

Corrosion Process Kinetic Parameters Determination
which is Flowing Past in Mixed Kinetics Conditions

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The method of simultaneous corrosion process kinetic parameters determination (corrosion current i_{cor} , Tafel coefficients b'_a, b'_c), in conditions when the partial cathodic reaction is simultaneously controller both transport rate of a charge through a boundary of phases and diffusion rate of a depolarizer and anodic is subject to legitimacies of the slow ionization theory is offered. In this case i, η - dependence is described by the equation:

$$i = i_{cor} \cdot \left\{ \exp\left(\frac{\eta}{b'_a}\right) - \frac{\exp\left(-\frac{\eta}{b'_c}\right)}{1 - \left[1 - \exp\left(\frac{\eta}{b'_c}\right) \cdot \frac{i_{cor}}{i_d}\right]} \right\} \quad (1)$$

where $b = b' \cdot \ln 10$, i_d -limiting diffusion current.

If the exponential curves of the equation (1) to expand in a series, being not limited quantity of the decomposition terms, we come to the equation of the polarization curve by the way of degree polynomial:

$$i(\eta) = K_0 + K_1\eta + K_2\eta^2 + K_3\eta^3 + \dots + K_n\eta^n \quad (2)$$

With due regard for McLaurian's formula we shall write (2) in the form:

$$i(\eta) = \left(\frac{\partial i}{\partial \eta}\right)_{\eta=0} \eta + \frac{1}{2!} \left(\frac{\partial^2 i}{\partial \eta^2}\right)_{\eta=0} \eta^2 + \dots + \frac{1}{n!} \left(\frac{\partial^n i}{\partial \eta^n}\right)_{\eta=0} \eta^n \quad (3)$$

Thus, if $K_0 = 0$, other coefficients of a degree polynomial are precisely connected with magnitudes of the relevant derivatives.

So, if a points set of experimental dependence $i_{exp}(\eta)$ to approximate by a degree polynomial, under condition of adequate approximating all kinetic parameters of corrosion system can be calculated through magnitudes of a polynomial coefficients, as:

$$\left\{ \begin{array}{l} K_1 = i_{cor} \left[\frac{1}{b'_a} + \frac{1}{b'_c} (1 - \beta) \right] \\ 2K_2 = i_{cor} \left[\frac{1}{b'_a{}^2} - \frac{1}{b'_c{}^2} (1 + 3\beta - 2\beta^2) \right] \\ 6K_3 = i_{cor} \left[\frac{1}{b'_a{}^3} + \frac{1}{b'_c{}^3} (1 - 7\beta - 12\beta^2 - 6\beta^3) \right] \\ 24K_4 = i_{cor} \left[\frac{1}{b'_a{}^4} - \frac{1}{b'_c{}^4} (1 + 15\beta - 50\beta^2 + 60\beta^3 - 24\beta^4) \right] \end{array} \right. \quad (4)$$

where $\beta = i_{cor}/i_d$.

The proposed approach can be easy realized with the help of the PC. It is possible to apply for this standart procedures of polynomial approximating. The equation (1) has two limiting cases: at $\beta \rightarrow 0$ the corrosion kinetic is

subjected by a slow charge transportation regularities ;. at $\beta=1$ the limiting stage of total process is the depolarizer transport to electrode surface. In these cases the system (4) is simplified and can be decided analytically. The relevant expressions [2], permitting to calculate kinetic parameters through approximating coefficients are received. These expressions afterwards were used as initial guesses for the system (4) solution.

Method tested on model i, η -curves calculated on the equation (1) over the overpotential interval from $-0,030$ V to $0,030$ V and at steps of 1 mV. Some calculations results are given in the table. As it is visible from the table insignificant (less than 0,1 %) magnitudes of all kinetic parameters determination percentage errors were observed in most cases. It is necessary however to note, that the simultaneous calculation of all parameters with usage of equations set (4) in some cases (for example $\beta > 0,7$) was accompanied by a fair quantity of iterations. For this reason the procedure of evaluations was changed a little: in the beginning calculated quantity β , and then on this quantity concluded the mechanism of corrosion process. Is exhibited, that in range $\beta < 0,05$ and $\beta > 0,95$ for calculations already it is possible to use the simplified set of equations (for activation and diffusion mechanisms) without precisions of calculation evaluations.

The method can be recommended for data processing of polarization measurings at corrosion examinations.

Table

Calculation b'_a, b'_c and i_{cor} on mixed kinetic model, ($\beta=0,5$, 1-model parameters, 2-computed parameters (numerator) and percentage error (denominator))

Kinetic parameters			
	b'_a , mV	b'_c , mV	i_{cor} , mA/cm ²
1	13,0000	52,0000	0,0100
2	<u>12,9927</u> 0,0557	<u>50,9521</u> 2,014	<u>0,0099</u> 0,1504
1	26,0000	39,0000	0,0100
2	<u>12,9933</u> 0,0514	<u>38,5813</u> 1,0736	<u>0,0099</u> 0,1318
1	26,0000	26,0000	0,1000
2	<u>25,9999</u> $6,121 \cdot 10^{-5}$	<u>26,0003</u> $1,200 \cdot 10^{-3}$	<u>0,1000</u> $1,579 \cdot 10^{-4}$
1	26,0000	52,0000	0,1000
2	<u>25,9998</u> $6,138 \cdot 10^{-4}$	<u>51,9989</u> $5,748 \cdot 10^{-3}$	<u>0,1000</u> $1,393 \cdot 10^{-3}$

References

- [1] Z.Nagy, D.A.Thomas, *J.Electrochem.Soc.* **133** (1986) 2013
[2] V.I.Korobov, I.A Medvedeva, *51 ISE Meet.*, Warsaw, Poland, 2000, abstract 3/6