The Capacity of a Bright Platinum Electrode in Various Electrolytes and its Dependence on the Treatment of the Electrode

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Extensive investigations carried out recently upon the capacity of the platinized platinum electrode [1] showed that the determination of the capacity may be utilized as a method for the measurement of the adsorption of hydrogen on platinum. By means of the determination of the capacity it was possible to find the dependence of hydrogen adsorption on the potential of the platinized platinum electrode and on the composition of the electrolyte.

The capacity of the bright platinum electrode was also the subject of repeated investigations. Bowden [2] found that it remains constant between the hydrogen and oxygen potentials. Armstrong and Butler [3] et al. found that during the change of potential from the hydrogen to the oxygen values there are arrests on the charging curve at certain potentials due to the removal (or deposition) of hydrogen or oxygen from the surface of the platinum. But as the charging curves („potential-charge" curves) of the bright electrode, given in the papers cited by us [2,3], do not seem to correspond to the equilibrium states of the electrode, the data now available on the capacity of the bright platinum electrode

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[1] Šlygin a. Frumkin, Sow. Phys., **4**, 246 (1933); Acta Physicochimica URSS, **3**, 731 (1935); **4**, 911 (1936); C. R. Acad. Sci. USSR, 1934.

[2] Bowden, Proc. Roy. Soc., (A) **125**, 446 (1923); Bowden a. Rideal, ibid., **120**, 53, 80 (1928).

[3] Butler a. Armstrong, Proc. Roy. Soc., (A) **143**, 89 (1933): **137**, 604 (1932); Armstrong, Himsworth a. Butler, ibid., **143**, 89 (1933).

unfortunately cannot be used in the same manner as those referring to the platinized platinum electrode.

It was found, indeed, that, e. g., for a platinized electrode, the arrest of the charging curve, corresponding to the removal of adsorbed hydrogen, ends at a potential of 0,3 to 0,4 V against the reversible hydrogen electrode, whereas in curves given by Butler and Armstrong this retardation only begins at 0,3 V. The difference between the bright and platinized electrodes can be most naturally explained in the following manner: the bright electrode must be quickly charged in order to diminish the influence of the depolarization processes, and the entire interval between the hydrogen and oxygen potentials is gone through in a few seconds. At such a rate of change of potential the process of removal of hydrogen may not keep place with the change of potential of the electrode. It attains a noticeable speed and consequently is only detected at a more anodic potential than that at which it occurs on the equilibrium curve. The same is, of course, true for the other arrests on the charging curves of the bright platinum electrode (deposition of hydrogen, removal and deposition of oxygen).

This retardation is the cause of the fact, that the process occuring at a given arrest does not terminate until potentials are reached, corresponding to the beginning of new processes. It is therefore very probable that there are regions on the charging curves of the bright platinum electrode where different processes overlap. All this does not allow of using the existing data on the capacity of the bright platinum electrode for the determination of the relation between the adsorption of hydrogen and oxygen and the potential of the electrode. We thought it therefore necessary to re-investigate the problem. In this part of our work we determined the capacity of the bright electrode using the method described in the work of Borissova and Proskurnin [4]. The electrode was polarized to a definite potential and at this potential a 50 hertz alternating current was applied, creating an alternating potential difference at the electrode-solution boundary, not exceeding $\pm$ 15 mV. It was always possible in this manner to hold the electrode sufficiently long at

[4] Borissowa u. Proskurnin, Acta Physicochimica URSS, 4, 819 (1936).

the chosen potential, to secure an equilibrium state corresponding to that potential and then to measure the capacity.

The results of our measurements agree, to a certain extent, with the data for the platinized electrode and we consider their publication to be of interest.

Description of apparatus

The apparatus (see Fig. 1) consists of two vessels: *A* which contains the electrodes to be tested and *B* which contains a large

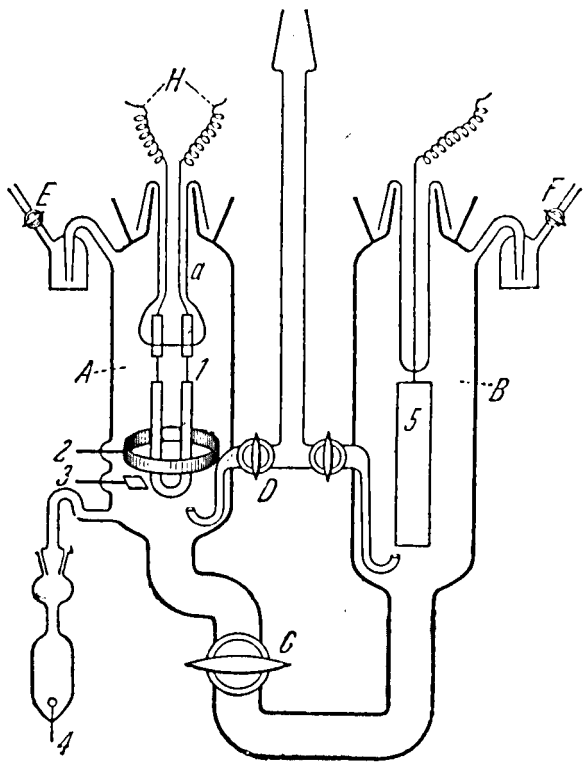

Fig. 1.

platinum electrode for the purification of the solution (see below). The electrode 1 to be investigated is prepared in the form of a ribbon of thin platinum (0,05 mm) 2×75 mm in size, fixed in the following manner: in the tube *a* connected to the vessel *A* by means of a ground glass joint, two thick platinum wires are fused,

to which the ends of the ribbon serving as the electrode to be tested are welded. Such an arrangement allows the electrode to be glowed in an atmosphere of hydrogen or oxygen. Before heating the electrode, it is necessary to force the liquid from the vessel *A* into *B*. This is done by closing the tap *E*, opening *C*, *F* and *D* and introducing through *D* into *A* hydrogen (or another gas) which forces the liquid into *B*. When the liquid is forced out, the tap *C* is closed and after opening *E*, hydrogen is passed throught *A* in order to fully remove the oxygen. *E* is then closed, *C* and *A* are opened and hydrogen is continually passed through *D* finally to escape through the vessel *B*. The heating current is then applied to the wires *H* using a voltage of 4 to 8 volts. The electrode under investigation can be brought to white glow almost instantaneously. In addition to the electrode to be tested, the vessel *A* contains an electrode *2*, through which the alternating current is passed to the electrodes *1* and *3*, the latter being used as a reference electrode during the measurement of the capacity (see the paper of Borisova and Proskurnin). Polarization with D. C. is applied to electrode *1* with the aid of a large platinized electrode *5* which is always kept in an atmosphere of hydrogen and measured against a calomel reference electrode *4*, connected to *A* by a narrow capillary tube.

The influence of purification of solution on the capacity

The results of the capacity measurements were greatly affected by the degree of purity of the solution. In pure solutions, the capacity at potentials near the reversible hydrogen potential (in an interval of 0,2 V on the anodic side) is high (about 1000 m. f./cm^2). If, however, the solution is insufficiently purified, such a high capacity is observed only during the first moment of immersion of the electrode into the liquid. It then begins to fall rapidly and may diminish during a few minutes to $^1/_3$ or $^1/_4$ of the initial value. Stirring of the solution by hydrogen or nitrogen under these conditions greatly accelerates the decrease of the capacity. This was studied in detail with HCl. The purest HCl of Kahlbaum contains traces of some impurities which lower the capacity. We purified our acid with a large platinized electrode in an atmosphere of hydrogen for 24

hours and more as described by Aten [5]. The high capacity of the electrode remains constant in an acid purified in such a manner for several hours.

The capacity curve in 1 norm. HCl

If the electrode is cleaned with chromic acid solution or with aqua regia and then heated to red glow in air, it gives in 1 norm. NCl the capacity curve shown in Fig. 2 (curve *a*). The shape of the

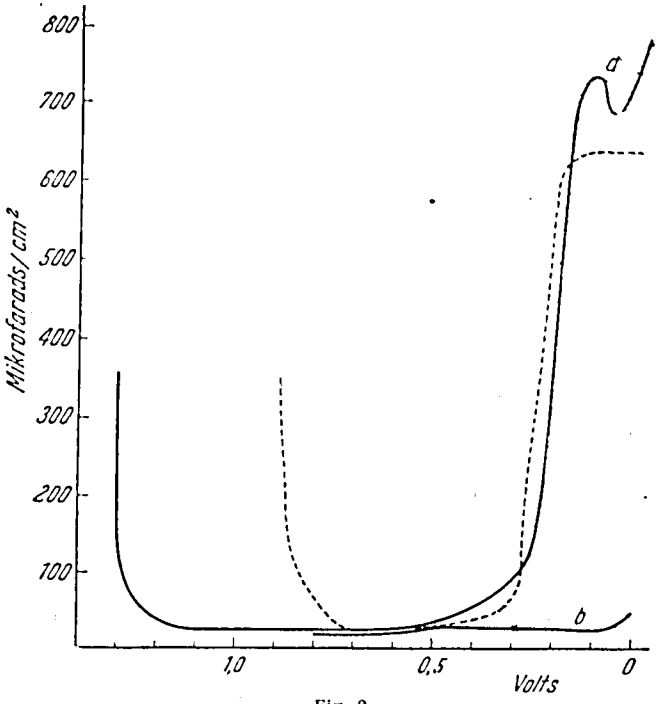

Fig. 2.

curve, as shown by a series of experiments, is very little influenced by the direction in which the curve is passed as well as by stirring the solution with hydrogen, oxygen or nitrogen.

Active and passive electrodes

We found that the shape of the capacity curve in HCl greatly changes if the electrode is heated in hydrogen and afterwards brought

[5] Aten, Rec. Trav. chim. Pays-Bas, **46**, 417 (1927).

into contact with a liquid saturated with hydrogen without coming into contact with air. The capacity curve of such an electrode is shown in Fig. 2 (curve *b*). The rise of such a curve in the hydrogen region, corresponding to the deposition of hydrogen begins at much more negative potentials than with a curve obtained as described above. In addition, the rise is very little. If the potential of this electrode is changed without reaching a more anodic polarization than 0,3 — 0,4 V with respect to the reversible hydrogen electrode, then the capacity curve preserves the shape *b* and it may be considered that the capacity changes more or less reversibly with the potential. If, however, the electrode is polarized to potentials more anodic than 0,4 — 0,6 V, then upon return to a more negative potential, the capacity now changes not according to curve *b*, but according to curve *a*. Although a further approach to the reversible oxygen potential somewhat increases the capacity, it does not change the shape of the curve. We shall call the electrode giving the curve *b* passive and the electrode giving the curve *a* active. Passive electrodes are also obtained with impure solutions. In these cases, after the electrode is exposed to a more anodic polarization than 0,4 — 0,6 V, its capacity changes upon returning to the hydrogen potential according to curve *a*, but if the electrode is then left in the impure liquid, it will finally give again the curve *b*.

It should be mentioned that passive as well as active electrodes retain the reversible hydrogen potential in an atmosphere of hydrogen and return to it sufficiently quickly after positive polarization [6].

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[6] The terms „active" and „passive" for bright electrodes have already been often used in electrochemical literature. An electrode is called active if the hydrogen overvoltage is small (viz. Hammet, J. Am. Chem. Soc., 46, 7, 1924; Armstrong and Butler, Proc. Roy. Soc., A, 143, 89, 1933; Volmer, Z. physik. Chem., (A), 172, 429, 1935). Hammet had already found that as a result of repeated anodic and cathodic polarisations, the overvoltage on a bright platinum electrode decreases. The same was confirmed by Armstrong and Butler. Bowden (Proc. Roy. Soc., A 125, 446, 1933) found that as a result of repeated anodic and cathodic polarizations the arrest on the charging curve between the hydrogen and oxygen potentials is increased. This increase of the length of the arrest he assumed to be due to the growing „activity" of the electrode, meaning by activity, as did the others, the rate of discharge of hydrogen.

The capacity of the active bright electrode in different electrolytes

We carried out measurements of the capacity in normal solutions of HBr, H_2SO_4 and KOH. The curves obtained are given in Fig. 3.

Discussion of results

Our results enable us to conclude that, qualitatively, the dependence of the capacity of the electrode on the potential for bright platinum is similar to the same dependence for platinized platinum. On all curves, we have a region of high capacity in the interval from the reversible hydrogen potential to 0,3 — 0,4 V on the anodic side, corresponding to the presence of a hydride film; then the capacity rapidly falls down to a small value, corresponding probably to the double layer region [1] and then again follows a region of high capacity, corresponding to the formation of oxides.

The similarity of the behaviour of the bright and platinized electrodes is also made evident by the fact that the influence of the electrolyte on the capacity curve in the case of the bright electrode is qualitatively the same as in the case of the platinized one. Namely, the length of the double layer region on the capacity curve is greatest in HBr and decreases in the following order: HBr > HCl > H_2SO_4 > KOH.

However, we also observe certain differences between the behaviour of both electrodes.

Firstly, we see that the capacity curve of the bright electrode rises in the oxygen region in the case of HCl at considerably more positive potentials than the curve of the platinized electrode (Fig. 3 dotted curve). This difference may be explained in two ways:

Using the terms „active„ and „passive" for the electrodes which were studied in our work, we leave open for the present the question as to whether the activity and passivity of our electrodes signifies merely the difference in the rate of discharge (ionization) of hydrogen, or whether the difference between these electrodes implies as well a difference in the amount of adsorbed hydrogen under equilibrium conditions and the energy of the metal-hydrogen bond. In preliminary experiments we found that the overvoltage on our passive surface was only slightly higher than on the active one.

1. Bright platinum begins to oxidize at more positive potentials than platinized platinum.

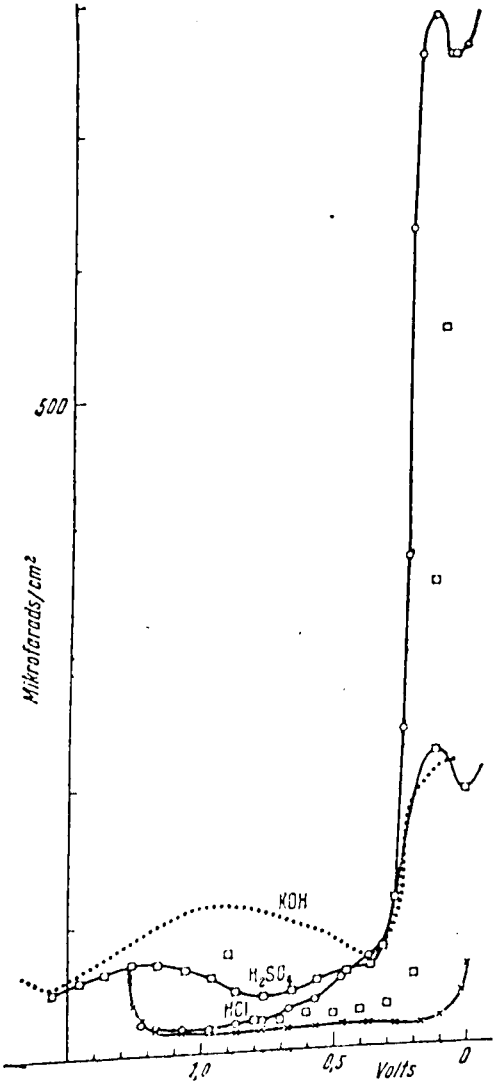

Fig. 3.

2. The oxidation of platinum proceeds so slowly, that under the conditions of our measurements (50 hertz A. C.) the oxides have no time to be formed or removed and therefore we do not detect

the influence of the oxidation of platinum on the capacity curves although this oxidation actually occurs.

In order to decide between these two explanations it is necessary to carry out the determinations of capacity while charging the surface at a smaller rate. However, at such low rates of charging, depolarization currents brought about by gases dissolved in the liquid begin to become important. In order to eliminate these difficulties we propose to carry out such determinations in the future using a „perfectly polarisable bright platinum electrode" (see below).

Another distinction is that, strictly speaking, the double layer region, i. e. the region in which the capacity changes comparatively little with the potential, is observed only in the case of HBr. In HCl (in the case of an active surface) we have almost no such region of constant minimum capacity since the minimum noted at 1,0 V corresponds to a surface already covered with oxygen, as follows from the data obtained with the platinized electrode. In the case of sulphuric acid, the minimum capacity in twice as high as the capacity in the double layer region in HBr or the minimum capacity of a passive surface in HCl.

This difference may be explained by assuming that on our active surface obtained with bright platinum, we have more firmly bound hydrogen than on a platinized surface. This hydrogen should be removed or deposited at more anodic potentials. The presence of the „bright" platinum of more firmly bound hydrogen than on platinized platinum is certainly rather unexpected. The behaviour of the active and passive electrodes is also of great interest. The earlier rise of the capacity curve of the active electrode in the hydrogen region may again mean the presence either of more firmly bound hydrogen which is deposited at more positive potentials or simply the retardation of the process of the deposition and removal of hydrogen on the passive electrode. In exactly the same manner, the low capacity of the passive electrode in the hydrogen region may mean either a retardation of the processes of the deposition of hydrogen, or a decrease in the quantity of adsorbed hydrogen.

„The perfectly polarizable electrode"

In order to solve these questions, measurements of the capacity of the bright platinum electrode should be carried out by charging

with currents of very low density. At present, a method is proposed by one of us (B. Ershler) which makes such measurements possible.

The method is based on the use of a practically „perfectly polarizable electrode" from bright platinum. An electrode is placed in a vessel containing only such an amount of liquid that the quantity of gases which it is able to dissolve is negligible in comparison with the capacity of the electrode. As has already been ascertained, such an electrode shows almost no leakage of electric charge and is practically perfectly polarized. The depolarization current of such an electrode does not exceed 10^{-9} A, while the surface equals 1 cm^2. Investigations with such an electrode are being carried out at present and the results will be published in a following communication.

Conclusion

It was shown that the capacity of the bright platinum electrode depends very greatly on the purity of the solution and on the previous treatment of the electrode. Heating in hydrogen gives an electrode having a small capacity in the hydrogen region. The influence of the composition of the electrolyte on the shape of the capacity curve of the bright platinum electrode is similar to that observed in the case of the platinized electrode. The difference between the curves of the bright and platinized platinum electrodes is essentially pronounced in the oxygen region; it can be explained probably by the slowness of the process of deposition and removal of oxygen. A new method of measuring the capacity of the bright platinum electrode is described.

In conclusion we are glad to express our gratitude to Prof. A. Frumkin, who suggested this work, for his help in its fulfilment.

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