING AND THE ELECTROCHEMICAL EQUIVALENT OF AN ALLOY

P RADHAKRISHNAMURTY

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

Electrochemical equivalent is defined in the context of the calculation of the current density of electrodeposition of alloys. In order to calculate the current efficiency of the alloy deposition process, it is necessary to know the mass of the alloy expected to be deposited per Faraday of electricity when no other electrode reaction than the alloy deposition occurs at the electrode surface. Since alloys do not have a fixed composition, in other words, since alloys do not obey the law of definite properties, it is not possible to calculate theoretically the mass of the alloy deposited per Faraday. Thus there exists no fixed value for the electrochemical equivalent of an alloy. However, the current efficiency for an alloy deposition process can easily be calculated, without any need to know or define the electrochemical equivalent of an alloy. An analysis of the alloy deposited can be obtained experimentally and the corresponding Faradays utilised can be calculated. The ratio of this quantity to the number of Faradays passed through the cell would give the current efficiency for the alloy deposition process. The above aspects are dealt with in detail in the paper.

Keywords: Alloy plating, electrochemical equivalent of alloy.

INTRODUCTION

Current efficiency (CE), is a concept of crucial importance in Electrochemistry. It is a simple concept. But its significance is not appreciated well by the scientific community in general and electrochemists in particular. This view is supported by the recent literature reports on 1) current efficiency of membranes [1,2] where the concept of transport number is used in place of current efficiency 2) current efficiency losses in bipolar cells [3], where the concept of CE is misinterpreted and misused, 3) invoking the concept of electrochemical equivalent of an alloy which serves only to make the calculation of CE more tedious.

Books on Electrochemistry [5-7] restrict the scope by applying the definition to metal deposition/dissolution process. Books on Standards do not even refer to Current Efficiency [8] or make the concept more confusing [9]. In this context it is not surprising that Current Efficiency of alloy deposition/dissolution process is defined in a complicated way and sometimes in a wrong way [8].

Definition of current efficiency

Before we deal with the CE of an alloy deposition/dissolution process, it is desirable to define of CE of a simple electrochemical reaction.

It is important to note that Current efficiency refers to electrode reactions (Half cell reaction(s)).

Let us consider a general half cell reaction,



The simplest definition of the CE of an electrochemical reaction such as given above is given by the equation [9].

$$CE_r = \frac{I_r}{I} \quad (2)$$

where I_r is the current due to the r th half cell reaction at a given electrode (anode or cathode). I is the current passing through the electrochemical cell. It is important to note that

the above definition of CE_r does not specify whether the cell under consideration is an electrolysis cell or a battery (Galvanic Cell). Therefore, the definition applies to both types of cells. It is again important to note that the above definition does not specify whether the half cell reaction is cathodic or anodic, and therefore, the definition applies to both types of reactions.

While I can be experimentally measured, I_r can not be. Therefore, the above eq. does not help us to calculate CE directly. We have to express I_r in terms of experimentally measurable quantities so that we can calculate CE , using them. I_r is given by the equation

$$I_r = \frac{n_r F d\xi_r}{dt} = \frac{n_r F dn_i}{v_i dt} = \frac{n_r F dn_i M_i}{v_i M_i dt} \quad (3)$$

It is assumed that species X_i takes part only in r th reaction and in no other half cell reaction.

Electrochemical equivalent

Let
$$\frac{v_i M_i}{n_r} = W_{ir} \quad (4)$$

The quantity W_{ir} (a constant, $\neq f(t)$) is called the electrochemical equivalent of the species i in the r th electrode reaction. Equation (4) gives the simplest mathematical definition of W_{ir} . Its value can be calculated if the reaction in which the species takes part is given. We don't need to conduct an experiment to get the value of W_{ir} . Stated in words (eqn (4)) says, the electrochemical equivalent of a substance (species), is the relative mass ($v_i M_i$) of species i per equivalent of reaction, in which the substance (species) is involved. Note that the above definition, (eqn (4)), is much simpler than the other more often used definition given by equation (5)

$$W_{ir} = \frac{m_i}{CE_r} \frac{It}{F} \quad (5)$$

From equation (3), we get

$$\begin{aligned} \frac{I_r dt}{F} &= \frac{dm_i}{W_{ir}}, \therefore CE_r = \frac{I_r dt}{F} = \frac{dm_i}{W_{ir}} \frac{It}{F} \\ &= \frac{\int dm_i}{W_{ir} \frac{\int Idt}{F}} = \frac{m_i}{W_{ir} \frac{It}{F}} \end{aligned} \quad (6)$$

where
$$\frac{dm_i}{dn_i M_i} \quad (7)$$

m_i and It can be experimentally obtained and CE_r can be calculated.

Current efficiency of alloy deposition

An expression for CE of alloy deposition or dissolution process can be derived starting from the relation

$$\frac{m_1}{W_1 CE_1} = \frac{m_2}{W_2 CE_2} = \dots = \frac{m_a}{W_a CE_a} = \frac{It}{F} \quad (8)$$

$$\therefore \frac{\sum m_i}{\sum W_i CE_i} = \frac{m_a}{W_a CE_a} = \frac{It}{F} \quad (9)$$

Let us consider the case of a binary alloy for simplicity, in which case the summation would be over two terms.

$$\frac{m_1 + m_2}{W_1 CE_1 + W_2 CE_2} = \frac{m_a}{W_a CE_a} = \frac{It}{F} \quad (10)$$

$$m_1 + m_2 = m_a \quad (11)$$

$$CE_1 + CE_2 = CE_a \quad (12)$$

$$\therefore W_a CE_a = \frac{m_a}{\frac{It}{F}} \quad (13)$$

The quantity on RHS of eq.13 can be experimentally obtained. We can, therefore, get the product of W_a and CE_a from experimentally measured quantities.

Electrochemical equivalent of an alloy

$$W_a = \frac{m_a}{CE_a \frac{It}{F}} \tag{14}$$

Equation (14) is the mathematical statement of the definition of CE of an alloy. W_a , the electrochemical equivalent of an alloy, is the change in the mass of alloy that deposits/dissolves when one Faraday of electricity passes through an electrochemical cell when the current efficiency of the deposition/dissolution process is unity.

We show below that unlike in the case of half cell reactions involving a single metal, W_a the electrochemical equivalent of an alloy, does not have a fixed value even when the reactions of alloy are given and even when $CE_a = 1$.

From equation (8), we get

$$\frac{m_1}{W_1} + \frac{m_2}{W_2} = \frac{It}{F} (CE_1 + CE_2) = \frac{It}{F} CE_a \tag{15}$$

∴ We get from equations 11, 14 and 15

$$\frac{1}{CE_a} \left(\frac{m_1}{W_1} + \frac{m_2}{W_2} \right) = \frac{m_a}{W_a CE_a} = \frac{m_1 + m_2}{W_a CE_a} = \frac{It}{F} \tag{16}$$

$$\frac{1}{CE_a} \left[\frac{f_1}{W_1} + \frac{f_2}{W_2} \right] = \frac{1}{W_a CE_a} = \frac{\frac{It}{F}}{m_a} \tag{17}$$

where $f_1 = \frac{m_1}{m_a}$, $f_2 = \frac{m_2}{m_a}$ (18)

$$\therefore W_a = \frac{W_1 W_2}{f_1 W_2 + f_2 W_1} = \frac{m_a}{CE_a \frac{It}{F}} \tag{19}$$

We also have

$$\frac{m_1 + m_2}{W_1 CE_1 + W_2 CE_2} = \frac{m_a}{W_a CE_a} = \frac{m_1 + m_2}{W_a CE_a} = \frac{It}{F} \tag{20}$$

$$\therefore W_a = \frac{W_1 CE_1}{CE_a} = \frac{\sum W_i CE_i}{CE_a} \tag{21}$$

$$W_a = \sum W_i CE_i \text{ (if } \sum CE_i = CE_a = 1 \text{ is assumed)} \tag{22}$$

It is clear from equations (19) and (22) that W_a is a function of f_1 and f_2 or it is a function of CE_1 and CE_2 whose values depend on the experimental conditions. Therefore, the value of W_a also depends on experimental conditions even when the current efficiency for the alloy deposition/dissolution process is one. In other words, while the electrochemical equivalent of a metal is a fixed quantity whose value can be calculated when the reaction is specified, without recourse to any experiment, the electrochemical equivalent of an alloy, W_a , does not have a fixed value and can not be calculated just from the reactions responsible for the alloy deposition/dissolution. Its value depends on the composition of the alloy (which is decided by the conditions of experiment) and therefore, has to be obtained from experimentally measured quantities only.

An interesting point that should be noted here is the case, when an alloy of say A and B dissolves at one electrode and deposits at the other electrode with current efficiencies at both electrodes being unity. If the rates of dissolution and deposition of the component metals are not equal then we get two different values of W_a for the alloy of A and B even with CE equal to 1.

However, CE_a itself can be obtained from the experimental quantities -- the composition of the alloy, the values of m_a and It - that are needed for the calculation of W_a . Then the question arises: What do we need W_a for? The answer naturally can not be: To calculate CE_a ! (Value of CE_a can be obtained from experimentally measured quantities without ever needing the value of W_a).

In fact the procedure that is currently practiced to get the current efficiency of an alloy involves two steps (1) calculating W_a using the equation

$$W_a = \frac{W_1 W_2}{f_1 W_2 + f_2 W_1} \tag{23}$$

(2) And (2) calculating CE_a using the equation

$$CE_a = \frac{m_a}{W_a \frac{It}{F}} \quad (24)$$

Which is circuitous and complicated with no associated benefits.

A simpler method to calculate CE of an alloy

The current efficiency of alloy deposition/dissolution process, CE_a , can be obtained using the equation

$$CE_a = \left[\frac{\frac{m_1}{W_1} + \frac{m_2}{W_2}}{\frac{It}{F}} \right] \quad (25)$$

Note that we don't need W_a to calculate CE of an alloy.

Thickness of the alloy

To calculate the thickness of the alloy, the density of the alloy is calculated from the composition of the alloy using the equation

$$d_a = \frac{d_1 d_2}{f_1 d_2 + f_2 d_1} \quad (26)$$

and then the thickness t_a , is calculated using the equation,

$$t_a = \frac{m_a}{A d_a} \quad (27)$$

Here again d_a does not have a unique value. The value of d_a depends on the composition of the alloy. We can calculate the thickness directly, using the formula

$$t_a = \frac{1}{A} \left[\frac{m_1}{d_1} + \frac{m_2}{d_2} \right] \quad (28)$$

without ever needing to calculate d_a .

Model Calculations of W_a^{10}

1. Alloy composition	Sn:Ni	=	65:35
The reactions	Sn	=	$Sn^{2+} + 2e$
	Ni	=	$Ni^{2+} + 2e$

W_{Sn}	=	118.69/2	=	59.35
W_{Ni}	=	58.7/2	=	29.35
f_1	=	0.65	f_2	= 0.35

$$W_a = \frac{59.35 \times 29.35}{0.65 \times 29.35 + 0.35 \times 59.35} = 0.453 \text{ mg/C}$$

2. Alloy composition	Sn:Ni	=	65:35	
The reactions	Sn	=	$Sn^{4+} + 4e$	
	Ni	=	$Ni^{2+} + 2e$	
W_{Sn}	=	118.69/4	=	29.67
W_{Ni}	=	58.71/2	=	29.35
f_1	=	0.65	f_2	= 0.35

$$W_a = \frac{29.67 \times 29.35}{0.65 \times 29.35 + 0.35 \times 29.67} = 0.306 \text{ mg/C} = 29.56 \text{ g/F}$$

In reference 10, W_a is calculated using an incorrect equation,

$$W_a = \sum f_i W_i = (f_1 W_1 + f_2 W_2) \quad (29)$$

which gave values of 0.505 mg/C and 0.306 mg/C of W_a in the model calculations 1 and 2 respectively, given above.

The simpler method suggested by us can be used to calculate the CE_a as shown below.

In the model calculation 1 above, let us assume 40 g of the alloy is deposited/dissolved per Faraday of electricity ($It/F = 1$) passed through the cell. Then using eq.25, we get

$$CE_a = 40 \times \frac{0.65}{59.35} + 40 \times \frac{0.35}{29.35} = 0.915 = 91.5\%$$

In the model calculation 2 above, let us assume 25 g of the alloy is deposited/dissolved per Faraday of electricity ($It/F = 1$) passed through the cell. Then using eq.25, we get

$$CE_a = 25 \times \frac{0.65}{29.67} + 25 \times \frac{35}{29.35} = 0.846 = 84.6\%$$

The above illustration serves to highlight the central theme of this paper ---

- * that the electrochemical equivalent of an alloy is defined by wrong equations in literature giving rise to wrong results of CE_a
- * even when the correct equations are used for W_a , the calculation of CE of an alloy becomes complicated and round about process, and

* CE of an alloy can be calculated by a simple and direct method, without ever needing the value of W_a .

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Symbols

A Area of alloy (m^2)
 CE_r Current efficiency of r^{th} half cell reaction
 CE_a Current efficiency of alloy deposition or dissolution process
 d_i Density of metal i (kg/m^3)
 d_a Density of alloy (kg/m^3)
 f_i Mass fraction of metal "i" in the alloy
 F Faraday constant (C)
 I Current passing through the electrochemical cell (Amp)
 I_r Current due to the r^{th} half cell reaction (Amp)
 m_i Change in the mass of species "i" in time "t" (Kg)
 m_a Change in the mass of alloy in time "t" (Kg)
 M_i Molecular mass of species "i" (Kg/mol of species i)
 n_r Stoichiometric coefficient of electron in the half cell reaction (mol of electron/mol of reaction)
 d_{ni} Change in the number of moles of species "i" in time "dt" (mol)
 t Time (sec)

W_{ir} Electrochemical equivalent of species, i , in r^{th} half cell reaction (kg/C)
 W_a Electrochemical equivalent of alloy (kg/C)
 X_i Molecular formula of species "i"
 v_i Stoichiometric coefficient of species i (mol of i /mol of reaction)
 ξ_r Extent of reaction r (mol)

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