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THE COMPUTER SYSTEM FOR COULOSTATIC EXPERIMENTS. THE ADSORPTION MEASUREMENTS UNIT

Annotation. Mathematical model and corresponding computer application for determination of adsorption characteristics in coulostatic experiments on solid electrodes were developed. The model simulates coulostatic relaxation of the electrodes' potential while adsorption is considered as slow stage. Impact of the surface inhomogeneity on potential curves behavior is discussed. Kinetic and adsorption parameters of the electrode reactions under investigation were determined with use of an automated measuring system.

Model's adequacy was checked by comparison of real experimental data with output of computer simulation. Routines described above were developed as procedures of specialized unit within computer system for coulostatic measurements. Use of uniform data during the whole cycle of experiment series makes the simulation process more convenient for researcher and more effective with regard to time of calculation as well as reliability of results.

Key words: mathematical model,computer System, relaxation, adsorption, simulation.

1. Introduction. Kinetic effects caused by adsorption phenomena at the electrode/electrolyte interface make it possible to control the rate of the electrochemical processes as well as properties and structure of metal deposits. That is why studies on kinetics of electrochemical reactions taking place under adsorption of electrochemically inactive organic surfactants attract continuing interest despite the results already achieved. One of the most important tasks in this research direction is determination of quantitative relations between the inhibition coefficient and the surface coverage with organic substance (θ). Conventional technique is based on measurement of the double layer capacitance within the framework of the two parallel capacitors model. The coulostatic relaxation technique seems to be very promising for application in this area. It is based on injection of electric charge of controlled value into electrode system following with potential registration while charging circuit is open.

However, in the case of solid crystalline electrodes the interface reacts rather like so called constant phase element (CPE) than like a capacitor. It was shown earlier ([1]), that for adequate description of the relaxation process under coulostatic conditions one should replace the time derivative in corresponding equation with the functional

$$\frac{D^n E}{Dt^n} \equiv \frac{1}{\Gamma(1-n)} \int_0^t \frac{\mathbf{dE}(\tau)/\mathbf{d\tau}}{(t-\tau)^n} \mathbf{d\tau} \qquad (1)$$

where n is a dimensionless parameter varying within interval from 0.5 to 1; Γ – Euler's gamma-function.

2. The problem. Kinetic and adsorption parameters of the electrode reactions under investigation were determined with use of an automated measuring system [2]. If the impedance of the electrode corresponds to the Ershler – Randles model then the relation between time and relaxation potential is described by

$$C_d \frac{dE}{dt} = -\frac{E}{R_F} \quad (2)$$

where R_F is the faradaic resistance; C_d is the double layer capacitance. Solution of (2) can be obtained easily:

$$E(t) = E_0 \exp(-t/R_F C_d) \quad (3)$$

E_0 is the initial potential of the relaxation.

The double layer capacitance can be used for determination of θ being represented as sum of capacitance for pure metal surface and that of covered with organic substance one (two capacitors joined in parallel). Then:

$$\theta = (C_d^0 - C_d^\theta)/(C_d^0 - C_d^1) \quad (4)$$

where C_d^0, C_d^θ and C_d^1 are the values of C_d at coverages 0, θ and 1, respectively. C_d^0, C_d^θ can be found from (3) directly; C_d^1 can be obtained by extrapolation from capacitance/ bulk concentration of organic substance diagram.

The fact that interface of solid electrodes with electrolytes does not behave like a capacitor in the most of cases changes the measurement routine radically; formal substitution of the time derivative in (2) by the functional (1) leads to the problem of n predetermination to arise. The old technique still works in the case of n=1 only. At n<1 the dissipation of the electric energy takes place even for very short injection pulses and goes on at relaxation stage. As it has been shown earlier [3], for n<1 the potential decreases slower in comparison with corresponding exponent of (3) type. Obviously, recording of relaxing potential must occur in wider time range and choice of its width set another problem for experimenter.

These problems can be solved on the basis of computer control of the couloststic experiment. That means that few relaxation curves in series should be registered only. 2-3 of them must be used for the time window determination, next 2-3 ones – for the coverage to be calculated.

To estimate the impact of the inhomogeneity on relaxation of the potential let's present corresponding equation in form

$$K_\theta (D^n E/Dt^n) + E/R_F = 0 \quad (5)$$

where

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$$K_\theta = \theta K_{org} - (1-\theta)K_{pure} \quad (6)$$

indices at K_{org}, K_{pure} reflect that value of K corresponds to covered with organic substance or pure metal surface. Measurements at different θ allow to calculate θ, as usual:

$$\theta = (K_{pure}-K_\theta)/(K_{pure}-K_{org}) \quad (7)$$

Laplace transformation of (5) represents potential transform in the form

$$\overline{E}(s)=\frac{s^{n-1}\cdot E_0}{s^n + 1/KR_F} \quad (8)$$

In general case it was shown [1] that time dependence of the potential can be expressed as linear combination of Mittag-Leffler's functions. Here we consider the case of maximal inhomogeneity of the surface: n=0.5. For this value (8) can be re-written as

$$\overline{E}(s)=\frac{E_0}{s^{0.5}(s^{0.5} + 1/KR_F)} \quad (9)$$

In time domain (9) transforms into

$$E(t) = E_0 \exp(a^2 t)\mathrm{erfc}(at^{0.5}) \quad (10)$$

where a= $1/KR_F$. Right part of (10) is well-known tabulated function. To register the same decrease of (10) as for (3) one must use time window two orders wider than that of exponent.

In general case - $0.5<n<1$ – calculation of θ includes an algorithm for reconsruction of electrochemical system's impedance in complex plane where Re(s)=0 with following application of available program packages to simulate alternative electrical circuits of the object under investigation.

The reconstruction of the impedance includes such steps.

1. Definition of a set of functions with next properties:

a) approximation of relaxation curves under the given error level;

b) the set must include functions describing the potential relaxation for simple models (for example, n=0.5; 1);

c) the set must make it possible to represent Laplace transforms as a linear combination of analytical functions.

2. Numerical filtration of registered signal with some LF filter.

3. Normalization of records to E_0=1.

4. Approximation with linear combination of probing functions.

5. Reconstruction of the impedance as linear combination of corresponding transforms.

Such approach allows to avoid improper integrals to be calculated; including additional probing functions to the set makes possible decrease of the approximation error to given restriction.

3. Results. Model's adequacy was checked by comparison of real experimental data with output of computer simulation. Routines described above were developed as procedures of specialized unit within computer system for coulostatic measurements. Use of uniform data during the whole cycle of experiment series makes the simulation process more convenient for researcher and more effective with regard to time of calculation as well as reliability of results.

REFERENCES

1. Kapitonov A.G. Mathematical model of electrical charge relaxation on solid phase electrodes. Adequacy issues. //System technologies. –2 (67). – Dnepropetrovsk, 2010. – p. 96-99.
2. Obraztsov V., Kapitonov A., Parfyonov Yu., Danilov F. Automated system for coulostatic measurements. // Elektrokhimiya. - V.27. -№10.- 1991. - p. 1378-1380.
3. Kapitonov A.G. Specificity of computer processing of electrical charge relaxation curves at solid electrodes. //System technologies. –2 (73). – Dnepropetrovsk, 2011. – p. 32-35.

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Компьютерная система для кулоностатических экспериментов. Модуль адорбционных измерений

Розработана математическая модель и реализовано соответствующее компьютерное приложение для расчетов адсорбционых характеристик в кулоностатических экспериментах. Модель описывает релаксацию электродного потенциала при условии замедленной стадии адсорбции. Рассматривается влияние неоднородности поверхности на ход потенциальних кривых. Адекватность модели проверялась путем сравнения реальных экспериментальных данных с результатами компьютерного моделирования. Описанные выше процедуры были разработаны как процедуры специализированного блока в компьютерной системе для кулостатических измерений. Использование единых данных в течение всего цикла серии экспериментов делает процесс моделирования более удобным для исследователя и более эффективным с точки зрения времени расчета, а также надежности результатов.

Комп'ютерна система для кулоностатичних експериментів. Модуль адорбційних вимірювань

Розроблено математичну модель та реалізовано відповідний комп'ютерний додаток для розрахунків адсорбційних характеристик в кулоностатичних експериментах. Модель описує релаксацію електродного потенціала за умови сповільненої стадії адсорбції. Розглядається вплив неоднорідності поверхні на хід потенціальних кривих. Адекватність моделі перевірена шляхом порівняння реальних експериментальних даних з результатами комп'ютерного моделювання. Описані вище процедури були розроблені як процедури спеціалізованого блоку в комп'ютерній системі для кулопатичних вимірювань. Використання единих даних протягом всього циклу серій експериментів робить процес моделювання більш зручним для дослідника і більш ефективним з точки зору часу розрахунків, а також надійності результатів.

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