High Activity Fuel Cell Electrodes

THE INFLUENCE OF ELECTROCATALYST SUPPORTS

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By making more efficient use of the platinum and by extending the reaction zone into the catalyst support, a fuel cell electrode has been developed to give excellent current output with extremely low platinum loadings.

One of the standard methods of reducing the high cost of platinum metal catalysts is to put them on high surface area supports. However, very little fundamental work has been done on the influence of electrocatalyst supports on the performance of low loading platinum fuel cell electrodes, especially to see if they can be induced to participate in the overall electrochemical reaction.

Basic Requirements

The basic requirements of any electrocatalyst are:
(1) Rapid adsorption of the reacting gas, moderate heats of adsorption and rapid desorption of the reaction products. The general principles governing the choice of electrocatalysts are similar to heterogeneous catalysis, namely electronic structure and geometry of atomic structure.
(2) Corrosion resistance.
(3) Chemical stability at the operating potential.
(4) Electrical conductivity.

The last three requirements are specific to fuel cell electrocatalysts as well as electrocatalyst supports, and these further limit the choice of suitable materials.

Platinum on carbon or graphite electrocatalysts, containing 0.5 to 10 weight per cent of platinum, have been extensively used in both low temperature alkali and acid fuel cells as catalysts for the anodic oxidation of hydrogen. The main role of carbon or graphite is to act as an inert conducting extender. Though further improvement may be achieved through the choice of better supports or by using improved techniques for dispersing the platinum on the supports, the advance is likely to be limited since practically all the electrochemical reaction takes place on the platinum surface.

Recent work by General Electric Co., U.S.A. (1) has shown that when coarse tungsten carbide (1–2 m^2/g) is used as electrocatalyst supports for platinum in acid electrolytes, its performance on pure hydrogen is higher than that of platinum supported on high surface area carbon blacks (300 m^2/g), suggesting that there is some "synergistic" effect. However, the reason for the enhanced performance has not been clarified. Furthermore, Niedrach and Weinstock (2) have shown that mixtures of platinum with certain oxides, notably those of tungsten (WO_3, W_2O_5, WO_2), are less susceptible to poisoning by carbon monoxide when operating on impure hydrogen streams. However, no definite conclusions were drawn concerning the function of the oxide during the anodic oxidation of pure hydrogen.

Platinum Activated Tungsten Oxide Electrodes

WO_3 is an acid resistant, insulating oxide. However, in the presence of platinum, water vapour and hydrogen, it rapidly forms hydrogen tungsten bronzes (3). These compounds (4) have a general formula H_xWO_3 ($0.3 < x < 0.5$) (5) and are structurally analogous to sodium tungsten bronzes
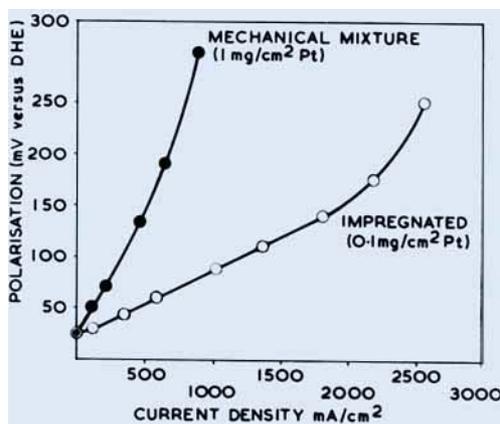
Fig. 1 *Comparison between methods of platinising tungsten trioxide electrodes. Tested in 5N H₂SO₄ at 30°C, 1 atm H₂, iR corrected.*

(Na_xWO_3). They are acid resistant metallic conductors (pseudo-metals) and could function as intermediates in the anodic oxidation of hydrogen on platinum/tungsten trioxide electrodes, thus providing an alternative path for the reaction

$$WO_3 + xPt\text{-}H \rightarrow H_xWO_3 + Pt \rightarrow WO_3 + xe^- + x\,H^- \quad (1).$$
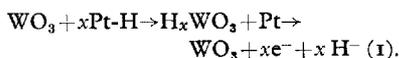
This mechanism would depend on the electron transfer step on the platinum being slow relative to the chemisorption of hydrogen and its migration to the oxide. As yet there is no conclusive evidence for the exact mechanism of anodic dissolution of hydrogen on platinum (6, 7). Even in the event of "fast" electron transfer on the platinum, however, the "bronze route" could have importance in practical electrodes (for example, hydrophobic electrodes (8)) where some platinum will certainly be out of electrolyte contact and therefore unable to oxidise hydrogen in the usual manner. This platinum, which would normally be wasted on substrates such as carbon, may be used because it can still form reduced compounds with oxide which is also in contact with electrolyte.

Reaction (1) then should enable low platinum loadings to be used, without serious losses in performance, by making more efficient use of the noble metal and extending the reaction zone into the catalyst support.

Some preliminary experiments to test this hypothesis, reported recently by Hobbs and Tseung (9), are reproduced here, together with some more recent results on platinum/graphite catalysts.

In order to investigate the participation of tungsten trioxide in the anodic oxidation of hydrogen, tantalum carbide and graphite were chosen as the control substrates. Tantalum carbide is acid resistant, possesses adequate conductivity, does not form bronze-type intermediate oxides and has a particle size in the same region as the tungsten trioxide used (~0.1 micron, calculated from Coulter Counter measurements). Graphite powder (500 m²/g) serves as another standard, since past experience shows that quite good performance can be obtained when it is used as electrocatalyst substrates.

In this experiment, it is essential to use a small platinum loading (~0.1 mg/cm²; that is, ~0.4 per cent by weight) because higher loadings may mask the oxide function. Platinum was deposited on the substrate by either (a) mechanical mixtures with Johnson Matthey platinum black, or (b) impregnation with chloroplatinic acid solution followed by hydrogen reduction at 50°C.

The powders were tested as hydrophobic gas electrodes (8) on gold plated platinum screens in 5N H₂SO₄ at 30°C. Fig. 1 shows that platinum/tungsten trioxide prepared by impregnation is much better than mechanically mixed powder. Thus the degree of platinum dispersion and intimacy of contact between the two phases has considerable influence on the electrode performance.

Fig. 2 shows the initial performance of three electrodes. The Pt/WO_3 electrode has by far the best performance, suggesting that oxide participation is highly significant. But differences in electrode structure (10), such as platinum dispersion, aggregate size and wetting characteristics, make any final conclusions difficult on this result alone.

However, when tested over longer periods, the high initial performance of platinised WO_3 electrodes could not be maintained.
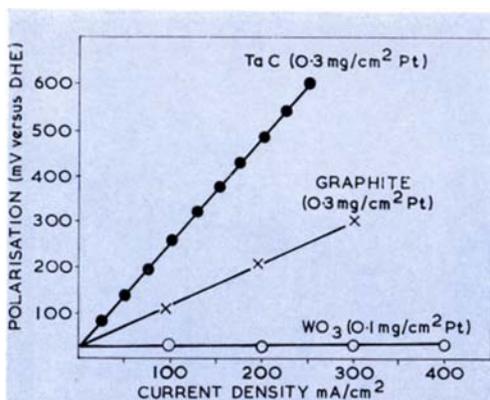
Fig. 2 *Relative performances of impreg-nated platinised electrodes of tantalum carbide, graphite and tungsten trioxide. Tested in 5N H_2SO_4 at $30°C$, 1 atm. H_2, iR corrected.*

The other two "control" electrodes suffered no loss in performance when tested for 24 hours, while the performance of the platinised WO_3 electrodes dropped to half the original figure and continued to fall below that of the "control" electrodes after several days.

This problem was overcome by pre-treating electrodes in hydrogen at $250°C$, when the high initial performance could be maintained on repeated testing over a period of 3 days. The hydrogen treatment resulted in the tungsten trioxide becoming partially reduced, as shown by a permanent light blue colour.

Future work will be directed at deter-mining the exact role of the oxide by using solid electrodes, and the factors affecting long-term performance.

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Platinum Furnaces in Lunar Rock Study

Among the studies to be carried out on the lunar samples brought back by the Apollo 11 astronauts is an investigation of their melting behaviour and of the nature of the crystalline phases in equilibrium with the liquid. This is being un-dertaken at the Grant Insti-tute of Geology, University of Edinburgh, and involves the use of a bank of eight Johnson Matthey platinum-wound electric furnaces. Twelve samples at a time will be held in each furnace for periods varying from a few hours to thirty days at temperatures around 1500°C and will then be water-quenched to maintain the equilibrium conditions established. Samples can also be studied at very high pressures, ranging up to 40,000 atmospheres.

Interpretation of the results will be a complex process but valuable information is expected to be obtained on the conditions below the surface of the moon.