

The Analysis of Underpotential Deposition by Multilayer Adsorption Model

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Abstract

The underpotential deposition of zinc was investigated on carbon steel and nickel. The relationship between the deposition potentials and the corresponding amounts of charge for deposited layers shows a very similar trend to the multilayer adsorption mechanism. The experimental results fit a mathematical model derived on the basis of the BET equation for the underpotential deposition.

1. INTRODUCTION

The deposition of monolayer-thick metal film occasionally occurs on a foreign substrate at the potential less negative than the reversible potential of bulk phase deposition. This phenomenon is thus called underpotential deposition (UPD). The characteristics of UPD have been investigated for various metal-substrate systems.¹⁻⁹⁾ Quantitative studies, however, have been limited to a few cases such as the deposition of copper on noble metals.^{2, 6, 8)} The UPD of zinc was investigated mostly on the iron-group metal substrates,^{1, 6, 7, 9)} where it was regarded as an explanation for the anomalous codeposition of zinc and iron-group metals. A major difficulty for the quantitative study on zinc was the simultaneous evolution of hydrogen.

Kolb et al.^{5, 6)} argued that the positive shift of electrodeposition potential was due to the

strength of charge transfer reaction between substrate surface and UPD adsorbate. They correlated the UPD phenomenon to the difference of work function value between substrate and deposit. Many experimental results show that a steady-state of UPD layer can be maintained at a constant potential.^{8, 9)} The exact thickness appears to be system-dependent. In most cases, however, the UPD reactions lead to the formation of only monolayer or sub-monolayer.¹⁻⁶⁾ The experimental evidence for more than one layer near the reversible potential of bulk phase deposition has also been reported.^{8, 9)}

In this work, a mathematical model describing the equilibrium state of UPD product was derived in the same manner as the well-known BET adsorption model. It was then evaluated by fitting the experimental data (presented in our previous report⁹⁾) on the UPD of zinc.

2. DERIVATION OF MODEL

The many experimental results of UPD shows that, when the electrode potential is maintained at a value which is less negative than the reversible potential of bulk phase deposition, a steady-state partial coverage of the surface is obtained^{8,9)}. Fig. 1 shows the relationship between the electrode potential and the corresponding amount of charge for UPD. The curves represent respectively the results obtained on carbon steel in sulfate and chloride solution, and also on electroplated nickel in sulfate solution.

All three curves display the features of an isotherm for a multilayer adsorption process. In the underpotential range, the surface coverage of zinc increases as the potential becomes more negative. Each curve has a knee which indicates the monolayer adsorption. The position of the knee is related to the electrodeposition potential at the completion of a zinc monolayer before it grows to a multilayer. Considering the theoretical amount of charge for a closed-packed monolayer, 0.52mC/cm^2 (a basal plane of hexagonal-closed-packed zinc), it must be a fraction of monolayer. However, the amount of charge after the knee becomes much higher than that for a monolayer. It corresponds to the electrodeposition of a multilayer which probably commences just before the deposition of bulk layer. The presence of this layer has been mentioned in several papers.^{8,9)}

The shape of curves in Fig. 1 rules out a simple Langmuir monolayer. It suggests instead

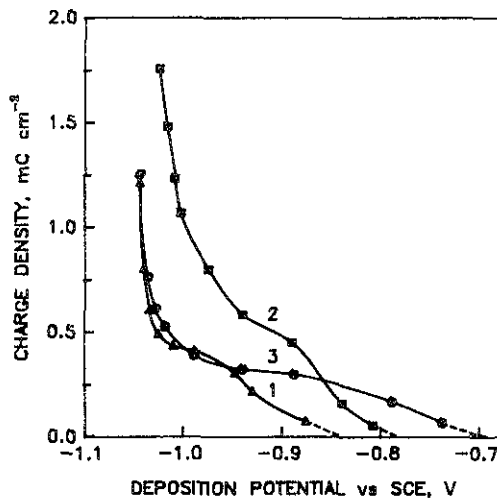
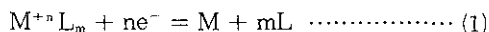


Fig. 1. Calculated charge densities of reduced zinc as a function of electrodeposition potential in 0.5 M ZnSO_4 (curve 1) and 0.5 M ZnCl_2 (curve 2) on carbon steel, and in 0.5 M ZnSO_4 on electroplated nickel (curve 3) (pH 3.0, temperature 25°C , cathode rotating speed 2500rpm, sweep rate 100mV/sec).

that the model derived by Brunauer, Emmett, and Teller¹⁰⁾ to describe the adsorption of a vapor on a solid surface also fits the underpotential deposition of metal. At equilibrium, the electrode can be described as consisting of patches of uncovered surface of area A_0 , patches of single layer of area A_1 , patches of double layer of area A_2 , etc. The steady-state is reached where the rate of dissolution from the layer of i -atom thickness equals the rate of electrodeposition on the layer of $(i-1)$ -atom thickness. If the electrochemical process is represented by the equation,



where m is the coordination number of ligand, then the equilibrium condition is

$$A_i k_{a,i} C_M C_L e^{\frac{\alpha_c F U}{RT}} = A_{i-1} k_{c,i-1} C_M^+ e^{-\frac{\alpha_a F U}{RT}} \dots\dots\dots (2)$$

where $k_{a,i}$ and $k_{c,i-1}$ are respectively the rate constants of electrodeposition and dissolution on i th and $(i-1)$ th layers, C_M^+ , C_M , and C_L are the concentrations of metal ions, metal, and ligand, α_c and α_a are the transfer coefficients for the cathodic and anodic processes, U is the electrode potential, F is Faraday's constant, R is gas constant, T is absolute temperature.

Assuming a simple reaction with one rate determining step,

$$\alpha_c + \alpha_a = n \dots\dots\dots (3)$$

where n is the charge of the cation. The equation above becomes

$$A_i = \frac{k_{c,i-1}}{k_{a,i}} \frac{C_M^{+n}}{C_M C_L} e^{-\frac{nFU}{RT}} A_{i-1} \dots\dots\dots (4)$$

The further assumption of the BET model is that the rate constant, k_c for deposition is the same for all layers and the rate constant k_a is the same for all layers but the first one, $k_{a,1}$. Then,

$$A_i = \left[\frac{k_c}{k_a} \frac{C_M^{+n}}{C_M C_L} e^{-\frac{nFU}{RT}} \right]^i \frac{k_a}{k_{a,1}} A_0 \dots\dots (5)$$

Noting the following relations and defining the parameters X and C ,

$$\frac{k_c}{k_a} \frac{C_M^{+n}}{C_M C_L} e^{-\frac{nFU}{RT}} = e^{-\frac{nF(U-U_{rev})}{RT}} = X \dots\dots (6)$$

and

$$\frac{k_a}{k_{a,1}} = e^{\frac{E_i - E}{RT}} = C \dots\dots\dots (7)$$

where U_{rev} is the reversible potential, E_i and E are respectively the activation energy for anodic dissolution of the first layer and the other layers. X reciprocally represents the state of underpotential deviation from the reversible potential.

The relation between the area of the i -atom layer and the area of the uncovered layer may be written as

$$A_i = X^i C A_0 \dots\dots\dots (8)$$

and the total surface area is

$$A = A_0 + \sum_{i=1}^{\infty} X_i C A_0 = A_0 (1 + C \sum_{i=1}^{\infty} X^i) \dots\dots (9)$$

The total charge density Q and that for a monolayer Q_m can be written as

$$Q = \frac{1}{A} \frac{nF}{N\sigma} \sum_{i=1}^{\infty} i A_i = \frac{1}{A} \frac{nFA_0}{N\sigma} C \sum_{i=1}^{\infty} i X^i \dots\dots (10)$$

and

$$Q_m = \frac{1}{A} \frac{nFA_0}{N\sigma} (1 + C \sum_{i=1}^{\infty} X^i) \dots\dots\dots (11)$$

where N is Avogadro's number, and σ is the area occupied per atom. From Eq. 10 and 11,

$$\frac{Q}{Q_m} = \frac{\sum_{i=1}^{\infty} i A_i}{A_0 + \sum_{i=1}^{\infty} A_i} = \frac{C \sum_{i=1}^{\infty} i X^i}{1 + C \sum_{i=1}^{\infty} X^i} \dots\dots\dots (12)$$

Insertion of the algebraic equivalents of the series yields

$$\frac{Q}{Q_m} = \frac{CX}{(1-X)^2} = \frac{CX}{(1-X)[1+(C-1)X]} \dots\dots\dots (13)$$

and this equation can be written as

$$\frac{X}{Q(1-X)} = \frac{1}{CQ_m} + \frac{(C-1)X}{CQ_m} \dots\dots\dots (14)$$

The plot $X/Q(1-X)$ vs. X is a straight line, and two parameters are calculated as

$$Q_m = \frac{1}{S+I}, C = \frac{S}{I} + 1 \quad \dots\dots\dots (15)$$

where S and I respectively represent the slope and the intercept.

3. EVALUATION OF MODEL

Fig. 2 and 3 are adsorption isotherms and linear plots obtained from data in Fig. 1. The experimental results fit the linear BET plot up to about $X=0.4$, which is consistent with the case of gas adsorption on a solid where the linear range is $0.05 < X < 0.3$.⁽¹⁰⁾

The monolayer charge Q_m can be obtained from Eq. 15. The difference between the activation energy for the dissolution of zinc from the first layer on carbon steel substrate and that from the other layer on the previously electrodeposited zinc E_1-E can be obtained from Eq. 7. The calculated values are listed in Table 1.

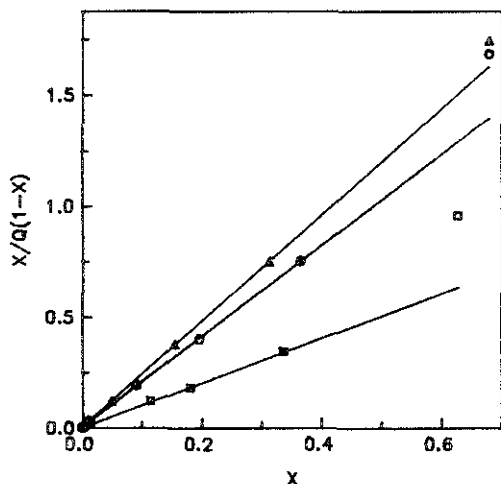


Fig. 2. Isotherms corresponding to Fig. 1.

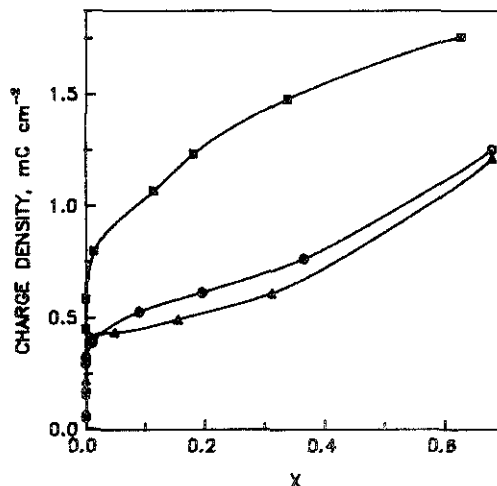


Fig. 3. Evaluation of Fig. 2 by BET adsorption model.

The surface area of substrate was assumed constant for all experiments. The value of Q or Q_m will be changed by true roughness factor; however, the trend appeared in Fig. 2 and 3 will be maintained.

In Fig. 2, all three curves have a similar shape with sharp knee, characteristic of the high value of C . This means that the difference of two activation energies, E_1-E is very large. Therefore, the electrodeposition of zinc is preferred on carbon steel than on zinc itself, and it occurs in the underpotential range. Since the values of intercepts are extremely small, the determination of the value of C by Eq. 16 can not be precise enough. In Table 1, only the estimates of minimum values are listed.

Table 1. Calculated Constants

Condition	Q_m mC/cm ²	$E_1 - E$ kJ/mol
Steel in Sulfate	0.42 ± 0.03	> 11.7
Steel in Chloride	0.99 ± 0.09	> 9.5
Nickel in Sulfate	0.49 ± 0.04	> 10.3

4. CONCLUSION

Zinc can be electrodeposited on carbon steel and electroplated nickel in the underpotential range. The coverage of the carbon steel substrate by zinc in sulfate and chloride solutions as well as the coverage of nickel by zinc in sulfate solution can be described by the BET-type equation. This suggests the validity of the BET assumption that the surface coverage corresponds to a thermodynamic equilibrium controlled by the cathodic potential. The effect of the electrolyte needs further study.

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