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Abstract

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ON A “SUSPENSION” ELECTRODE

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It is known that metal particles suspended in an electrolyte are capable, upon collisions, of imposing their potential on a metal electrode (^{1}). The essence of this phenomenon consists in the discharge of the capacitance of the particles during collisions with the electrode (^{2}). This effect has been widely used in studying the mechanism of a number of catalytic reactions in solutions (^{3}). However, only recently was the process of charge transfer by suspension particles during their collisions with an electrode polarized by means of an external source first investigated (^{4}). In the works cited, the aim was to accomplish removal of charge from the electrode by a suspension under equilibrium conditions (charging curves analogous to those obtained on massive electrodes (^{5}) were studied). Recently, polarization curves of “suspension” electrodes taken under nonequilibrium conditions have been described ($^{6-9}$). Such curves are the subject of discussion in the present paper.

The current density at the surface of the current collector is equal to the sum of the usual “Tafel” current, determined by the mean potential of the current collector $\overline{\varphi}_1$, and the current i_c carried by the suspension. The latter term is equal to

$$i_c = -\frac{1}{S}\sum_i \overline{\nu_i}\,\overline{\Delta q_i}, \tag{1}$$

where S is the working surface of the current collector; $\overline{\nu_i}$ is the mean frequency of collisions of the i-th particle with the electrode; $\overline{\Delta q_i}$ is the mean charge received by it from the electrode in one collision (for definiteness we consider a cathodic process; the charge acquired by a particle upon collision with the electrode is negative). We transform (1) as follows:

$$i_c = -\frac{1}{S}\overline{\nu}\sum_i \overline{\Delta q_i} = -\frac{1}{S}\overline{\nu}\,\overline{\Delta q}. \tag{2}$$

Here $\overline{\nu}$ is the mean frequency of collisions of particles with the current collector; $\overline{\Delta q} = \sum_i \overline{\Delta q_i}$ is the mean charge acquired by the entire suspension in one effective collision. If the capacitance of unit surface of a particle in the range of potentials considered is constant, then

$$\overline{\Delta q} = C(\overline{\varphi}_3 - \overline{\varphi}_2)\sum_i S_i = C\overline{\Delta\varphi}\sum_i S_i, \tag{3}$$

where S_i is the surface of the i-th particle; C is the capacitance; $\overline{\varphi}_2$ and $\overline{\varphi}_3$ are the mean values of the potentials of the suspension particles immediately before and after collision with the electrode; $\overline{\Delta\varphi}$ is the mean difference of these potentials. Since under real experimental conditions the contact time of the particles with the electrode is much less than the mean time between collisions $\overline{t}$,

$$\overline{\nu} \cong 1/\overline{t}. \tag{4}$$

Under stationary conditions the charge $\overline{\Delta q}$ is expended in carrying out the electrochemical reaction on the suspension particles during the time $\overline{t}$. This process of charge consumption is nothing other than a galvanostatic transition (at zero external current) from the potential $\overline{\varphi}_3$ to $\overline{\varphi}_2$. As is known, far from the equilibrium potential φ_0 it is described by the equation (^{10})

$$\overline{\Delta\varphi} = -\frac{RT}{\alpha F}\ln\left[\frac{\alpha F i_0 \overline{t}}{CRT}e^{-\alpha F(\overline{\varphi}_3-\varphi_0)/RT} + 1\right], \tag{5}$$

where α is the transfer coefficient; i_0 is the exchange current of the electrochemical reaction occurring on the suspension particles. Near φ_0, according to (11),

$$\overline{\Delta\varphi} = (\varphi_3 - \varphi_0)\left(1 - e^{-nFi_0\overline{t}/\nu RTC}\right), \tag{6}$$

where ν is the stoichiometric number; n is the number of electrons participating in the reaction. From (1)–(5) we obtain:

$$i_c = -\frac{g\sigma}{S}\,\frac{\alpha F\,\overline{\Delta\varphi}\,i_0 e^{-\alpha F(\overline{\varphi_3-\varphi_0})/RT}}{RT\left[e^{-\alpha F\Delta\varphi/RT} - 1\right]}, \tag{7}$$

and from (1)–(4) and (6)

$$i_c = -\frac{g\sigma}{S}\,\frac{nFi_0\overline{\Delta\varphi}}{\nu RT\ln\left[(\varphi_3-\varphi_0)/(\varphi_2-\varphi_0)\right]}. \tag{8}$$

In (7) and (8), g is the powder charge; σ is its specific surface ($g\sigma = \sum_i S_i$). Let us consider several special cases.

We shall assume that the contact between the particles and the current collector is good, so that during the contact time the particles have time to acquire the electrode potential. In this case $\varphi_3 = \varphi_1$, $\Delta\varphi = \varphi_1 - \varphi_2$; denote $\eta = \varphi_1 - \varphi_0$. If the time $\bar{t}$ is very small or the rate of reaction on the particles is very low, so that $\overline{\varphi_2} \simeq \overline{\varphi_1}$, the exponent in the denominator of (7) may be expanded in a series for small $\Delta\varphi$. In this case

$$i_c \simeq \frac{g\sigma}{S}\, i_0 e^{-\alpha F\bar{\eta}/RT}. \tag{9}$$

It follows from (9) that under such conditions the suspension electrode operates like an ordinary electrode with an exchange current increased by $g\sigma/S$ times. Equation (9) is valid provided that $\bar{t}$ is still much less than the contact time of the particles with the electrode. If $\bar{t}$ is so large that, in the intervals between collisions with the electrode, the particles have time to acquire the equilibrium potential, then $\Delta\varphi = \varphi_1 - \varphi_0 = \eta$. In this case equation (7) ceases to be valid, since for small $\varphi_2 - \varphi_0$ equation (5) is inapplicable. This does not prevent us, however, by using (2) and (3) and bearing in mind that in the stationary hydrodynamic regime $\bar{t} = \text{const}$, from obtaining a linear relation between current and overvoltage at any η:

$$i_c = -\frac{g\sigma}{S}\frac{C}{\bar{t}}\eta. \tag{10}$$

A comparison of equations (7) and (8) with experiment was carried out for the reactions of hydrogen evolution and ionization on various metal powders. In the experiments an ordinary electrochemical cell with a magnetic stirrer was used. The current collector was a plate of platinum gauze placed at the periphery of the cell, perpendicular to the suspension flow; a thin platinum wire—a probe—was fixed on it with the aid of glass. The probe was located near the surface (at a distance of 0.3–0.5 mm from it) along the axis of the plate on both sides. In the experiments the overvoltage of the current collector η and the potential difference between the probe and the current collector were measured for each value of η. The probe potential is equal to φ_2, if the total capacitance of the probe is significantly less than the total capacitance of the particles colliding with it at a given moment, and its polarizability is high. In our experiments the currents carried by the suspension were tens of times greater than the Tafel currents through the current collector (see below). Since the current collector and the probe were made of the same material, it may be assumed that, in order to maintain the probe potential equal to $\overline{\varphi_2}$, it is sufficient to expend only a few percent of the excess charge present at the moment of collision. Figure 1 gives the polarization curves for carbonyl nickel. At high $\bar{\eta}$ (Fig. 1a) $\overline{\Delta\varphi}$ differs from η by more than 100 mV. This makes it possible to check equations (7) and (8) in a single experiment. For such for verification, the dependences of the quantities $\Phi' = \Delta\varphi \exp(-\alpha F\bar{\eta}/RT)/[\exp(-\alpha F\Delta\varphi/RT) - 1]$ and $\Phi = \Delta\varphi/\ln[\bar{\eta}/(\bar{\eta} - \Delta\varphi)]$ on i_c were plotted in the regions of large and small η, respectively, and from the slopes of the resulting straight lines the exchange current on nickel particles was calculated. The linearity of the dependences obtained (curves 5 in Fig. 1a and b) and the comparatively good agreement

Fig. 1. Hydrogen evolution on carbonyl nickel in 1 N KOH at 20°. $\sigma = 0.426$ m^2/g; $g = 2.72$ g; $S = 0.6$ cm^2. 1 –dependence of $\bar{\eta}$ on the total current, 2 –on the Tafel current, 3 –on i_c; 4 –$\Delta\varphi$; 5 –Φ' and Φ

of the exchange-current values ($2.06\cdot10^{-7}$ A/cm^2 at small $\bar{\eta}$ and $1.57\cdot10^{-7}$ A/cm^2 at large; it was assumed that $\nu/n = 1$, $\alpha = 0.58$ (^{12})) indicate the applicability of equations (7) and (8). On the other hand, the values of i_0 lie almost within the scatter of the literature data for smooth nickel electrodes (^{13}).

The influence of the specific surface area of the powder and of the suspension concentration on the polarization curves was studied (see Table 1). The values of σ were determined

Table 1

Polarization characteristics of suspensions during H_2 evolution near the equilibrium potential. 20°. $S = 0.6$ cm^2

Suspension	σ, m^2/g	g, g	Conc., g/L	Slope of curve $i_c - \eta$, A/V · cm^2	Slope of curve $i_c - \varphi_2$, A/V · cm^2	Slope of curve $i_c - \Phi$, A/V · cm^2	$i_0 \cdot 10^7$, A/cm^2
Carbonyl Ni, 1 N KOH	0.426	2.72	120	0.143	0.91	0.157	2.06
Hydrated Ni, 1 N KOH	0.73	2.43	100	0.182	0.24	0.213	1.82
Same	0.73	2.43	160	0.172	0.23	0.200	1.72
Same	0.73	1.22	60	0.069	2.72	0.130	2.22
Raney Ni, 1 N KOH	24.0	0.66	30	0.500	10.0	1.57	1.50
Same	20.0	1.63	100	1.50	33.3	4.00	1.87
Same*	10.3	0.70	30	0.286	0.80	0.480	1.35
Pt black, 1 N KOH*	11.6	0.70	30	0.088	0.50	0.198	0.25

Figure 2

Figure 1: Figure 2

Suspension	σ, m^2/g	g, g	Conc., g/L	Slope of curve $i_c - \eta$, A/V • cm^2	Slope of curve $i_c - \varphi_2$, A/V • cm^2	Slope of curve $i_c - \Phi$, A/V • cm^2	$i_0 \cdot 10^7$, A/cm^2
Pt black, 1 N H_2SO_4*	11.6	0.70	30	0.21	3.0	0.830	1.03
Pd black, 1 N KOH*	1.1	1.50	90	0.116	0.32	0.192	1.77

* In these experiments $S = 0.8$ cm^2.

by the BET method. In all experiments the stirring rate was the same (1250 rpm). Only the initial portions of the polarization curves were studied. Despite the large differences in the specific surface areas of nickel, the exchange currents calculated from the experimental dependences

with the aid of equation (8), agree well. The same values of i_0 were also obtained in experiments on the ionization of H_2 on the same suspensions. Figure 2 shows in greater detail the results for one of the Raney nickel specimens. As can be seen, the linearity of the polarization curve at rather high $\bar{\eta}$ is combined with a very small difference between $\bar{\eta}$ and $\Delta\varphi$ (cf. Fig. 1). This is also to be expected on the basis of equation (10), obtained under the assumption $\varphi_3 \cong \varphi_1$. In (8) it was experimentally proved that, as a result of ohmic difficulties during collisions, on the average only 2% of the total charge of the particles is transferred. This means that $\varphi_3 - \varphi_0 = 0.02\bar{\eta}$ (under the condition $C = \text{const}$). In our experiments, as is evident from Fig. 1 and Table 1, $\varphi_2 - \varphi_0$, and hence the smallest possible values of $\varphi_3 - \varphi_0$, are almost always comparable with $\bar{\eta}$. It follows from this that the average contact time under our hydrodynamic conditions was substantially greater than in (8), and the assumption $\varphi_3 = \varphi_1$ is valid. Thus, the linearity of the polarization curve at large η indicates not the slowness of electron transfer during contact (^{6,8}), but the smallness of the frequency of collisions of particles with the electrode, which ensures fulfillment of the condition $\varphi_2 \cong \varphi_0$.

Fig. 2. Hydrogen evolution on Raney nickel in 1 N KOH at 20°. $\sigma = 24$ m^2/g; $g = 0.66$ g; $S = 0.6$ cm^2. The designations $1, 2, 3$ are the same as in Fig. 1;

crosses—$\Delta\varphi$.

In experiments with suspensions of platinum and palladium blacks (see Table 1), there was not observed, as in the case of nickel, any closeness between the exchange currents on powders and on smooth electrodes (^{12}). In this connection one should note the approximate equality of the activities of Raney nickel and of platinum and palladium blacks also in (8). Such a large decrease in the exchange-current density on platinum and palladium upon development of their surface has not yet found a satisfactory explanation.

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