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STATE OF THE CATHODE SURFACE DURING THE GENERATION OF SOLVATED ELECTRONS IN HEXAMETHYLPHOSPHORUS TRIAMIDE

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UDC 541.138

The state of the surface of copper and platinum cathodes in the electrochemical generation of solvated electrons in solutions of lithium chloride and sodium bromide in hexamethylphosphorus triamide was studied by the method of measurement of the capacitance. It was shown that the electrodes can exist in two states: passive and active. The mechanism of generation depends on the state of the surface. On a passive electrode there is a thermionic emission of electrons, and on an active electrode their electrochemical dissolution.

Earlier we studied the kinetics of the generation of solvated electrons (SE) in hexamethylphosphorus triamide (HMPA) [1-4]. It was shown [4] that the mechanism of the generation of SE depends on the state of the surface of the metallic electrode, on the degree of its passivation. However, the change in the electrode surface was judged only according to indirect data, i.e., according to the change in the kinetic parameters of the electrochemical generation of solvated electrons; there were no direct data on the state of the surface.

For a study of the state of the surface we used a pulsed method of measuring capacitance [5]. The pulse duration was 3-5 μsec. The working electrode was an electropolished copper or platinum wire. The preparation of the electrode surface was cited in [1]. The counterelectrode for measurement of the capacitance was a platinum cylinder, the area of which far exceeded the area of the working electrode. For the rest, the design of the cell was analogous to that described earlier [4]. For an investigation of the nature of the limiting currents of the discharging of the proton donor, we used a rotating disc electrode of copper or platinum [1]. The rate of rotation was determined with a strobotachometer. The measurements were performed in solutions of lithium chloride and sodium bromide in HMPA. The purification of the solvent and preparation of the solutions were cited in [6]. Redistilled sulfuric acid was used as the proton donor. The potentials were measured relative to a lead reference electrode at room temperature [1]. The solution was mixed with a stream of purified argon.

Originally we investigated the state of the surface corresponding to the conditions of [4], i.e., when the polarization curves were recorded in the presence of solvated electrons in the volume of the solution on passive and active electrodes.

If a platinum electrode is immersed in a solution of lithium chloride in HMPA, the electrode has a capacitance of 1.9 $\mu F/cm^2$. If we take into consideration the fact that the minimum capacitance of a mercury electrode in a 0.2 M sodium perchlorate solution in HMPA is 3.7 $\mu F/cm^2$ [7], while the roughness factor of a platinum electrode is evidently greater than one, we can conclude that the surface of the electrode has a passive state under the conditions cited above. If such an electrode is subjected to cathodic polarization, or its potential is shifted toward negative values, creating a concentration of SE in the volume of the solution of the order of 10^{-3}-10^{-4} M by the generation of SE on an auxiliary cathode, we can obtain an even more passive electrode with capacitance 0.8-1.1 $\mu F/cm^2$. In Fig. 1, curves 1 and 2 present the cathodic polarization curve and the

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 13, No. 2, pp. 216-220, February, 1977. Original article submitted June 13, 1975.

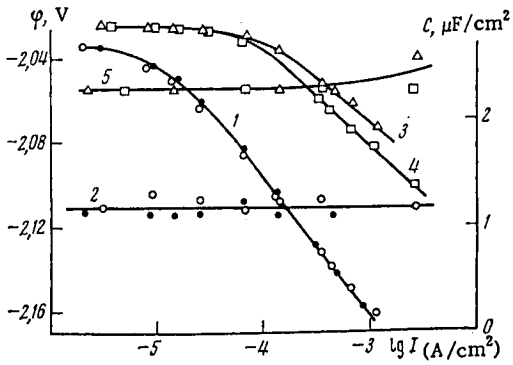

Fig. 1

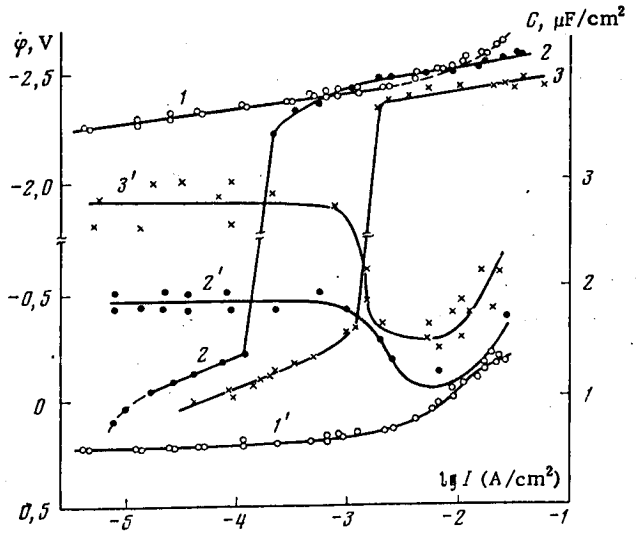

Fig. 2

Fig. 1. Dependence of the potential φ (curves 1, 3, 4) and the capacitance C (curves 2, 5) on the cathodic current density I for passive (1, 2) and activated (3-5) platinum electrodes in a solution of 0.5 M LiCl in HMPA in the presence of SE (7°C). 3) Mixing with a stream of argon; 4) without mixing; 5) with and without mixing.

Fig. 2. Dependence of the potential φ (curves 1-3) and capacitance C (curves 1'-3') on the cathodic current density I for a copper electrode (25°C): 1, 1') solution of 0.34 M LiCl in HMPA in the absence of SE; 2', 3') solution of 0.35 ± 0.03 M LiCl in 0.06 M H_2SO_4; 2, 2') measurements from large currents to small ones; 3, 3') measurements from small currents to large ones.

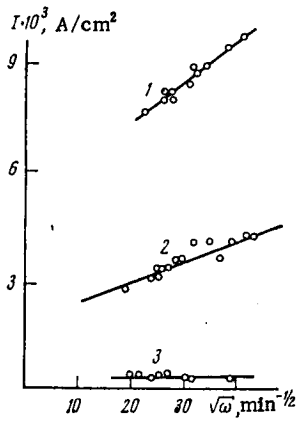

Fig. 3. Dependence of the limiting current (I) on the rate of rotation of a disc electrode ω in a solution of 0.2 M LiCl with additions of $4.24 \cdot 10^{-2}$ (1), $1.61 \cdot 10^{-2}$ (2), and $2.75 \cdot 10^{-2}$ M H_2SO_4 (3) with a copper electrode (1, 2) and a platinum electrode (3), 25°C.

curve of the dependence of the capacitance on the current density in the presence of SE in solution. The rate of generation of SE on such a passive surface does not depend on the mixing, and the state of the surface is unchanged during the recording of the curve. If the electrode is anodically polarized in a solution containing SE, with a current of 10^{-1} A/cm² for 30-90 sec, there is an activation of the surface; the rate of generation increases by approximately an order of magnitude and begins to depend on the mixing (curves 3 and 4), while the capacitance increases to 2.3 μF/cm² (curve 5).

The data for a platinum electrode are compared with the data for a copper electrode in Table 1.

Table 1 presents the electrode capacitance after immersion in the corresponding solution and the capacitance after cathodic polarization or after the creation of an appreciable concentration of SE in the volume of the solution; the values of the capacitance after anodic activation are also given.

For a copper electrode, measurements of the capacitance were performed after the corresponding treatment and disappearance of SE in the volume of the solution. In the presence of SE in solution, the values of the capacitance, especially on active electrodes, are greatly distorted on account of the pseudocapacitance associated with the reaction of solvated electrons.

TABLE 1. Dependence of the Electrode Capacitance ($\mu F/cm^2$) on the Conditions of Its Preliminary Treatment in Solutions of 0.3 M LiCl and NaBr in the presence of SE at 5°C

System	At the time of immersion	After cathodic polarization	After anodic activation	At the anodic limiting current
Copper–LiCl	2,1±0,3	1,6±0,2	3,5±0,3	3,2±0,1
Copper–NaBr	2,2±0,2	0,45±0,05	2,4±0,2	2,4±0,2
Platinum–LiCl	1,8±0,1	0,9±0.1	2,3±0,2	

Table 1 also presents the data obtained in the region of the anodic diffusion limiting currents, i.e., at a concentration of SE in the layer near the electrode close to zero. These values are close to the values determined after the disappearance of SE in solution for an electrode through which no current passes.

As can be seen from the table, the greatest degree of activation is achieved on a copper electrode in a solution of lithium chloride. A value of the capacitance of the active surface around 3.5 $\mu F/cm^2$ is preserved when the cathodic and anodic curves are taken in a solution of lithium chloride in the presence of SE. The polarization curves obtained on such a surface are analogous to those described earlier [4]. The data of Table 1 also indicate that platinum electrodes have a greater tendency for passivation than copper electrodes.

Thus, the results obtained confirm our earlier conclusion [4] that in the presence of SE in the volume of a solution of lithium chloride and sodium bromide in HMPA, two different states of the surface of copper and platinum electrodes can be realized – passive and active. Two mechanisms of cathodic generation correspond to the two different states of the surface: thermionic emission and electrochemical dissolution of electrons [4, 8].

Now let us consider the state of the surface of the copper electrode in the absence of SE in the volume of the solution.

The capacitance of a copper electrode immersed in a solution of lithium chloride with an addition of a proton donor (H_2SO_4) is 2.9 ± 0.2 $\mu F/cm^2$, i.e., greater than in a solution of lithium chloride without proton donor (see Table 1). This indicates that the initial passivation of a copper electrode is caused by some sort of basic compounds, soluble in an acid solution of lithium chloride.

If the cathodic polarization curve is taken in such a solution on a copper electrode from low currents to high ones, then the active state of the surface corresponds to the branch of liberation of hydrogen (curves 3 and 3' of Fig. 2). In the region of transition from the branch of liberation of hydrogen to the branch of generation, there is a passivation of the electrode, and the capacitance decreases. The rise in the capacitance when the current is further increased is caused by the pseudocapacitance due to an increase in the concentration of SE in the layer near the electrode.

When the cathodic curve is recorded from high currents to low ones, immediately a passive state of the surface is established (curves 2 and 2' – branch of generation of electrons). Passivation decreases upon transition to the branch of liberation of hydrogen, but it does not disappear entirely, and the transition to the branch of liberation of hydrogen occurs at lower current densities in comparison with the corresponding surfaces when the curve is taken from low currents to high ones.

The nature of the limiting currents of discharging of the proton donor depends on the state of the electrode surface. Figure 3 presents the dependence of the limiting current of the liberation of hydrogen on the rate of rotation of a disc electrode. The measurements were performed under conditions close to the conditions of measurement of the capacitance (Fig. 2). For an active copper electrode (when the curves are recorded from low currents to high ones), the values of the limiting currents I_{lim} depend on the rate of rotation ω (Fig. 3, curves 1 and 2). However, the straight lines I vs $\sqrt{\omega}$ do not pass through the origin, which is an indication of a diffusion kinetic nature of the currents, caused by incomplete activation of the surface. On a platinum electrode the limiting currents are of a passivation nature (Fig. 3, curve 3). This is due to the greater tendency of platinum for passivation in comparison with copper, which has already been noted above (see Table 1).

Figure 2 also presents the cathodic polarization curve (1) and the curve of the change in the capacitance

(1') for a copper electrode in lithium chloride solution, containing no proton donors. As can be seen, under these conditions there is an immediate passivation of the surface. The rate of generation on such an electrode does not depend on the mixing and the direction of recording of the polarization curve.

Thus, the data on the values of the capacitance agree with the assumption advanced in [2], that in the transition from the region of liberation of hydrogen to the region of generation of SE there is a passivation of the electrode surface. The possibility of realization of a more active surface in the presence of acid in the volume of the solution shows that passivation is at least partially due to the formation of basic compounds of the alkali metals.

The dispersion of the data pertaining to the polarization curves [1, 2] is due to the different degree of passivation of the electrodes. Passivation is partially random in nature – poisoning of the electrode surface by destruction products of the solvent or by impurities. This phenomenon is evidently most pronounced on a platinum electrode possessing high catalytic activity. However, in the ground state of the surface, preliminary preparation of the surface can be set: cathodic polarization induces passivation; while anodic polarization destroys the passivating effect both of a film of basic compounds of metals and of the film of decomposition products of the solvent. In the presence of SE in the volume of the solution, an active state is also preserved when the cathodic polarization curve is recorded; in the absence of SE, passivation occurs when the cathodic polarization curve is recorded.

Data on the presence of a passive film on the surface of the electrode under definite conditions permit us to draw conclusions from the results obtained earlier [2]. During the liberation of hydrogen, discharging evidently occurs on a surface free of film (the difference in the overvoltage on various metals in HMPA is close to the difference of the overvoltages in aqueous solutions). When definite conditions are observed, the liberation of hydrogen occurs on an active surface, comprising a substantial fraction of the entire surface.

A generation of SE in their absence in the volume of the solution occurs on the passive surface. The influence of thin films on the mechanism of generation was discussed earlier [4]. However, passivation can also induce the formation of thick films, blocking part of the surface, which is eliminated from the generation process.

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