

# Note on the theory of three-dimensional growth of the porous passivating layers on metals

Andrew V. Noskov · Elena P. Grishina

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**Abstract** An analytical relationship “the current peak height—the potential sweep rate” is derived for the three-dimensional film formation under ohmic resistance control. The model takes into account both the changing of the coverage degree and the thickening of the surface film. It is shown that a criterion for definition of the growth type (2D or 3D) of the surface film can be offered. An offered model is tested for anodic oxidation of silver in sulfuric acid solution.

**Keywords** Layer-pore resistance model · Three-dimensional growth · Current peak · Thickening rate · Silver · Voltammetry

## Introduction

Passivation of the metal surface is a very important subject matter that has been extensively studied by the linear potential sweep voltammetry. Different theories, depending on the passivating film properties, have been proposed to explain a formation and growth of these films.

In [1–3] a layer-pore resistance model have been offered and evolved. This approach takes into account the electrochemical process under ohmic resistance control. According to this model, the current peak height ( $I_m$ ) increase linearly with the square root potential sweep rate ( $V=dE/dt$ ):

$$I_m = \sqrt{\frac{zF\rho\kappa S^2}{M}}(1 - \theta_m)\sqrt{V}, \quad (1)$$

and straight line  $I_m - \sqrt{V}$  is extrapolated to the zero of coordinate system. Here,  $z$  is the number of electrons,  $F$  is the Faraday,  $S$  is a geometrical surface area of the electrode,  $K$  is the specific conductivity of the electrolyte,  $M$  is the molecular weight of the passivating compound,  $\rho$  is the density of the passivating compound,  $\theta_m$  is a fraction of covered surface with anodic reaction products at  $I_m$ .

At the derivation of Eq. 1, a two-dimensional growth scheme was proposed for porous layer formation, i.e., for passivation there is a change of the covered surface fraction ( $\theta$ ) only, and thus a passive film thickness keeps constant (a simple film spreading model).

There has been a considerable amount of interest in the anodic formation of the surface films on the silver electrodes in various solutions [4–8]. In [4], AgCl films were formed galvanostatically on Ag and were investigated by the scanning electron microscopy (SEM). A two-dimensional growth scheme was proposed for AgCl film formation. At the same time, in opinion of the author of [5], the thickness of a porous surface layer does not keep constant for electrochemical process and is increased continuously. Similar results are founded in [6]. Authors studied AgBr films growth on a surface of the silver anode and concluded that the experimental polarizing curve shows a broader maximum than that simulated by the layer-pore resistance model [1–3]. The agreement between experimental and calculated current/potential curves is not very satisfactory in this regard. Thus, the present theoretical approaches require modification.

Effort of the similar problem decision was undertaken in the mentioned publication [6]. Authors have assumed some modifications of the layer-pore resistance model taking into account a film thickening for electrochemical process. It is shown that the evolved three-dimensional model describes an experimental finding better in comparison with two-

A. V. Noskov (✉) · E. P. Grishina  
Institute of Solution Chemistry, Russian Academy of Sciences,  
Academicheskaya str., 1.,  
Ivanovo 153045, Russia  
e-mail: avn@isc-ras.ru

dimensional one. However, a relationship between the current peak height and potential sweep rate for 3D film growth is absent.

It is the objective of the present paper to elaborate the three-dimensional model of the layer-pore resistance (offered in [6]) and to establish the analytical relation describing a dependence of the current peak height ( $I_m$ ) on the potential sweep rate ( $V$ ). We offer a simple criterion to distinguish between 2D and 3D film growth.

## Experimental

The polarization measurements with linear potential sweep were performed with a stationary Ag-electrode in the glass three-electrode cell. The working electrodes were made of polycrystalline Ag (99.99% purity) in the form of the plate whose geometrical area was 1 cm<sup>2</sup>. The potential of the working electrode was measured against a mercury sulfate one connected to the working electrode cell compartment through a luggin-haber capillary tip. All potentials are referred to normal hydrogen electrode. The auxiliary electrode was a platinum foil located in a separated cell compartment.

Before the electrochemical measurements, the working electrode was degreased with alcohol, etched in nitric acid for 2 min, rinsed with distilled water, and dried with filter paper.

To the polarization measurements, we used a PI-50 potentiostat and LKD-4 recorder. The temperature was maintained by MK-70 ultracryostat in the range from -25 to -10 °C with an error of ±0.5 °C. The electrolyte solution was 5 M H<sub>2</sub>SO<sub>4</sub> prepared from sulfuric acid ( $\rho = 1.86 \text{ g}\cdot\text{cm}^{-3}$ ) of chemically pure grade together with distilled water.

## Theoretical consideration

We shall assume that rate of the film thickening is proportional to “driving force” of the reaction [6]:

$$\frac{dl}{dt} = \lambda' \Delta E \quad (2)$$

where  $l$  is a film thickness,  $t$  is a time,  $\Delta E = E - E_{st}$  is an overvoltage,  $E_{st}$  is an open circuit potential,  $\lambda'$  is a proportionality factor. Equation 2 is predicted that a film thickness increase linearly with  $t$  under potentiostatic conditions. This behavior was been observed experimentally for the anodization of copper by SEM [9]. The thickening rate of the anodic film depends on  $\Delta E$ .

Integration of the Eq. 2 gives a dependence of the film thickness on time:

$$l = l_0 + \lambda V t^2, \quad \lambda = \frac{\lambda'}{2}, \quad (3)$$

where  $l_0$  is a constant of integration.

Then, according to the Ohm's law, under potentiodynamic conditions ( $\Delta E = Vt$ ), a resulting current depend on the overall resistance of the system  $f(t, \theta(t))$ :

$$I = \frac{Vt}{f(t, \theta(t))}, \quad (4)$$

$$f(t, \theta(t)) = R_0 + \frac{l_0 + \lambda V t^2}{\kappa S(1 - \theta(t))}, \quad (5)$$

where  $R_0$  is an ohmic drop in the circuit, excluding the surface process.

On the other hand, in according to the Faraday's law, under the three-dimensional growth, a current depends both on the changing rate of the coverage degree and on the thickening rate of the film:

$$I = \frac{zF\rho S}{M} \left[ l \frac{d\theta}{dt} + \theta \frac{dl}{dt} \right]. \quad (6)$$

Taking Eq. 3 into account gives [6]:

$$\frac{d\theta}{dt} = \frac{1}{l_0 + \lambda V t^2} \left[ \frac{M}{zF\rho S} I - 2\theta \lambda V t \right]. \quad (7)$$

The intensity of the current reaches a maximum value  $I_m$  for given value of  $t$  which will denote  $t_m$  (the corresponding coverage degree is  $\theta_m$ ). An expression may be found for  $I_m$  by deriving  $I(t, \theta(t))$  (the formula 4) with respect to  $t$  and setting it to zero. Hence, we get:

$$\frac{V}{I_m} = \frac{df(t, \theta(t))}{dt} \Big|_{t=t_m} \quad (8)$$

It is easily to get by taking into account Eqs. 5 and 7 that a relationship “a current peak height ( $I_m$ )—a potential sweep rate ( $V$ )” can be submitted under the three-dimensional growth of the porous layer by the implicit form:

$$V = \frac{M}{zF\rho\kappa S^2(1 - \theta_m)^2} I_m^2 + \frac{2\lambda(1 - 2\theta_m)}{\kappa S(1 - \theta_m)^2} \Delta E_m I_m \quad (9)$$

It is necessary to note that the second term in the Eq. 9 is negatively as a rule since the covering fraction is close to 1 under the current peak. It means that the current peak height can be bigger for the three-dimensional growth than for simple film spreading model (at the same values of parameters).

Equation 9 can be written down as:

$$\frac{V}{I_m^2} = \frac{M}{zF\rho\kappa S^2(1 - \theta_m)^2} + \frac{2\lambda(1 - 2\theta_m)}{\kappa S(1 - \theta_m)^2} \frac{\Delta E_m}{I_m} \quad (10)$$

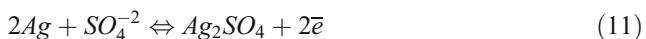
As follows from 10, a criterion for definition of growth character (2D or 3D) of the passivating layer and a calculation method of parameters of its functioning can be offered. A foundation of this method is an analysis of

experimental values for the current peak ( $I_m$ ) and the overvoltage peak ( $\Delta E_m$ ) at various potential sweep rates ( $V$ ). An essence of the method is in the following:

- (1) it is necessary to make an experimental plot of  $\frac{V}{I_m^2}$  vs  $\frac{\Delta E_m}{I_m}$ ;
- (2) if this plot is a straight line and parallel with an abscissa axis, it corresponds to two-dimensional growth of the film;
- (3) if this straight line is sloping, it corresponds to three-dimensional growth of the film;
- (4) it is necessary to determine a magnitude of the section which is cut off on ordinate axis by this straight line. The above-mentioned magnitude is equal to the first term on the left hand-side of Eq. 10. Then it is possible to calculate a covering fraction at the current peak,  $\theta_m$ , by using information concerning molecular weight and density of the film;
- (5) it is necessary to calculate a value for  $\lambda$  by using a slope of this straight line and an information above. A parameter  $\lambda$  characterizes quantitatively a thickening rate of the film.

**Experimental testing**

In [10], we have examined the electrochemical oxidation of silver in potentiodynamic polarization in aqueous sulfuric acid between  $-25$  and  $80$  °C. On the cyclic recordings, there were both a single anodic current maximum and a single cathodic current maximum, indicating the occurrence of a single electrode process. This process is reversible electrochemical formation of a resistive porous layer of silver sulfate:



It is found [10] that above  $25$  °C some of the anodic products dissolve and are not reduced in the cathodic half-cycle. The dissolution appears to be a purely chemical process. The foregoing model can't be applied to anodic oxidation of silver in sulfuric acid solution above  $25$  °C since this model does not take into account a chemical dissolution. However, this process (chemical dissolution) is absent below zero [10]. For this reason, we have tried to apply the advanced 3D-growth model to the electrochemical oxidation of silver for  $-25$  and  $-10$  °C.

In Table 1 the values for  $I_m$  and  $\Delta E_m$ , which were found by us for various potential sweep rate ( $V$ ), are shown. Figure shows the findings—  $\frac{V}{I_m^2}$  vs  $\frac{\Delta E_m}{I_m}$  plots. It can be seen that dependence  $\frac{V}{I_m^2}$  vs  $\frac{\Delta E_m}{I_m}$  is linear. This proves that relationship 10 has been confirmed experimentally. It corresponds to three-dimensional film growth. From the cut section value of ordinate axis on figure,  $\theta_m$ , the fractions

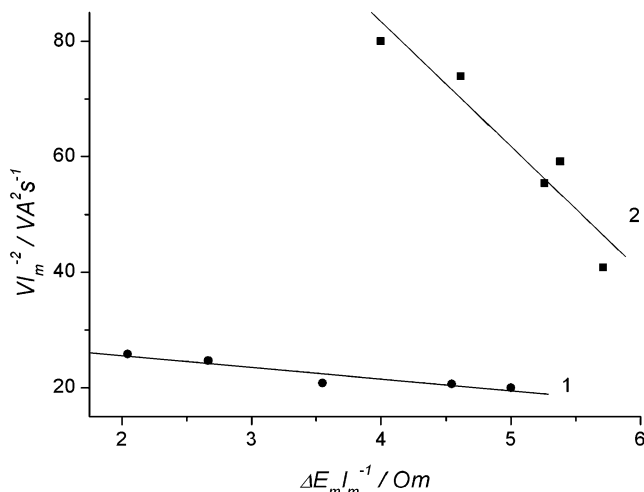
**Table 1** Current peak values and overvoltage peak values for various potential sweep rate of silver potentiodynamic polarization in aqueous sulphuric acid (5 M)

| $V/V \cdot s^{-1}$ | $T=-10$ °C |                | $T=-25$ °C |                |
|--------------------|------------|----------------|------------|----------------|
|                    | $I_m/A$    | $\Delta E_m/V$ | $I_m/A$    | $\Delta E_m/V$ |
| 0.002              | 0.010      | 0.05           | 0.007      | 0.04           |
| 0.010              | 0.022      | 0.10           | 0.013      | 0.07           |
| 0.020              | 0.031      | 0.11           | 0.019      | 0.10           |
| 0.050              | 0.045      | 0.12           | 0.026      | 0.12           |
| 0.200              | 0.088      | 0.18           | 0.050      | 0.20           |

of the covered surface at  $\Delta E_m$  were been found to be equal to 0.997 (at  $-25$  °C) and to 0.996 (at  $-10$  °C). The values for  $\theta_m$  have been calculated by using of the references data [11]:  $z=2$ ,  $\rho=5.45$  g·cm<sup>-3</sup>,  $K=22.6$  Ohm<sup>-1</sup>·m<sup>-1</sup> (at  $-25$  °C) and  $K=37.3$  Ohm<sup>-1</sup>·m<sup>-1</sup> (at  $-10$  °C). A value for  $\lambda$ , a thickening rate of the film can be found by using a slope of the linear  $\frac{V}{I_m^2}$  vs  $\frac{\Delta E_m}{I_m}$  plot. From this, the value for  $\lambda$  is equal to  $1.93 \cdot 10^{-7}$  m·V<sup>-1</sup>·s<sup>-1</sup> (at  $-25$  °C) and to  $0.60 \cdot 10^{-7}$  m·V<sup>-1</sup>·s<sup>-1</sup> (at  $-10$  °C). These are reasonable values, since, for example, tacking into account a date of [9, Fig. 1] value for  $\lambda$  for copper in acid solution has been found to be equal to  $16.65 \cdot 10^{-7}$  m·V<sup>-1</sup>·s<sup>-1</sup>.

**Summary**

A theoretical investigation of the porous film formation on the metals was carried out. It is shown that a conclusion concerning the growth type of the passivating layer can be made by the analysis of experimental dependence of the current peak value and the overvoltage peak value on the



**Fig. 1** Dependence of  $\frac{V}{I_m^2}$  on  $\frac{\Delta E_m}{I_m}$  for silver potentiodynamic polarization in aqueous sulphuric acid (5 M) at various temperature:  $-10$  °C (1);  $-25$  °C (2)

potential sweep rate. An offered model is tested for anodic oxidation of silver in sulfuric acid solution.

## References

1. Muller WJ (1931) *Trans Faraday Soc* 27:737
2. Calandra AJ, de Tacconi RN, Pereiro R, Arvia AJ (1974) *Electrochim Acta* 19:901
3. Devilliers D, Lantelme F, Chemla M (1986) *Electrochim Acta* 31:1235
4. Fleischmann M, Thirsk H (1959) *Electrochim Acta* 1:146
5. Giles RD (1970) *J Electroanal Chem* 27:11
6. Birss VI, Wright GA (1982) *Electrochim Acta* 27:1429
7. Abd El Rehim SS, Hassan HH, Ibrahim MAM, Amin MA (1998) *Monatshefte fur Chemie* 129:1103
8. Zaky AM, Assaf FH, Abd El Rehim SS, Mohamed BM (2004) *Appl Surf Sc* 221:349
9. Haseeb ASMA, Schilardi PL, Bolzan AE, Piatti RCV, Salvarezza RC, Arvia AJ (2001) *J Electroanal Chem* 500:543
10. Grishina EP, Rummyantsev EM (1999) *Surf Engin and Appl Electrochem* 3:26
11. Maximova IN (ed), Pravdin MN, Razuvaev VE, Sergeev SV, Fedotov NB (1980) *Rastvori electrolitov v visoko- i nizkotemperaturnom rezhimah. Izdatelstvo Leningradskogo universiteta. Leningrad.*