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SURFACE CHEMISTRY OF THE PLATINUM ELECTRODE.

By B. Ershler and A. Frumkin.

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Earlier investigations have shown that with the help of polarisation measurements [1] adsorbed layers of oxygen and hydrogen can be detected on the surface of a platinum electrode, whereas direct adsorption measurements [2] indicate the presence of cations and anions adsorbed from the solution through an exchange adsorption mechanism. In a series of papers from these laboratories [3] it was shown that in the case of large strongly platinised electrodes both methods can be applied simultaneously, and a fairly complete picture of the state of the electrode surface can thus be obtained. The main advantage presented by these electrodes is that on account of their large surface the influence of the residual dissolved gases on the potential of the electrode is negligible and any intermediate value of the potential in the region between the hydrogen and the oxygen potential imparted to the electrode can be conserved for a practically indefinite time. This makes it possible to carry out adsorption measurements at different potentials and to effect the charging of the electrode with small current densities in such a way that the potential of the electrode is changed from the hydrogen to the oxygen value over a period of several hours. The "charging" curves (*i.e.*, the curves giving the relation between the potential of the electrode ϕ and the amount of electricity imparted to the electrode Q) obtained under these conditions show a close approach to reversibility, especially in the hydrogen region, and are very well reproducible even in minute details. It was shown that various conclusions as to the adsorption of hydrogen and oxygen on platinum can be drawn from these curves. In particular, the shape of the adsorption isotherm of hydrogen can be determined, and it can be shown that, to a first approximation, there is a linear relationship between the amount adsorbed and the thermodynamic potential of adsorbed hydrogen, as in the case of Na films on W. The binding energy of hydrogen depends very much on the nature of the dissolved electrolyte; it increases in the order $HBr < HCl < H_2SO_4 < KOH$, thus proving the strong polarity of the platinum hydrogen bond.[3(a)] From two charging curves taken in solutions of different p_H the change of the ionic adsorption with variation of potential can be calculated with the aid of a thermodynamic relation [3(c)] and can be compared with the adsorption curves as found by direct experiment.[3(b)] From the totality of data obtained by measurements of polarisation and adsorption the influence of atoms and ions on the metal-solution potential difference can be determined. The measurement of charging

[1] Bowden and Rideal, *Proc. Roy. Soc. A*, 1928, **120**, 59; Bowden, *ibid.*, 1929, **125**, 446; Butler and Armstrong, *ibid.*, 1932, **137**, 604; Armstrong, Himsworth and Butler, *ibid.*, 1933, **143**, 89.

[2] Frumkin and Obrutschewa, *Z. anorg. Chem.*, 1926, **158**, 84; Frumkin and Donde, *Ber.*, 1927, **60**, 1816; Kolthoff and Kameda, *J. Am. Chem. Soc.*, 1929, **51**, 2888; Frumkin, *Sow. Phys.*, 1933, **4**, 246.

[3] Frumkin and Šlygin, *C.R. Ac. Sc. URSS*, 1934, **2**, 176; (*a*) Šlygin and Frumkin, *Acta Physicochimica URSS*, 1935, **3**, 791; (*b*) Šlygin, Frumkin and Medwedowsky, *ibid.*, 1936, **4**, 911; (*c*) Frumkin and Šlygin, *ibid.*, 1936, **5**, 819.

curves serves also as a convenient tool for the comparison of platinum black deposits obtained under different conditions and for the study of the recrystallisation of platinum black on heating.[3(a), (c)]

Nevertheless, the data obtained with platinised electrodes are, in one respect, incomplete, since the true area of these electrodes is unknown. It was therefore desirable to work out similar methods which could be applied to a bright electrode.

Experimental.

A difficulty was encountered owing to the depolarising action of the inevitable traces of dissolved gases, which becomes relatively more important with a small electrode surface. This difficulty may be overcome by two methods. The one consists in using large current densities, so that the diffusion effect becomes negligible, the change from the hydrogen to the oxygen potential occurring in a short interval of time. This method was applied in a recent paper by J. Pearson and J. A. V. Butler.[4] The curves obtained with such large currents (of the order of 1 amp./cm.^{2}) clearly correspond to conditions which are very far from equilibrium, as shown, for instance, by the large discrepancy between the anodic and cathodic curves. Another method was developed by one of the present authors.[5] The harmful influence of dissolved substances which are electrochemically active is eliminated by decreasing the volume of the liquid which is in contact with the electrode (a platinum wire with a surface of 0·78 cm.^{2}) to a few mm.^{3}. The oxygen dissolved in this small volume was removed by gentle cathodic polarisation. The cell used is shown in Fig. 1. It consisted of a capillary (*b*) widened at the end where a carefully ground joint (*c*) was inserted. A small platinum wire (*d*) was sealed into the bottom of the capillary, making contact with the electrode (*f*) to be investigated. The end of the syphon from the large hydrogen electrode, with respect to which the potential of the electrode under investigation was measured and through which the polarisation was effected, was led into the cup of the cell (*a*). With a cell of this kind the action of dissolved gases on the potential is reduced to a minimum, the depolarising currents being of the order of 10^{-11} amp. The charging curves could therefore be taken with very small currents, usually from 3×10^{-8} to 3×10^{-7} amp, the whole of the change from the hydrogen to the oxygen potential occurring in times of the order of an hour. The curves thus obtained show more detail and better approach to reversibility than those obtained with high current densities. In contrast with the latter, the stage referring to adsorbed oxygen and hydrogen can be distinguished on both the anodic and cathodic curves.[5(e)] The method here described has an important additional advantage: the danger of poisoning the electrode by traces of impurities present in every solution is very much reduced if the electrode comes into contact only with a very small amount of the liquid. For further experimental details the original paper must be consulted.[5(d)]

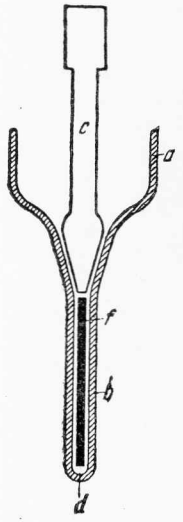

FIG. 1.

In Fig. 2 an example of curves obtained with 0·5 N. Na_2SO_4 + 0·02 N. H_2SO_4 is given, the zero on the potential scale indicating the reversible hydrogen potential in this solution. The current density was $2{\cdot}77 \times 10^{-7}$ amp./cm.^{2}. The electrode was initially cleaned by heating in air and the oxide layer removed by appropriate cathodic polarisation. The dotted curve gives the change of potential observed during two minutes after the interruption of the anodic polarisation. The current was then reversed and the cathodic polarisation started. The total quantity of hydrogen adsorbed at the reversible hydrogen potential, as determined by this method, corresponds to the number of platinum atoms on the surface, if we assume that the true surface area of the electrode slightly exceeds (by a factor of about 1·4) its apparent area.

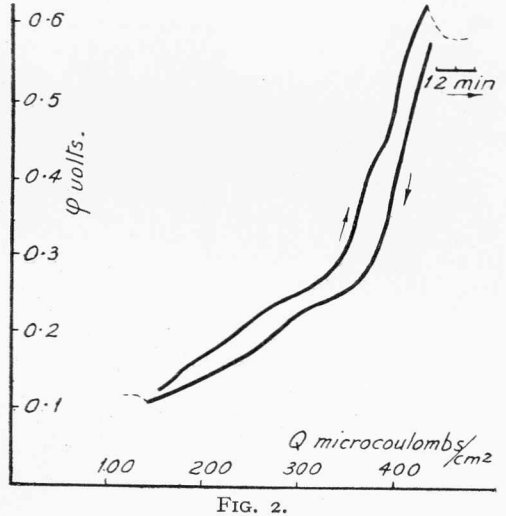

FIG. 2.

With the treatment of the electrode described above the charging curves obtained are very well reproducible and the influence on their shape of exceedingly small quantities of chemically active substances adsorbed at the platinum electrode can be traced.[5(e)] This is shown by Fig. 3; curve (*a*) is an anodic curve obtained with a solution of N. Na_2SO_4+0·02 N. H_2SO_4; the other curves were obtained after addition of successive portions of Na_3AsO_4 to the solution. The curves observed in the presence of As are very similar to those described by Pearson and Butler as corresponding to an "inactive state" of the electrode. A detailed account of the influence of different poisoning substances on the charging curves will be given in a paper shortly to be published in the *Acta Physicochimica URSS*.

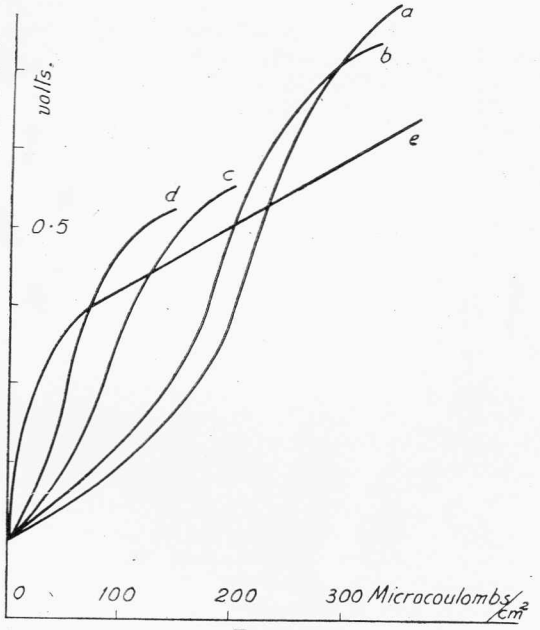

FIG. 3.

The poisoning of a platinum electrode by A_s

a—initial curve.		
b—$4 \cdot 10^{-9} g$	A_s	
c—$2 \cdot 10^{-8} g$	A_s	
d—$4 \cdot 10^{-8} g$	A_s	
e—$2 \cdot 10^{-6} g$	A_s	

[4] *Trans. Faraday Soc.*, 1938, **34**, 1163.

[5] (*d*) B. Ershler, *Acta Physicochimica URSS*, 1937, **7**, 327; *cf.* also (*e*) B. Ershler, G. Deborin and A. Frumkin, *ibid.*, 1938, **8**, 565. These papers seem to have escaped the attention of Pearson and Butler, as they state: "... curves of that kind cannot be obtained with bright electrodes using small currents. ..."

The study of the charging curves may be of considerable importance in regard to the theory of over-voltage, as they make it possible to investigate separately one of the steps involved in the evolution of hydrogen, *viz.*, the reaction $H_3O^+ + Pt + \epsilon \rightarrow H_2O + Pt[H]$. In our opinion, however, no definite conclusions can be drawn until quantitative data on the kinetics of this reaction will be available. At the present moment the work is being continued on these lines.

Summary.

Various methods of investigating the surface of platinised and bright platinum electrodes have been described and the more important results obtained briefly summarised.

Karpov Chemical Institute,
Electrochemical Laboratory of the Moscow State University.

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