

Novel Method of Electrical Storage

TRANSFER OF HYDROGEN BETWEEN ELECTRODES OF PALLADIUM ALLOYS

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Different pairs of palladium alloys can form a series of secondary cells that depend for their operation, both during charging and discharging, solely on the transfer of hydrogen from one electrode to the other. Cells may be prepared with a low internal resistance and future studies of a wider range of palladium alloys are likely to extend the range of working voltages available.

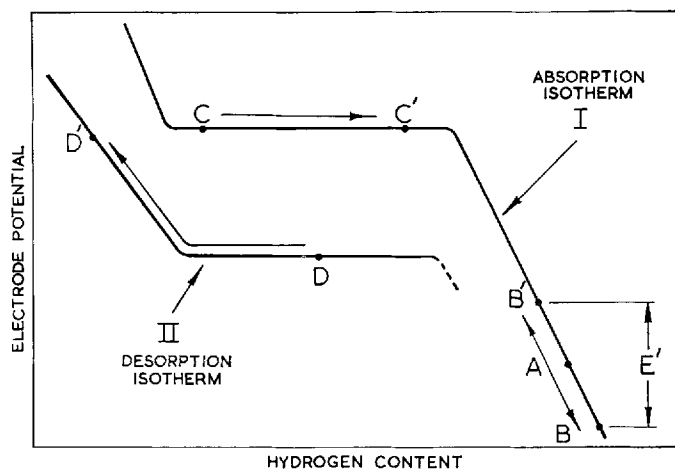
Measurements of the electrical resistance of palladium and palladium alloys are a useful guide to their hydrogen contents (1). When palladium wires that contain hydrogen are immersed in electrolyte—and the method of measurement involves passing a direct current through the specimen—the initial “apparent” value of the resistance can be lower than true, but then “drifts up” to close to the true value (2, 3). Latterly, the relationships between electrode potential E , and hydrogen content have become satisfactorily established (1, 4) and are illustrated (ca. 25°C —somewhat distortedly) as I in the diagram. Inquiry into the origin of the “resistance drift”, described above, initiated a study of the effects of applying a small voltage (say E' in the diagram) between pairs of palladium electrodes. If, before E' was applied, both electrodes had the same hydrogen content, and this corresponded to a potential such as A , it was found that the subsequent current flowing between them decreased exponentially with time until only a very small residual current was passing. At this point, the potential of the cathodic electrode had changed to B and the potential of the anodic electrode to B' . The potential difference $|B-B'|$ almost equalled the value $|E'|$ which had been applied initially. Furthermore, summation in coulombs of the total current

flow showed (3) that the net chemical change had been the transfer of hydrogen from the anode to the cathode; i.e. the summation was equivalent to the difference in hydrogen content between A and B or A and B' . Finally, if E' was removed and the electrodes connected together externally, current flow again occurred, and again decreased exponentially, until both electrodes reassumed the potential and hydrogen content corresponding to A . It then followed (3) that the effect of drifting resistances, during measurements of a continuous wire, corresponded to increasing polarisation of a current being conducted in parallel through the electrolyte.

Subsequently, further experiments with the cell formed by pairs of electrodes confirmed (3) (as would be expected from inspection of the diagram) that if the potential of each of these had been on the plateau containing C and C' (where α - and β -phase hydrides co-exist in the solids) rather than at A , much more hydrogen would have to be transferred between them, after applying E' , before their individual potentials altered sufficiently to oppose E' and so polarise the cell.

Now, alloys of palladium are known that exhibit similar forms of relationship to I but with quantitative differences—an example is shown as II in the diagram. Suppose such an

alloy is one electrode of a pair and palladium is the other, and further suppose that C and D represent the initial hydrogen content and electrode potential of palladium and the alloy respectively. Then, on connecting externally, the alloy should lose hydrogen corresponding to the intercept of D-D', and the palladium gain an equal amount C'-C. Moreover, for much of the time the constant differences between the



Schematic diagram of relationships between electrode potential and hydrogen content

“plateau” potentials should be reflected by a constant discharge current. Conversely, regions of constant charging rate should be observed if a potential—corresponding to, but slightly in excess of E' —is then imposed so that hydrogen is retransferred from palladium to the alloy. Examples of some preliminary results have been published recently by the author (5).

There is no unique principle involved. For example, oxygen transfer may similarly be expected if two different oxides form the electrodes. However, fast rates of diffusion of hydrogen in palladium confer an advantage in that the concentration of hydrogen in the surface layers need not rise steeply above that deeper in the interior. Furthermore, although some deformation of the electrodes may occur after several cycles of charging, the resistance of palladium to embrittlement on absorption of hydrogen is superior to metals such as titanium which form hydrides of a related type.

At present, it is difficult to assess whether these “hydrogen-transfer” cells have any practical utility. As yet, the maximum voltage (25°C) from electrodes of two palladium alloys, selected from the range examined so far, is less than 100 mV when their hydrogen contents correspond to their respective ranges of α - and β -phase co-existence. Even then, at the “upper” end of this scale, the “potential

plateau” regions are imperfectly invariant over wide ranges of hydrogen content, and at the lower end ($E \sim O$ on the hydrogen scale) the pressures of hydrogen gas in equilibrium with the electrodes become considerable; and this gas has to be prevented from interdiffusing to avoid chemical discharge of the cell on storage. On the other hand, the operating principles are independent of the electrolyte, so that, provided this is not strongly oxidising, it can be strongly conducting and thus reduce the internal cell resistance. Further, a low impedance to current flow across the surfaces of the electrodes can be obtained by plating on a layer of palladium black—which often does not affect seriously either the relationships between electrode potential and hydrogen content or the ease of diffusion of hydrogen into the solid substrate.

References

- 1 See e.g. J. C. Barton and F. A. Lewis, *Talanta*, 1963, **10**, 237
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- 3 A. W. Carson, T. B. Flanagan and F. A. Lewis, *Trans. Faraday Soc.*, 1960, **56**, 1311, 1324
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- 5 J. C. Barton, J. A. S. Green, and F. A. Lewis, *Nature*, 1963, **197**, 1293