A study on current density for PKL electrochemical cell

[1]K.A.Khan,Md. [2]Khairul Islam,[3]Sayed Bony Amin, [4]Khandaker Kabir Hossain

[1]Department of Physics, Jagannath University, Dhaka-1100, Bangladesh

[2]Senior Experimental Officer, Nuclear Medical Physics Institute, Bangladesh Atomic Energy Commission

[3]Senior Experimental Officer, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission

[4]Experimental Officer, Institute of Nuclear Science andTechnology, Bangladesh Atomic Energy Commission,

Abstract

It is a known fact that different morphologies of electrodeposited metal can appear at the different positions of the electrode surface. This means that the local current density during electrodeposition of a metal varies from point to point on an electrode surface. This is due to the factors: the geometry of the system, the conductivity of the solution and electrodes, the activation overpotential, the hydrodynamics of the system.Although all factors effect the current distribution simultaneously, there are three main types of current distribution on a macroprofile. If the influence of overpotential is negligible, primary distribution is determined by the geometry of the system and the conductivity of the solution. In case of the secondary distribution the activation overpotential and in case of tertiary distribution both the activation and diffusion overpotentials also have to be taken into consideration.

Keywords: *Current density, Morphology, Overpotential, Electrode surface,Current distribution, Diffusion Current.*

I. Introduction

Even for a simple electrode configuration, the calculation of the current distribution is a complex problem and the difficulties further increase with increasing complexity of the geometry, especially if the limiting diffusion current varies over the electrode due to the different geometric and hydrodynamic conditions[1-30]. Because of this, analytical solutions can be found only for some cases (Wagner, Newman), while in other cases numerical solutions are available[31-60]. If the complete calculation cannot be performed, it is possible to estimate certain trends, using a dimensionless group called the Wagner number[61-100]. The current distribution on a macroprofile is very important in many electrochemical technologies and devices[100-140]. In electroplating, the current distribution determines the local variations in the thickness of the coating[141-160]. In electrowinning and electrorefining of metals, a non-homogenous current distribution can cause a short circuit with the counter electrode. In electroforming corner weakness and failure can occur due to nonuniform deposition[161-180]. This is very important in all three-dimensional electrodes, as well as in some storage batteries[181-190]. In all the cited cases a uniform current density distribution over the macroprofile is required for successful and efficient operation. In a metallic conductor, the free conduction electrons transport the charge, whereas in an electrolytic conductor it is the ions that move and carry the charge[191-200]. In order to include an electrolytic conductor in an electrochemical circuit it is necessary to make electrical contacts to and from the electrolyte by metallic conductors[201-210]. A metallic conductor immersed in an electrolyte solution is an electrode, and two electrodes connected electrolytically represent an electrochemical cell[211-215]. Obviously, a steady current flow in this circuit can only be maintained if there is a change of charge carrier at the metal-electrolyte interface by a chemical transformation involving the transfer of electrons across the interface, that is, by an electrochemical reaction. It constitutes the bridge between the current of electrons in the metallic part of the electrochemical circuit and the current of ions in the electrolytic part

of the circuit[216-218]. The conducting electrons move throughout the whole volume of metallic conductor, but in the electrolytic one only a part of volume is active, depending on the shape of electrodes[219-221].

II. Methodology
III. A *The Wagner number*

A dimensionless group called the Wagner number, W_a, is given by

$W_a = (d\eta_c/d_j)(K/l)$ ….. …… …….. …… ……..(1)

Where, $(d\eta_c/dj)$ is the slope of the cathodic activation overpotential-current density dependence,is the conductivity of solution, and l is a characteristic length. (Before the introduction of W_a, the parameter

$K_c = ķ(d\eta_c/dj)$ …….. …….. ……..(2)

was used, according to Kasper, Hoar, and Agar.) The Wagner number represents the ratio of the polarization resistance to the solution resistance. The larger it is, the more even is the current distribution in spite of non-uniform geometry. In general, the current distribution is the more uniform: the smaller the characteristic length of the system, the larger the conductivity of the solution, and the larger the slope of the activation overpotential-current density curve.

Obviously, the Wagner number can be used only to compare the current distribution in a cell with non-uniform geometry as the electrolyte is changed.

The situation is the same if the ability of an electrolyte to uniformly distribute the current density is experimentally determined using the method of Haring and Blum.

II. B *The effect of different parameters on the current distribution*

The quantitative estimation of the effect of the length of the system, of the conductivity of solution, and the parameters of electrochemical process can be done as follows. The voltage imposed on electrochemical cell, E_{cell}, is given by:

$E_{cell} = \eta_a + \eta_c + \rho. l. j$ …….. …….. ……. ….. . (3).

Finally, we have, $E_{cell}=b_a.\log(j/j_{o,a}) + b_c.\log(j/j_{o,c})[1/1-(j/j_L)] + \rho.l.j$ ……. ……. (4)

Where, η_a = anodic overpotential
η_c = cathodic overpotential
ρ = resistivity of the solution
l = distance between the parallel plane electrodes
j = current density
b_c =cathodic Tafel slope
b_a = anodic Tafel slope
j_L = limiting diffusion current density for the cathodic process
$j_{0,a}$ = the anodic exchange current density
$j_{0,c}$ = The cathodic exchange current density

In the case of complete ohmic control of the deposition process, it is obvious that the current density at the elevation near to the anode, j_n, can be expressed as

$J_n=j_f[(l+h)/l]$ …. ……. …….. ……. …… ……(5)

where j_f is the current density at the planar cathode surface far from the anode, l is the interelectrode distance, and h is the height of the elevation as denoted in Fig.1.

The situation is somewhat different in case of activation control-ohmic control. The voltage imposed on an electrochemical cell, E_{cell}, can be expressed not only as a function of j_f for the part of the cathode far from the anode [6], but also as a function of j_n for the cathode segment near to anode [7]:

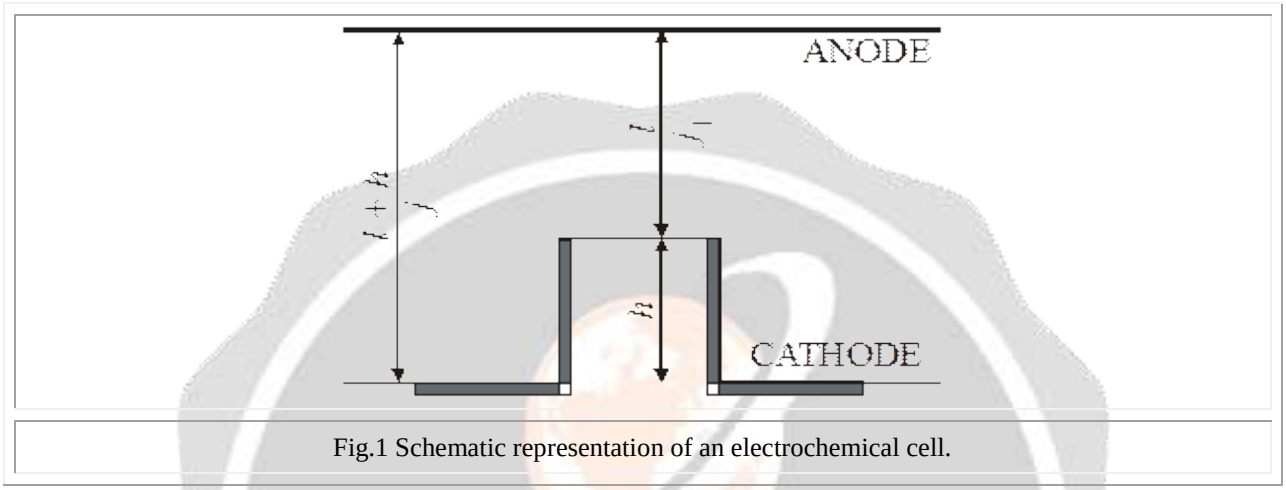

Fig.1 Schematic representation of an electrochemical cell.

$E_{cell} = (b_a/2.3)\ln(j_f/j_{oa}) + (b_c/_{2.3})\ln[(j_n/j_{oc})(j_L/(j_L\text{-}1)] + \rho.(l+h).j_f$ ……. …….. …….. ……. ….. (6)

$E_{cell} = (b_a/2.3)\ln(j_f/j_{oa}) + (b_c/_{2.3})\ln[(j_n/j_{oc})(j_L/(j_L\text{-}j)] + \rho.l.j_f$ …… …….. …….. ……. ….. ….. (7)

However, an estimation of the effects of different parameters on the current density distribution can simply be made by plotting [6] and [7], that is E_{cell}, as a function of current density at parts of the cathode near to, j_n, and far from the anode, j_f respectively.

Hence, the effect of the solution resistivity can be estimated by deriving the dependency of current density at the near part of the cathode on current density at the far part of the cathode from $E_{cell} - j_n$, with $E_{cell} - j_f$ dependencies calculated for different resistivities, while all other cell parameters are kept constant. It can be seen that, besides the conductivity of the electrolyte, the kind of the control of the deposition process also determines the current distribution. The result is shown in Fig.1 together with boundary dependences calculated using equation [5]. As can be seen, the larger the conductivity of the electrolyte, the better is the current density distribution. Also, the distribution is better under total activation control at low cell voltages and under total diffusion control at high cell voltages than under mixed activation-di.

II.C Experimental Work

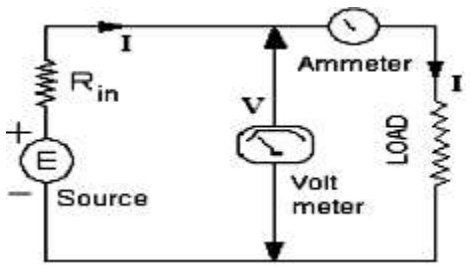

Fig.2 Design of an equivalent circuit for Current density

It is shown in Fig.2 about the design of an equivalent circuit for Current density.The ammeter is connected in series and the voltmeter is connected in in parallel combination.

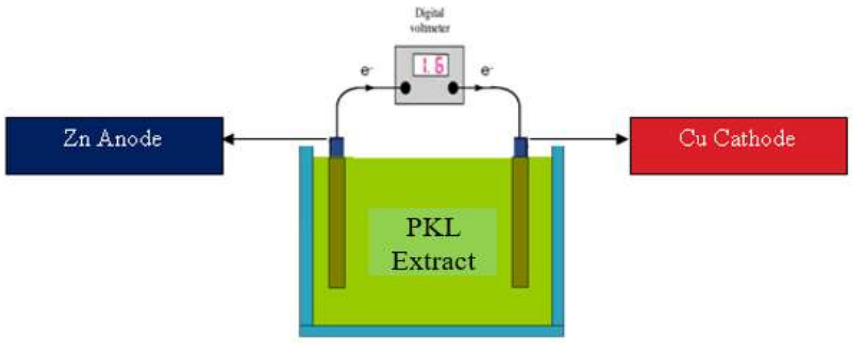

Fig.3 Experimental set up of an equivalent circuit for Current density of a PKL Cell

It is shown in Fig.3 about an experimental set up of an equivalent circuit for Current density of a PKL electrochemical Cell. The copper plate is used as a cathode and the zinc plate is used as an anode. The PKL extract is used as an electrolyte.

III. Results and Discussion

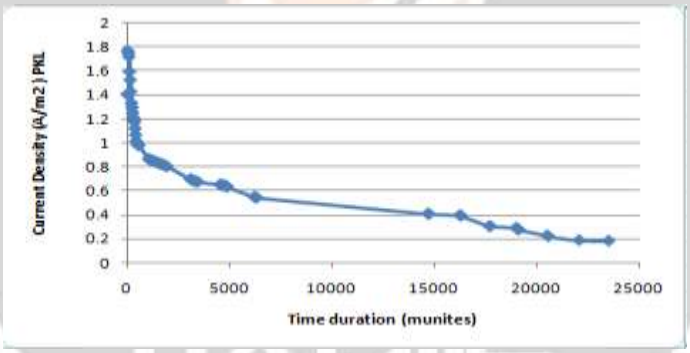

Fig. 4 variation of current density (A/m2) with the variation of time duration (minutes)

Fig.4 shows the variation of capacity (A/m2) with the variation of time duration (minutes). It is shown that the current density increases up to 1.8 (A/m2). Then the current density decreases gradually to 1.0, 0.8, 0.7, 0.6, 0.5 & 0.4 (A/m2) .Finally the current density decreases to 0.2 (A/m2).

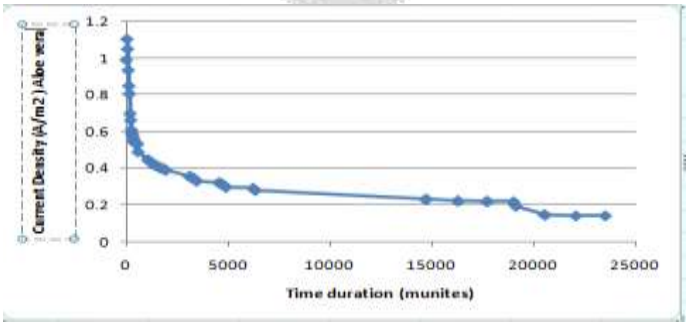

Fig. 5 variation of current density (A/m2) with the variation of time duration (minutes)

Fig.5 shows the variation of capacity (A/m2) with the variation of time duration (minutes). It is shown that the current density increases up to 1.16 (A/m2). Then the current density decreases gradually to 1.0, 0.8, 0.7, 0.6, 0.5 , 0.4, 0.3 & 0.2 (A/m2) .Finally the current density decreases to 0.15 (A/m2).

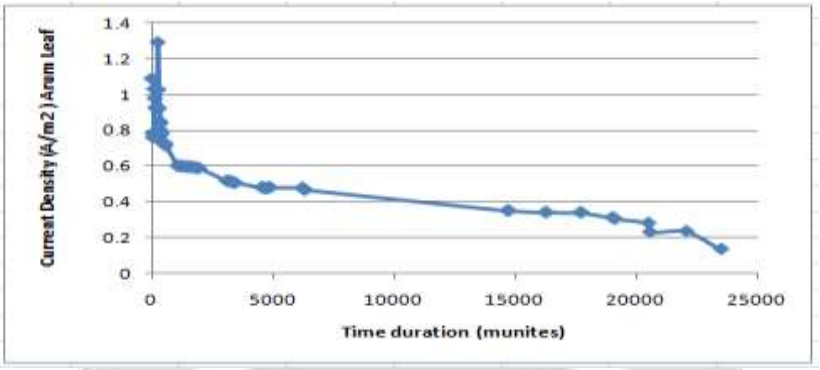

Fig.6 variation of current density (A/m2) with the variation of time duration (minutes)

Fig. 6 shows the variation of capacity (A/m2) with the variation of time duration (minutes). It is shown that the current density increases up to 1.31 (A/m2). Then the current density decreases gradually to 1.0, 0.8, 0.7, 0.6, 0.5 , 0.4, 0.3 & 0.2 (A/m2) . Again increases to 2.2 (A/m2) .Finally the current density decreases to 0.17 (A/m2).

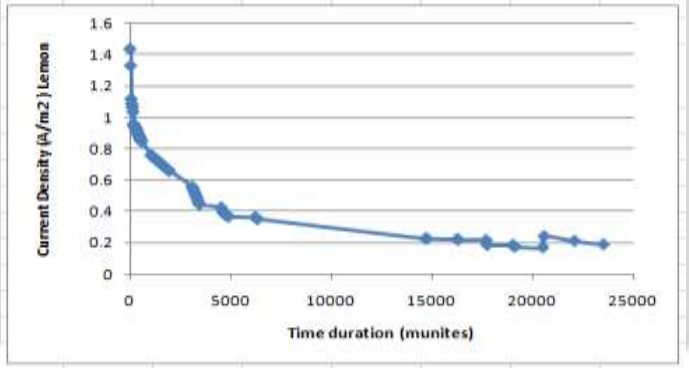

Fig. 7, variation of current density (A/m2) with the variation of time duration (minutes)

Fig.7 shows the variation of capacity (A/m2) with the variation of time duration (minutes). It is shown that the current density increases up to 1.43 (A/m2). Then the current density decreases gradually to 1.0, 0.8, 0.7, 0.6, 0.5 , 0.4, 0.3, 0.2 & 0.18 (A/m2) . Again increases to 2.2 (A/m2).Finally the current density decreases to 0.2 (A/m2).

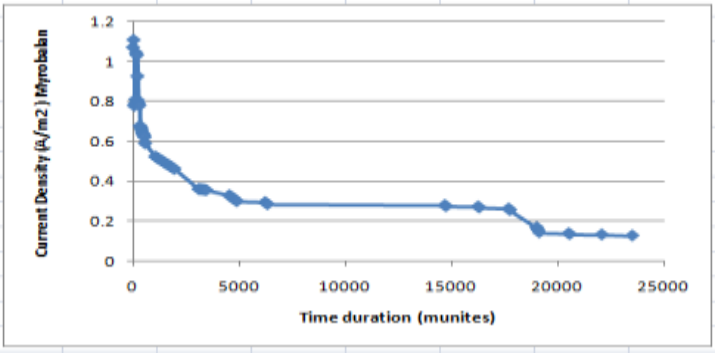

Fig. 8 variation of current density (A/m2) with the variation of time duration (minutes)

Fig.8 shows the variation of capacity (A/m2) with the variation of time duration (minutes). It is shown that the current density increases up to 1.15 (A/m2). Then the current density decreases gradually to 1.0, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2 & 0.18 (A/m2) . Finally the current density decreases to 0.15 (A/m2).

IV. Conclusions

In electrochemistry, exchange current density is a parameter used in the Tafel equation, Butler–Volmer equation and other electrochemical kinetics expressions. The exchange current density is the current in the absence of net electrolysis and at zero overpotential. Current density or electric current density is related to electromagnetism and is defined as the amount of electric current flowing through a unit cross-sectional area. It is a vector quantity. The SI unit of electric current density is ampere per square meter. The symbol "J" is used for electric current density. More the current in a conductor, higher will be the current density. However, the current density alters in different parts of an electrical conductor and the effect takes place with alternating currents at higher frequencies. ... It is all about the amount of current flowing across the given region.

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