Effect of elastic deformation on interfacial conductivity

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Reversible deformation has been observed to affect the kinetics of charge transport across an electrode–electrolyte interface. At a fixed current, a steady-state elastic extension of a platinum electrode increases the hydrogen overvoltage. The derivative of the overvoltage with respect to the strain was measured. The predominant component of this derivative is independent of the current. The argument in an exponential representation of the decay of the exchange current as a function of the extension has been found. An increase in the distance between the surface platinum atoms strengthens their bonds with adsorbed hydrogen atoms, thereby reducing the discharging current, but it does not have any substantial effect on the contribution of the overvoltage to the lowering of the activation energy. The effect observed here might be utilized to obtain new and independent information on the elementary event of the reaction.

The potential of an electrode with respect to an electrolyte, φ, is maintained by an electrical double layer at the interface.[1] If no current or only a low-density current is flowing, the potential shift of a solid electrode deformed elastically in a liquid electrolyte is of a thermodynamic nature—at equilibrium, with the electrode material involved and with corrosion of metal,[2] and also on an inert electrode in the polarizability region of the latter. It was in this region that this shift was first measured successfully by an estance method[3] (the estance is the derivative of the surface tension γ of a solid with respect to the charge density at the double layer, q). As φ is moved away from the polarizability region, the steady-state current of the discharging of ions at the electrode increases. The discharging process shunts the double layer and changes the nature of the potential shift completely. The shift acquires a kinetic nature. On an inert electrode, the equilibrium potential is set by the composition of the liquid phase, and a steady-state reversible deformation can affect only the increment in the potential with the current, i.e., the overvoltage. No information has been available on this effect or on its mechanism.

The resistance of the electrode and that of the electrolyte vary in an out-of-phase fashion upon elastic deformation. There is the possibility that these resistances can be cancelled completely by choosing the appropriate electrolyte concentration. In the present experiments we used high-purity reagents. The electrodes were made of 99.95%-pure platinum, in the form of a stretched wire 0.2 mm in diameter. The roughness factor of the wire, α, was varied from 2.6 to 16 by etching. The reproducibility of the properties of the surface, cleaned by electrolysis, was monitored by an

$Pt/5.5MKOH$; $\alpha = 16$; $j_\alpha = -60$ mA/cm^2 ($H_2\uparrow$)

$|\eta|$

$\delta_0\eta$

$|\eta|, \epsilon$

t

0.3 mV

0.8×10^{-3}

0.5×10^{-3}

20 ms

0.3×10^{-3}
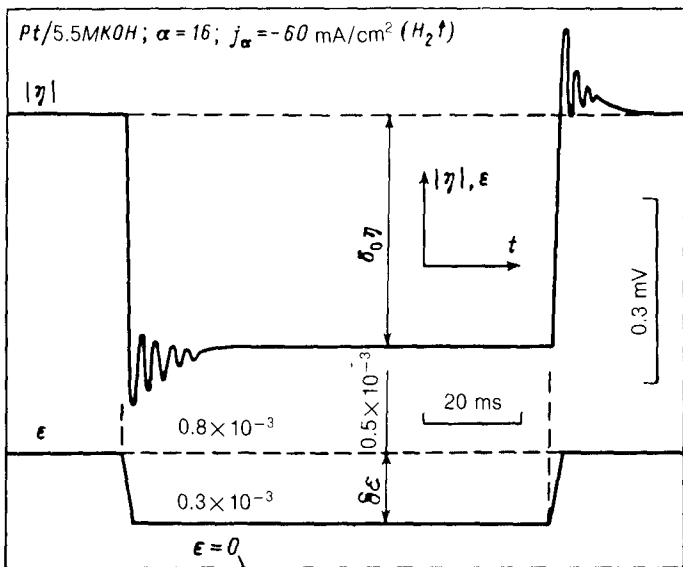
$\delta\epsilon$

ϵ

$\epsilon = 0$

FIG. 1. Effect of pulsed elastic deformation of an electrode on the hydrogen overvoltage at a fixed total current.

estance method. Measurements were carried out at 20 ± 2 °C in two deformation regimes.

1. The relative elongation ϵ was changed in a pulsed fashion from 8×10^{-4} to 3×10^{-4} over 2 ms (this was a compression). After a hold, the opposite change (an extension) was made. This was done at a fixed total current J. The overvoltage η was measured as a function of the time t (Fig. 1). In this case we have $J=Sj$, where S and j are the actual electrode area and the actual current density, $j_\alpha=\alpha j$, and $S/\alpha=0.36$ cm^2.

2. The relative elongation ϵ was varied periodically with an average value $\epsilon_0=7 \times10^{-4}$, an amplitude $\Delta\epsilon=2\times10^{-4}$, and a frequency $f=37$ Hz. The fundamental frequency of η, with an amplitude $\Delta_1\eta$, was measured as the current was swept in a linear fashion from the anodic region ($4OH^-=O_2+2H_2O+4e$) to the cathodic region ($2H_2O+2e=H_2+2OH^-$) (Fig. 2; $\delta_0\eta$ is the steady-state shift of η). The results in Fig. 2 correspond to an abrupt change in ϵ from 6×10^{-4} to 8×10^{-4} and a stepped change in the current J.

In the cathodic region we observed a reversible, steady-state decay of the absolute value of the hydrogen overvoltage during elastic compression of the platinum (Fig. 1). In the anodic region the decay of η during compression was considerably greater than the increase in η during extension, and the decay occurred over 30 ms. The spike in Fig. 1 is due to a reversible heating of the electrode during compression and the dependence of φ on the temperature T ($\partial\varphi/\partial T=+1.9$ mV/K at a cathode in $5.5M$ KOH). The height of the spike (0.1 mV) and its decay time (15 ms) correspond to
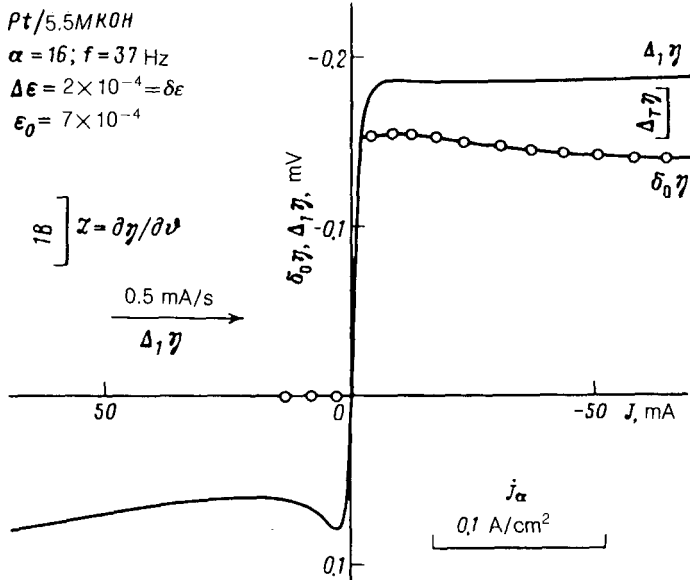
FIG. 2. Amplitude and steady-state shift of the overvoltage versus the current during periodic and pulsed elastic deformation of the electrode.

the results found with the help of a standard solution of potassium cyanoferrates (-1.5 mV/K). The oscillations are caused by transverse vibrations of the wire. The remaining shift, $\delta_0\eta$ ($+0.375$ mV for $\delta\epsilon=-5\times10^{-4}$ and $|J|=22$ mA), is free of effects due to the change in T and the charging of the double layer. To determine $\partial\eta/\partial\vartheta$, where $\vartheta=\delta S/S$ is the relative deformation of the actual area, we used a standard signal, namely, the oscillations in φ in the polarizability region.[3] With $\Delta\epsilon=5\times10^{-4}$, on the same electrode, the estance maximum $(\partial\gamma/\partial q)_m=(\partial\varphi/\partial\vartheta)_m=+0.7$ V corresponds to an amplitude $\Delta\varphi=71$ μV; here $\partial\eta/\partial\vartheta=(\partial\varphi/\partial\vartheta)_m(\delta_0\eta/\delta\epsilon)/(\Delta\varphi/\Delta\epsilon)=-3.7$ V. Corresponding measurements at other values of J, from -1 to -430 mA, showed that the change in $\partial\eta/\partial\vartheta$ in this interval was less than 20%.

The invariance of $\partial\eta/\partial\vartheta$ with respect to the cathodic current also follows from the experiments with periodic deformation (Fig. 2). At 37 Hz, the effect of the charging of the double layer is eliminated at $|j_\alpha|>30$ mA/cm^2, and the contribution $\Delta_T\eta$ of the thermal signal (the phase shift is taken into account here) is 30 μV and independent of the current. It follows that $\partial\eta/\partial\vartheta$ remains essentially constant over the $|j_\alpha|$ interval from 0.03 to 0.2 A/cm^2. From the set of data obtained on electrodes with α from 2.6 to 16 and a linear extrapolation to $J=0$, we find $\bar\eta_{\vartheta0}=(\partial\eta/\partial\vartheta)_{J=0}=-3.8$ V $\pm10\%$ for the steady-state, current-independent component of $\partial\eta/\partial\vartheta$ on platinum in 5.5M KOH.

In the coordinates $\partial\eta/\partial\vartheta-j$, the polarizability region $(\partial\varphi/\partial\vartheta-\varphi)$ degenerates to the point $j=0$. During periodic deformation, the effect of the charging of the double layer is seen at $jz<2\pi fCRT/\kappa F$, where C is the capacitance of the double layer, ze is

the charge transferred in an elementary event of the reaction, R is the universal gas constant, F is the faraday number, and κ is the η utilization factor, which is determined by the slow step of the reaction and which has a value $\kappa \approx 1/2$. As we move away from $j=0$ in either direction, the estance is positive,[3] $\partial \varphi / \partial \vartheta > 0$, on platinum. It adds to the positive branch of $\partial \eta / \partial \vartheta$, generating a maximum. It is subtracted from the negative branch in the region of the rise (Fig. 2). An invariance of $\partial \eta / \partial \vartheta$ with respect to the cathodic current is also observed on Ni, the alloy 80% Ni + 20% Cr, and Ir in 1–10M KOH and on Pt in 1–5M H$_2$SO$_4$. The measurements were carried out in intervals of j in which the Tafel equation $\eta(j) = (RT/\kappa zF)\ln(j/j_0)$ applies to the systems under study here, with $\eta z \gg RT/F$. Here j_0 is the exchange current, which is constant in this interval of j; the signs of η, z, j, j_0 are identical; and we have $\kappa = 0.45$ for platinum in 5.5M KOH.

Taking the Tafel equation into account, and differentiating η with respect to ϑ, we find, for $\eta z \gg RT/F$,

$$(\partial \eta / \partial \vartheta)_J = \bar{\eta}_{\vartheta 0} - \eta(\partial \kappa / \partial \vartheta)/\kappa, \tag{1}$$

$$\bar{\eta}_{\vartheta 0} = -(RT/\kappa zF)[1 + (\partial j_0/\partial \vartheta)/j_0], \tag{2}$$

$$(\partial j_0/\partial \vartheta)/j_0 = -1 - \kappa(zF/RT)\bar{\eta}_{\vartheta 0} \equiv -c, \tag{3}$$

$$(\partial J/\partial \vartheta)_\eta = J[1 + (\partial j_0/\partial \vartheta)/j_0 + \eta(zF/RT)\partial \kappa/\partial \vartheta]. \tag{4}$$

With $z = -1$, $\kappa = 0.45$, and the value $\bar{\eta}_{\vartheta 0} = -3.8$ V which has been found, we find $(\partial j_0/\partial \vartheta)/j_0 = -69$ from (3). In other words, there is an anomalously sharp decrease in the exchange current during elastic extension. A cold-hardened wire can withstand elastic extension up to $\epsilon_{max} = 2 \times 10^{-3}$. For a rough surface we would have $\vartheta = (\beta/\alpha)(1 - \nu)\epsilon$, where ν is the Poisson ratio, and β is the differential roughness factor.[3] Measurements of the estance on an electrode with $\alpha = 16$ yielded $\beta = 5.5$. With $\nu = 0.39$ (for platinum), the value of ϵ_{max} corresponds to $\vartheta_{max} = 0.4 \times 10^{-3}$. The experiments show that the relative change in the exchange current during the elastic deformation does not depend on the absolute value of the exchange current in the original state. In 5.5M KOH, an increase in the roughness factor of the platinum surface from $\alpha = 2.6$ to $\alpha = 16$ is accompanied by a fivefold decrease in the current density, while $(\partial j_0/\partial \vartheta)/j_0$ takes on values of -77 and -67, respectively (i.e., values which are not far apart). In a first approximation we can thus write

$$j_0(\vartheta, \alpha) = j_0(0, \alpha)\exp(-c\vartheta), \tag{5}$$

where the argument of the exchange current, c, is determined by the composition of the system. For platinum in 5.5M KOH we would have $c = 69$; the figure for 3.7M H$_2$SO$_4$ is an order of magnitude smaller.

Differentiating (1) with respect to η, and using $\partial \kappa / \partial \eta = 0$, we find

$$(\partial \kappa / \partial \vartheta)/\kappa = -\partial(\partial \eta / \partial \vartheta)/\partial \eta = j(\kappa zF/RT)\partial(\partial \eta / \partial \vartheta)/\partial j. \tag{6}$$

For platinum in 5.5M KOH with $\alpha = 16$ and $j = -2$ mA/cm^2, we find $(\partial \kappa / \partial \vartheta)/\kappa < 0.18$ and $\eta = -0.2$ V. Near this value of j, the condition $[(\partial \kappa / \partial \vartheta)/\kappa]/[(\partial \eta / \partial \vartheta)/\eta] < 0.01$ thus holds; this condition is equivalent to an independence of κ from the

elastic deformation. The value of κ may remain independent of φ and ϑ simultaneously if (for example) all the ions of the double layer behave like noninteracting particles at the time of the discharging, i.e., if they are unable to borrow energy from each other or to change their own fraction $(ze\eta/2)$ of the energy increment.

From the Frumkin equation we have $j = j_e \exp[(-G + \kappa z F\eta)/RT]$, where the effective activation energy G does not depend on η, and the coefficient j_e does not depend on η or ϑ. With $J = $ const we have

$$\partial G/\partial\vartheta = RT + \kappa z F\bar{\eta}_{\vartheta 0}. \tag{7}$$

The evolution of hydrogen from a basic medium would thus require $\partial G/\partial\vartheta = 1.74$ eV per H atom. The significant increase in G during elastic extension results from a strengthening of the bonds of the adsorbed hydrogen atoms with the platinum surface. The effect is to increase the energy required for a reorganization of the adsorption layer in the elementary event of the reaction. Because of the difference in equilibrium potentials, this effect should be more pronounced in a base than in an acid, in agreement with the anomalous increase in the estance during the adsorption of hydrogen from a basic solution.[3]

[1] A. N. Frumkin, *Zero-Charge Potentials*, Nauka, Moscow, 1979.
[2] A. R. Despic, R. G. Raicheff, and J. O'M. Bockris, J. Chem. Phys. **49**, 926 (1968).
[3] A. Ya. Gokhshteĭn, *Surface Tension of Solids and Adsorption*, Nauka, Moscow, 1976, p. 33, 186, 376.

Translated by D. Parsons