THE EFFECTS OF SALT AND OXIDE LAYERS DEPOSITED DURING DISCHARGE ON THE PASSIVATION OF ELECTRODES IN STORAGE BATTERIES

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Reactions occurring on the electrodes of storage batteries can generally be described as a simple conversion of the electrode material into the oxide or salt, or vice versa. The formation of thick phase oxide or salt layers will in effect determine the duration of electrode processes. The layers formed will insulate the electrode surface and produce concentration polarization or other difficulties.

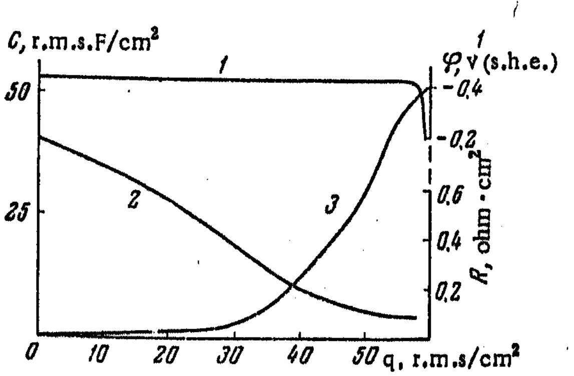

Fig. 1. A lead electrode in 8 N sulfuric acid. 1) Charge curve, 2) capacitance, and 3) resistance components of impedance.

In this report we will restrict ourselves to the examination of factors responsible for the reduction of electrode capacity, and of the part played in this by the deposits formed.

The capacity of electrodes is reduced by the fact that conditions arise on the electrode or near it, which tend to retard or entirely stop the primary electrochemical processes. Under the direction of B. N. Kabanov, we previously investigated the causes of this phenomenon by using iron and silver electrodes in alkaline solutions, or lead and lead dioxide in sulfuric acid [1, 2]. With these as an example we can examine some typical cases illustrating the effects of reaction product deposits on the electrode processes. The investigation was carried out by combining the recording of the polarization and charge curves, with capacitance and the resistance components of the impedance measured simultaneously at high-frequency alternating currents (30,000 hertz). Since it was important to know whether the principal electrochemical process ceased due to the electrode becoming passive towards this particular process, or as a result of a concentration polarization in the pores of the active electrode mass, we did our best to eliminate all possible concentration effects by using smooth electrodes.

It is a known fact that an iron anode, when polarized in alkali, will become coated with hydrated iron oxide, which has a very high electrical resistance. When, however, measurements were carried out on a discharged electrode by the use of alternating current, no resistance was observed; consequently, $Fe(OH)_2$ must have been deposited in loose layers. In a previously published paper [1], we already pointed out that iron may be rendered passive by the absorption of oxides on the electrode surface in quantities insufficient to give even a monomolecular layer. The capacitance of double layers on such electrodes decreased insignificantly during passivation – by approximately one third. All this indicates that the adsorption passivation of iron is responsible for the reduced capacity of iron electrodes in alkaline solutions. Charge curves of iron electrodes show that iron metal, which had been rendered passive to the reaction $Fe \rightarrow Fe(OH)_2$ in the first stage of the reaction would not undergo any further oxidation. On smooth electrodes, in the absence of concentration complications, we expanded one half as much electricity for the oxidation of the divalent iron to trivalent, $Fe(OH)_2 \rightarrow Fe(OH)_3$, as for the formation of the divalent iron, $Fe \rightarrow Fe(OH)_2$.

Let us examine a lead electrode in sulfuric acid; in Figure 1 we have plotted the charge curves and simultaneously recorded capacitance and resistance components of the electrode impedance towards an alternating current. Curve 1 gives the charging process with a direct current, curve 2 the capacitance, and curve 3 the resistance. As may be seen from the curves, the reaction Pb → $PbSO_4$ came to a standstill when the electrode became 90% coated with an insulating layer of $PbSO_4$ (capacitance showed a 90% drop). With the surface being so incompletely covered, we could not entirely attribute the ceasing to the electrical insulation of the surface. If that had been the case, then the process should have continued on the uncovered portion of the surface ten times as fast after the passivation as before, and with the overvoltage for this reaction being low, the potential could not have changed so abruptly towards the end of Curve 1. The phenomena in this case seem to be much more complex. Quite probably, the still uncovered surface undergoes adsorption passivation, caused by a change in the current density and the acid concentration near the free lead surface. We must also note that the change in the resistance observed, after the current was turned off, gave no grounds to assume that the reaction Pb → $PbSO_4$ ceased as a result of some concentration phenomena in the pores of the coated layer. The fact that lead sulfate can undergo further recrystallization, makes any treatment of the results even more difficult. However, we can safely state that, when the layer is not too thick and a large portion (10%) of the surface remains uncovered, the ceasing of the reaction Pb → $PbSO_4$ can not be accounted for without invoking some sort of absorption polarization.

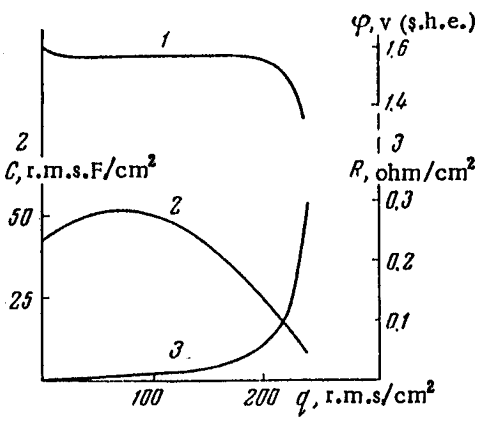

Fig. 2. A PbO_2 electrode, electrodeposited on gold, in 8 N sulfuric acid.
1) Charge curve, 2) capacitance, and 3) resistance components of the impedance.

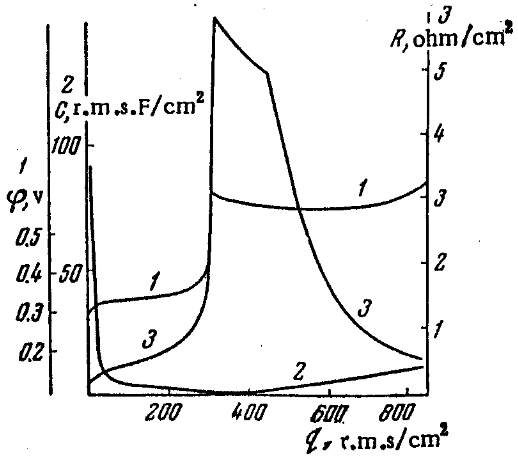

Fig. 3. A silver electrode in 10 N KOH.
1) Charge curve, 2) capacitance, and 3) resistance components of impedance.

The problem becomes even more complex when we pass over to a lead dioxide electrode. In Figure 2 we have plotted curves similar to those given in Figure 1, but recorded on a smooth lead dioxide electrode. The electrode was prepared by electrodeposition of lead dioxide on a gold wire.

As the figure shows, we saw the same behavior on both a lead dioxide and a lead electrode. It is quite natural for identical electrochemical reactions occur on both electrodes – the electrode material (lead or lead dioxide, which is an even better conductor of electricity) is converted to lead sulfate. However, difficulties arose when we started processing the data obtained on lead dioxide. It is known that the capacity of electrodes in lead storage batteries increases when the acid is diluted, while just the contrary behavior was observed on lead dioxide electrodes. To resolve the question as to what caused such a discrepancy, we compared the capacities of smooth lead and lead dioxide electrodes at different acid concentrations, and showed that the capacity of a smooth lead dioxide electrode increased with dilution just as in the case of lead metal. A theory was proposed that the capacity of the positive electrode in a lead storage battery is not reduced by passivation, as is the case on a smooth electrode, but by the appearance of concentration polarization. This theory is in excellent agreement with E. I. Krepakova's experiments [2]. Coated plates of a lead storage battery were discharged in an excess of the electrolyte, in 2 and 10 N H_2SO_4, and a very small current was used in order to avoid concentration polarization which results from decreased acid concentration in the pores of the active mass. Under such conditions the capacity in 2 N H_2SO_4 was 15% higher than in 10 N H_2SO_4; consequently, when some measures were taken to decrease the concentration polarization, the capacity of positive as well as of negative plates, increased with decreasing acid concentration. Thus, the reduced capacity of lead and smooth lead dioxide electrodes, as well as of coated positive electrodes (at very low current densities), was caused by the insulation of most of the surface and the passivation of the remaining uncovered portion.

A silver electrode in alkaline solutions behaves somewhat differently. In Figure 3 we have plotted the curves obtained (in cooperation with G. L. Vidovich) with a silver electrode in 10 N KOH. The legend is the same as in Figures 1 and 2. The first plateau ended after the surface became fully coated with an insulating layer of Ag_2O. Initial discharging was accompanied by a sharp drop in the capacitance which at the end of the first plateau declined to approximately 1% of its original value. However, the Ag_2O layer did not render the metal entirely passive; practically complete passivation did not take place till much later and at higher potentials. Actually, as the polarization was continued the silver metal retained its activity while discharge proceeded on the second anodic plateau, where the nonconducting Ag_2O was being converted to the conducting Ag_2O_2. Thus, by properly selecting the current density, it was possible to extend the second plateau to several times the length of the first. When the current density was regulated so as to yield a 0.565-0.57 v potential (against a mercurous oxide electrode in the same solution) the second plateau could be made very long. At about 0.6 volts (against a mercurous oxide electrode in the same solution) the silver became almost completely passive. When current densities were used such that the second-plateau reaction would proceed at voltages above this value, the second plateau was not longer than the first. A comparison between the anodic and cathodic charge curves also showed that practically no silver oxidation took place at potentials above 0.6 v.

Therefore, the true passivation of silver occurs at potentials more postitive than the one at which the reaction $Ag \rightarrow Ag_2O$ comes to a stop on the first anodic plateau.

From what has been said so far, one can readily see that under some conditions the oxide and salt layers, which had deposited, will have practically no insulating or passivating effect on the electrode, even though they may have a high electrical resistance, while in other cases the insulation of the surface may lead to adsorption passivation.

LITERATURE CITED

[1] B. N. Kabanov, and D. I. Leikis, J. Phys. Chem. 20, 995 (1946); Proc. Acad. Sci. USSR, 58, 1685 (1947); D. I. Leikis, Dissertation, Institute of Phys. Chem. Acad. Sci. USSR, 1948.

[2] B. N. Kabanov, D. I. Leikis, and E. T. Krepakova, Proc. Acad. Sci. USSR, 98, 989 (1954).