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Kinetic Study of the Effect of Benzoic Acid Derivatives on Copper Electrodeposition

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Abstract: The effect of anodic oxygen bubbles on the rate of mass transfer in presence of benzoic acid, p-nitro, p-chloro and p-aminobenzoic acids were studied by measuring the limiting current of cathodic deposition of copper from acidified copper sulphate solution using lead anode. It is found that the rate of deposition decreases by adding organic substances. The rate of deposition depends on the type of inhibitor as well as its concentration. The ability of inhibitors to decrease the limiting current is as follows: p-nitrobenzoic > p-chlorobenzoic > p-aminobenzoic acid. The thermodynamic parameters prove that the reaction is diffusion controlled.

Keywords: kinetic, benzoic acid, electrodeposition

INTRODUCTION

In electrodeposition of metals usually an insoluble anode is used where oxygen evolution takes place. Anodic oxygen evolution could adversely affect the performance of the cell by increasing the ohmic drop ^[1-3] and disturbing the uniformity of current distribution ^{[4-8].} On the other hand, anodic oxygen bubbles were found to enhance the rate of mass transfer at the cathode ^[9-12] to the modest degree in vertical parallel electrode cell. In electrorefining, a soluble copper anode is used where the anodic reaction is copper dissolution instead of O₂ evolution. Electrorefining and electrodeposition of copper are diffusion controlled processes whose rate depends on the physical properties of solution.

The aim of the present work is to study the effect of some organic substances as benzoic acid, p-nitro, pchloro and p-aminobenzoic acids on the rate of electrowining of copper at different temperatures.

MATERIALS AND METHODS

Experimental: Fig. 1 shows the cell and the circuit used in the present work. The cell consisted of a rectangular plastic container having the dimensions $5 \times 5 \times 10$ cm with electrodes filling the whole cross section. The cathode was a rectangular sheet of 10cm height and 5cm width, the anode was a lead sheet of similar dimensions, and electrode separation was 5 cm. In case of measuring the limiting current under natural convection, a copper anode was used instead of the lead anode.

The electrical circuit consisted of 6 volt D.C. power supply connected in series with the cell and a multirange ammeter. A voltammeter was connected in parallel with the cell to measure its voltage.

Polarization curves from which the limiting current was determined were constructed by increasing the current stepwise and measuring the steady state cathode potential against a copper reference electrode placed in the cup of a luggin tube whose tip was placed at about 1mm from the cathode surface. To make sure that the decrease of cu⁺⁺ concentration during polarization was negligible in case of using lead anode, the limiting current was measured again potentiostatically using a fresh solution. The galvanostatic and the rapid potentiostatic methods gave almost the same limiting current. Before electrolysis the cathode and anode were isolated from their backs and sides with epoxy resin except at the contact with the feed wires. Six concentrations of CuSO₄ were used namely, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 M. In all cases, 1.5M H₂SO₄ was used as a supporting electrolyte. All chemicals were of A. R. grade, distilled water was used in preparing all solutions. Temperature was 25±1°C. Each experiment was repeated twice using a fresh solution. Cu++ concentration was checked using iodometry ^[12].

RESULTS AND DISCUSSION

Potentiodynamic cathodic polarization curves: Fig. 2 shows the cathodic polarization curve for copper electrodeposition from sulphate solution under the influence of adding different amounts of p-nitrobenzoic acid. It is obvious that in the organic free solution, the

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current, first increases linearly, then tends to exhibit limiting current plateau with increasing the cathodic potential. It is generally accepted that electrodeposition of Cu⁺⁺ ions takes place through two steps:



Fig. 1: The electrolytic cell and the electrical circuit showing the position of the two parallel vertical plates and the reference electrode



Fig. 2: The relation between I & V in presence of nitrobenzoic acid at 303° K and 0.15 M CuSO₄

It was assumed that the first step in this process occurred slowly and the rate was controlled by equilibrium between Cu⁺⁺ and Cu⁺ at the electrode surface. However, addition of organic substances to the sulphate solution increases the cathodic polarization and decreases the value of limiting current density. The observed changes in the cathodic polarization in the presence of organic compound suggest that it must be acting as inhibitor, which is confirmed by the observation that at any given over potential, the current density for copper deposition from solutions containing organic compound is lower than that found for the corresponding organic free solution. This inhibition of the organic compound on the copper electrodepoition reaction may be due to the adsorption of organic compound on the cathode surface and/or the complexation of Cu^{++} with the organic compound.

As the organic concentration in the bath increased, most of the Cu⁺⁺ ions become complexed. For given concentration, the rate of transport of copper organic complex is lower than for Cu⁺⁺ ion because of the lower value of the diffusion coefficient of a complexed ion^[13]. Therefore, the current plateau decreases with increasing organic concentration as predicted in figure (2) due to a lowering of the uncomplexed Cu⁺⁺ ions.

Table 1: limiting current of different organic compounds (mA) at different temperatures

()					
Organic	$Cx10^{-4}$	298°K	303°K	308°K	313°K
compounds	mol I	210	270	215	2.1.5
	0	210	270	315	345
	2.9	200	260	295	310
n-	5.7	195	250	270	285
nitrobenzoic	11.4	190	240	250	280
muoooniioite	17	180	230	235	260
	22.7	175	200	225	245
	27.8	170	190	215	225
	0.0	260	270	315	345
	2.5	255	265	290	325
n ahlara	5.0	205	260	280	280
p-ciliolo banzoia	10.0	200	250	270	240
benzo1c	15.0	190	240	255	280
	20.0	185	230	240	260
	25	180	210	230	255
	0.0	260	270	315	345
	11.29	190	265	305	325
_	22.48	180	260	295	310
p-	44.53	175	255	285	295
aminobenzoic	66.15	170	250	270	280
	87.35	165	245	255	265
	108	160	230	235	245
	0.0	260	270	315	345
	5.72	200	260	295	330
	17.37	195	250	275	310
benzoic acid	34.39	190	240	250	245
	51.10	180	230	235	280
	67.47	175	200	225	270
	83.54	170	190	215	225

Values of limiting current for all solutions at different temperatures using lead anode are given in table (1). Noticeably, the limiting current decreases with increasing the organic additives concentration and increases with temperature. The mass transfer coefficient was calculated from equation (1)

$$k = \frac{1}{ZFC_{o}}$$
(1)

I = limiting current density, z valency, F Faraday constant, C_0 concentration of CuSO₄.

From table (2) we notice that velocity (V) and mass transfer coefficient (k) for all organic compounds are decreased with increase of the mole fraction of the organic compounds.

Fig. 3 shows that when lead anode was used, in absence of the organic substance, the blank data fits well into equation which agrees with the earlier finding derived from the hydrodynamic boundary layer theory ⁽¹²⁾.

$$J = 1.096 (Re. Fr) - 0.176$$
(2)

The gas discharge velocity V used in calculating J, Re and Fr was calculated from equation (3) Ahmed et al ^[12] predicted that (k α V^{0.18})

V = (IRT)/(4PF)(3)

In presence of organic substance, the following relation was obtained:

$$k \alpha (V)^{D}$$

where "b" is constant depending on organic substances.

Table 2: The variation of k and v for different organic compounds at 303° K

Ogranic compound	$Cx10^{-4}$ mol l ⁻¹	I _l (mA) Organic	V.10 ⁵ cm.s ⁻¹	k.10 ⁶ cm.s ⁻¹
	2.0	260	1.67	8.08
	2.9	200	1.07	8.98
n	5.7	200	1.07	8.20
<u>p-</u>	11.4	230	1.01	7.05
muobenzoic	22.7	230	1.40	7.95
	22.7	220	1.42	7.0
	27.8	215	1.38	7.43
	2.5	265	1./1	9.11
	5	260	1.67	8.95
p-chloro	10	250	1.61	8.64
benzoic	15	290	1.51	8.12
	20	230	1.48	7.91
	25	225	1.35	7.28
	5.72	260	1.67	8.98
	17.37	250	1.61	8.64
р [.]	34.39	240	1.55	8.29
Benzoic	51.10	230	1.48	7.95
	67.47	200	1.29	6.91
	83.54	190	1.23	6.56
	11.29	265	1.71	9.16
	22.48	260	1.67	8.95
p-	44.53	255	1.64	8.81
aminobenzoic	66.15	250	1.61	8.64
<u></u>	87.35	245	1.58	8.46
	108	230	1.48	7.95

Plot log k against log V for different organic compounds gave a good straight line as shown in figure (4) and table (2). The values of the slope (b) were found to be constant for all studied additives and its values approximately equal one as shown in table 3, which indicates that the discharge velocity of oxygen gas is affected by the presence of additive compounds to same extent as the mass transfer coefficient does.

Table 3: Values of (b) for different organic substances using lead anode.

6	
Organic substance	b
p-nitrobenzoic acid	1.06
p-chlorobenzoic acid	1.077
benzoic acid	1.05
p-aminobenzoic acid	1



Fig. 3: Overall mass transfer correlation at vertical plates

Effect of organic substance on the limiting current: The limiting current in absence of organic compound (I_{b}) and in presence of organic compound (I_{org}) , is related to the percentage of inhibition by the equation:

 $\% inhibition = [I_b - I_{org}] / I_b X 100$ (4)

Fig. 5 and table 4 show that the percentage inhibition caused by organic compounds ranges from 1.85% to 29.63%.

The percentage inhibition was found to be dependent on types of inhibitor and its concentration. The percentage inhibition increases as concentration increases. The order of inhibition is as follows: pnitrobenzoic > p-chloro > benzoic > p-aminobenzoic acid.

The obtained results show that the presence of organic compound has an inhibiting effect on the kinetics of the copper discharge process, pointed out by the decrease of the exchange current intensity. The inhibition enhancing due to increasing the organic compound concentration could be related to the strong adsorption of organic compound constituents on the copper electrode surface, which is in agreement with the decay of the current intensity observed on the polarization curves.

The presence of organic compound changes the mechanism of the copper electrodeposition as it can be seen from the decreasing of the cathodic transfer coefficient. A possible explanation for this fact is the increasing role of an additional reaction that produces the same mechanical species (Cu⁺) as those involved in the rate determining reaction ^[14].

Table 4: The effect of concentration of organic compounds and the % inhibition of the limiting current at 303° K



Fig. 4: The relation between log k and log V for different organic compounds at 303° K

Ogranic compound	Cx10 ⁻⁴ mol 1 ⁻¹	I _l (mA) blank	I _l (mA) Organic comp.	% inhibition
	2.9		260	3.704
	5.7		260	3.704
n nitrohanzaia	11.4	270	250	7.407
p-muodenzoic	17	270	230	14.82
	22.7		220	18.52
	27.8		215	20.37
	2.5		265	1.852
	5		260	3.704
p-chloro	10	270	250	7.407
benzoic	15	270	240	11.11
	20		230	14.82
	25		225	16.67
	5.72		260	3.704
	17.37		250	7.407
Panzoia	34.39	270	240	11.11
Belizoic	51.10	270	230	14.83
	67.47		200	25.93
	83.54		190	29.63
	11.29		265	1.852
	22.48		260	3.704
<u>p-</u>	44.53	270	255	5.504
aminobenzoic	66.15	270	250	7.407
	87.35		245	18.52
	108		230	20.39

Adsorption isotherm: It is generally assumed that the adsorption of the inhibitor at the metal solution interface is the first step in the action mechanism of inhibitors in aggressive acid media. Four types of adsorption may take place in the inhibiting phenomena involving organic molecules at the (meta-solution) interface, namely:

- 1. Electrostatic attraction between charged molecules and the charged metal.
- Interaction of uncharged electron pairs in the 2. molecules with the metal.
- Interaction of electron with metal 3.
- A combination of the above^[15]. 4.

Chemisorption involves sharing or charge transfer from the inhibitor molecule to the surface in order to form coordinate bond. In fact, electron transfer is typical for transition metals having vacant low energy electron orbital.

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are those of Langmuir, Frumkin, Parsons, Temkin, Flory-Huggins and Bockris-swinkels^[16-19]. All these isotherms are of the general form: f

$$(\theta, \mathbf{x}) \exp(-\alpha \theta) = \mathbf{KC}$$

where f (θ, x) is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm. Inhibitor adsorption characteristics were estimated by using the Langmuir isotherm $^{[20, 21]}$, equation (6):

(5)

$$KC = (\theta/1 - \theta) \tag{6}$$

Where K is the equilibrium constant of adsorption process, C is the concentration and θ is the surface coverage.

The degree of surface coverage (θ) at constant temperature was determined from $^{[\overline{2}2]}$:

$$\theta = (I_b - I_{org})/I_b \tag{7}$$



Fig 5: The relation between percentage inhibition and concentration for all organic substances at 303° K



Fig. 6: The relation between $\theta/1-\theta$ and C for different organic compounds at 303° K

Table 5 gives the data between $(\theta/1-\theta)$ vs C for all organic substances of the surface coverage θ with concentration variation at 303K. From equation (6) a plot of $(\theta/1-\theta)$ vs. C should yield straight line, thus figure (6) shows straight line indicating that all the inhibitors verify Langmuir adsorption isotherm.

Figure (7) shows the Flory-Huggins adsorption isotherm plotted as $\log \theta/C$ vs. $\log(1-\theta)$ for CuSO₄/H₂SO₄ organic compounds at 303K yields a straight line with slope x and intercept log (xk). Table (6) shows the values of x and k, the experimental data fits Flory-Huggins adsorption isotherm which represented by:

 $\log \theta / C = \log(xK) + x \log (1 - \theta)$ (8)

Here x is the number of water molecules replaced by one molecule of the inhibitor. It is clear that the surface coverage data are useful for discussing adsorption characteristics. The adsorption of inhibitors at metal solution interface may be due to the formation of either electrostatic or covalent bonding between the adsorbents and the metal surface atoms ^[23, 24].

The free energy of adsorption ($\Delta G_{ads.}$) at different concentrations was calculated from equation:

$$\Delta G_{ads.} = -RT \ln (55.5K)$$

The values of $\Delta G_{ads.}$ are given in table (6). In all cases, the $\Delta G_{ads.}$ values are negative and lie in the range of -12.652 to -22.019 kj/mol. The most efficient inhibitors show the most negative $\Delta G_{ads.}$ value. This suggests that they are strongly adsorbed on the metal surface. The negative values of $\Delta G_{ads.}$ indicate the spontaneous adsorption of the inhibitor. This is usually characteristic of strong interaction with metal surface. It is found that the $\Delta G_{ads.}$ values are more positive than -40kJ/mol indicating that inhibitors are physically adsorbed on the metal surface. Similar results have also been reported by Talati et. al ^[25].



Fig. 7: The relation between $\log \theta/C$ and $\log 1 - \theta$ for different organic compounds at 303° K

Effect of organic additives: It is known that many additives are usually capable of adsorption on the cathodic substrate and even might trap in the deposit. additives also increase the deposition Some overpotential. This may be due to either the need for the electron transfer to occur through the adsorbed layer or to a complex formation at the electrode surface. A complexation of the metal cation in solution is also proposed. In many cases the use of additives is till done in an empirical way. Indeed, the number of these organic or non organic substances is very large. Moreover, their action could be different in function of the substrate, the ion to reduce and the electrolytic conditions. For example, additive re-orientation on the electrode surface has been observed ^[26, 27] depending on the surface coverage or as a function of pH. A synergetic effect, often noticed when several additives are added to the solution even confuses the issue.

An explanation for the decrease of the rate of deposit may be due to that water molecules bounded by hydrogen bond to an acid are less nucleophilic than water molecules bounded by a hydrogen bond with each other. Also the results obtained in case of acid are interpreted on the basis that the metal surface is preferentially covered by acid molecules^[28].

Acids increase the local solution viscosity at cathode surface with a consequent decrease in the diffusivity of copper ion and the decrease in the rate of deposition with increasing the concentration of acids, which is attributed to acid molecules slower the natural convection flow arising from the density difference between bulk solution and solution at the electrode surface due to the attraction force between the cathode surface and coo⁻ group of the acid.

Rate of deposition and the limiting current is observed to decrease in the presence of electrolyte or acids probably due to the decrease of the conductivity of

(9)

solution mixture in the presence of acids. The limiting current is found to be lower in the presence of the acids added to solution than in absence of acids. The decrease of rate will depend on the acids composition and its structures, the protolytic action and oxygen solubility. It is found that the rate of electrodeposition increases in the following order:

p-nitrobenzoic > p-chloro > benzoic > p-aminobenzoic acid.

This is explained on the basis that nitro group is electron withdrawing group which make the –COOH group to be more ionized i.e. acid reacts with copper ion easily. The equilibrium will be shifted to right and less copper deposited.

Cu ====
$$Cu^{++} + 2e^{-}$$

2-COOH + Cu^{++} ===== -(COO)₂Cu

The –I effect of nitro group is more than Cl⁻ ion. This explains the rate of deposition of 4-nitro is more than 4-chlorobenzoic. For 4-aminobenzoic, amino group is electron releasing group which has +I effect, so the dissociation of COOH group will be less than in case of benzoic acid.

It is found that the rate of deposition decrease by increasing the concentration of acids. This is explained on the basis that, this substance adsorbed on the surface of cathode led to an inhibition effect.

Effect of temperature: The electrodeposition of copper in presence of different inhibitors was studied by measuring the limiting current over the temperature range from (298-313°C). Table (1) shows the limiting current obtained in presence of organic additives at different temperatures. The results indicate that the rate of electrodeposition increases with increasing the temperature. The above behaviour is indicative of the occurrence of the electrodeposition through physical adsorption of additive on the metal surface. Desorption is aided by increasing the reaction temperature.

The value of I_1 obtained at different temperatures permits the calculation of activation energy E_a according to Arrhenius equation:

$$\log I_1 = -E_a/2.303RT + \log A$$
(10)

The plot of I_1 against 1/T gave a straight line where A is Arrhenius constant, R is the gas constant and T is the

absolute temperature. The slope of which is proportional to E_a . The activation energy of the process is an important parameter for determining the rate controlling step. If the rate controlling step is the diffusion of the species in the boundary layer then E_a is generally ≤ 28 kJ/mol, while E_a values usually > 43 kJ/mol when adsorption of the species on the metal surface and subsequent chemical reaction take place.

Table 7 shows that the values of E_a are lower than 43 kj/mol; characterizing that diffusion processes are controlling the electrodeposition reaction.



Fig. 8: The relation between ΔS^* and ΔH^* for all organic compounds

Thermodynamic treatment of the reaction: The values of the enthalpy of activation ΔH^* , entropy of activation ΔS^* and free energy of activation ΔG^* can be obtained by using equations:

$$\Delta \mathbf{H}^* = \mathbf{E}_a - \mathbf{R} \mathbf{T} \tag{11}$$
$$\frac{\Delta S^*}{R} = \ln(A) - \ln\left(\frac{BTe}{h}\right) \tag{12}$$

$$\Delta \mathbf{G}^* = \Delta \mathbf{H}^* - \mathbf{T} \Delta \mathbf{S}^* \tag{13}$$

Table (7) shows that the entropy ΔS^* possesses negative values, indicating a highly ordered organic species in the solution under investigation. From the table (7) and Fig. (8), it is also noticed that the weak dependence of ΔG^* on the composition of the organic additives can be attributed largely to the general linear compensation between ΔH^* and ΔS^* for the given temperature.

Table 6: values of k, x and ΔG_{ads} of organic compound in Langmuir and Flury-Huggins

Organic compounds	Langn	nuir		Flury-Huggins	3
	k	$\Delta G_{ads.}$	x	k	$\Delta G_{ads.}$
	K	kJ.mol ⁻¹	А		kJ.mol ⁻¹
p-nitrobenzoic	97.887	21.309	2.809	81.194	19.655
p-chloro benzoic	83.496	20.914	0.5848	130.46	22.019
benzoic acid	51.512	19.714	0.5416	81.194	20.844
p- aminobenzoic	14.117	16.501	6.419	2.975	12.652

Cx10 ⁻⁴ mol 1 ⁻¹	I_l	θ	1-θ	θ/1- θ	log1-θ	logθ/c
p-nitrobenzoic						
2.9	260	0.04	0.96	0.04	-0.01	2.11
5.7	260	0.04	0.96	0.04	-0.02	1.81
11.4	250	0.07	0.93	0.08	-0.03	1.81
17	230	0.15	0.85	0.17	-0.07	1.44
22.7	220	0.19	0.81	0.23	-0.08	1.92
27.8	215	0.2	0.80	0.26	-0.09	1.87
p-chloro benzoic						
2.5	265	0.02	0.95	0.02	-0.01	1.97
5	260	0.04	0.96	0.04	-0.02	1.90
10	250	0.07	0.93	0.08	-0.03	1.84
15	235	0.13	0.87	0.15	-0.06	1.84
20	230	0.15	0.85	0.17	-0.07	1.83
25	210	0.22	0.79	0.29	-0.11	1.8
Benzoic						
5.72	260	0.04	0.96	0.04	-0.02	1.63
17.37	260	0.07	0.93	0.04	-0.03	1.58
34.39	241	0.11	0.89	0.08	-0.05	1.51
51.10	230	0.15	0.85	0.17	-0.07	1.45
67.47	200	0.26	0.84	0.23	-0.13	1.42
83.54	190	0.29	0.81	0.26	-0.15	1.40
<u>p-aminobenzoic</u>						
11.29	265	0.02	0.98	0.02	-0.01	1.22
22.48	260	0.04	0.96	0.04	-0.02	1.15
44.53	255	0.06	0.94	0.06	-0.025	1.09
66.15	250	0.07	0.93	0.08	-0.03	1.05
87.35	245	0.09	0.91	0.10	-0.04	1.03
108	230	0.15	0.85	0.17	-0.07	1.14

Am. J. Applied Sci., 5 (3): 234-241, 2008

Table 5: The data of the adsorption isotherm at 303k

Table 7: thermodynamic parameters for electrodeposition of copper in presence of organic substances

Ogranic compound	$C_{\rm w} 10^{-4} {\rm m} {\rm s} 11^{-1}$	Ea	ΔΗ*	ΔS^*	ΔG^*
	CX10 III011	kJ.mol ⁻¹	kJ.mol ⁻¹	J.mol.k ⁻¹	kJ.mol ⁻¹
	0.0	21.38	18.9	136.5	59.61
	2.9	20.15	17.67	140.8	59.65
	5.7	20.0	17.45	141.8	59.73
p-nitrobenzoic	11.4	18.0	15.29	149.1	59.75
	17	16.38	13.96	154	59.89
	22.7	15.08	12.60	159.9	59.96
	27.8	15.0	12.50	159.6	60.06
	0.00	19.33	16.55	142.52	59.44
	2.5	21.05	15.58	137.83	59.64
	5	19.33	16.85	143.83	59.74
p-chloro benzoic	10	17.5	15.01	150.30	59.82
-	15	18.3	15.85	147.9	59.95
	20	17.1	14.66	152.2	60.04
	25	16.33	13.85	155.1	60.07
	0.00	19.33	16.85	142.83	59.44
	5.72	17.33	14.85	149.96	59.56
	17.37	14.78	12.3	153.8	59.65
Benzoic	34.39	14.4	11.92	160.4	59.75
	51.10	13.65	11.17	163.4	58.88
	67.47	12.92	10.45	166	60.03
	83.54	11.11	8.63	172.71	60.12
	0.00	19.33	18.85	142.83	54.44
	11.29	21.14	18.66	137.3	59.6
	22.48	21.5	19.02	136.47	59.71
p-aminobenzoic	44.53	20.74	18.26	139.24	59.77
-	66.15	19.67	17.19	143	59.55
	87.35	17.34	14.86	154	59.88
	108	16.55	14.06	154.3	60.04

CONCLUSION

The study of the effect of benzoic acid derivatives on cupper electrodeposition led to the following important conclusions:

- 1. Rate of copper deposition decreases by adding organic compounds.
- 2. Rate of copper deposition depends on the type and concentration of the organic compound.
- 3. Rate of copper deposition increases by increasing temperature.
- 4. The copper electodeposition is diffusion controlled.
- 5. The discharge velocity of oxygen gas is affected by the presence of additive compounds to same extent as the mass transfer coefficient does.

REFERENCES

- 1. H. Voget, 1981. Electrochim. Acta, 263: 1311.
- S. Sides and C. W. Tobias, 1982. J. Electrochem. Soc., 129, 2715.
- 3. C. W. Tobias, 1959. J. Electrochem. Soc., 106:833.
- 4. J. E. Funk and J. F. Thrope, 1972. J. Electrochem. Soc. 8:436.
- 5. P. A. Damma, 1974. J. Electrochem. Soc, 121:1286.
- 6. S. Mohanta and T. Z. 1977. Fahidy, J. Appl. Electrochem., 7:235.
- V. A. Ettel., B. V. Tilak and A. S. Gendron, 1974. J. Electrochem. Soc., 121:867.
- L. Sigtist et al, 1979. Int. J. Heat Mass Transfer, 22:1393.
- 9. M. G. Fouad, F. N. Zein and M. I. Ismail, 1971. Electrochimical Acta, 16:1477.

- G. H. Sedahmed, S. S. Iskander, I. A. S. Mansour and M. A. Fawzy, 1980. Surface Technology, 11:67.
- 11. A. M. Ahmed and H. M. Faid-allah, 1987. J. Electrochem. 3:255.
- 12. E. Mattsson and J. O'M. Bockris, 1959. Trans. Faraday. Soc., 55:1586.
- J. Lipkowski and P. N. Ross. 1992. Adsorption of Molecules at Metal Electrodes, VCH Publishers, New York, Weinheim, Cambridge.
- 14. F. Donnue and K. Nobe, 1965. J. Electrochem. Soc., 112:886.
- 15. G. Poling, 1976. J. Electrochem. Soc., 114:1209.
- 16. O. Ikeda, H. Jimbo and H. Jaumura, 1982. J. Electroanal. Chem., 137:127.
- 17. R. Parsons, 1964. J. Electroanal. Chem., 7:136.
- J. O. M. Bockris and D. A. J. Swinkels, 1964. J. Electrochem. Soc., 111:736.
- 19. B. Ateya, B. E. El-Anadouli and F. M. El-Nizamy, 1984. Corros. Sci, 24:509.
- E. E. Oguize, B. N. Okolue, C. E. Ogukwe, A. I. Onuchukwu and C. Unaegbu., 2004. Bull. Electrochem., 20:421.
- 21. E. E. Ebenso, U. J. Ekpe, B. I. Ita, O. E Offioong and U. J. Ibok, 1999. Mater. Chem. Phys., 60:79.
- 22. E. E. Ebenso, 2003. Bull. Electrochem., 19:209.
- 23. M. A. Quraishi, and R. Sardar, 2002 Bull. Electrochem., 18:515.
- 24. J.D. Talati and J. M. Darji, 1988. J. Ind. Chem. Soc., 65:94.
- 25. E. Yung and L. Romankiw, 1989. J. Electrochem. Soc., 136:756.
- 26. W. Plieth, 1992. Electrochim. Acta, 37:2115.
- L. Bonou, M. Eyraud. R. Denoyel and Y. Massiani, 2002. Electrochim. Acta, 47:4139.
- 28. D. Stoychev and C. Tsvetanov, 1996. J. Appl. Electrochem., 26:741.