

Raney-type Platinum Metal Catalysts

EXTENDED-SURFACE ELECTRODES IN FUEL CELLS

The formation and numerous applications in the laboratory and on a chemical plant scale of Raney nickel have been familiar for many years. This hydrogenation catalyst is prepared by alloying nickel with aluminium and subsequently dissolving out of the resulting brittle inter-metallic compound the aluminium constituent, leaving a highly active catalyst consisting of a porous, extended-surface skeleton of nickel. The alloying process is strongly exothermic, and the brittle product must be crushed to a powder. Raney nickel is far more active as a catalyst than powdered nickel of equivalent particle-size.

During recently reported investigations on electrode structures for use in fuel cells carried out by H. Krupp, H. Rabenhorst, G. Sandstede and G. Walter of the Battelle Institute, Frankfurt, and R. McJones of the Cummins Engine Company of Columbia, Indiana (*J. Electrochem. Soc.*, 1962, **109**, (7), 553), modified Raney-type platinum, palladium and rhodium catalysts were found to provide excellent fuel electrodes under certain conditions. To date no fully satisfactory low-temperature fuel electrode has been developed to oxidise hydrocarbons at a useful rate at temperatures below 200°C. Partially oxidised hydrocarbons such as methanol are, however, much more readily and more completely oxidised, but at least some of the reactions involved in the stepwise oxidation at the anode must be accelerated catalytically. Electrodes must therefore incorporate a suitable catalyst that above all is able to accelerate the acceptance of electrons from the fuel by the anode. It is thought that the activity of such catalysts is related to the number of crystallographic defect structures in their surfaces and in the report under discussion Raney-type catalysts were investigated since they may be produced at room temperatures, thus avoiding re-

crystallisation enhanced at higher temperatures. Earlier work had referred to methods of construction of Raney-type electrodes and these methods were followed.

Electrode specimens were prepared in the form of porous discs by compressing a mixture of skeleton metal powder and Raney powder, followed by dissolution of the aluminium constituent. The skeleton powder in each electrode was the same as the active constituent of the Raney alloy, and the latter had an active metal concentration less than the stoichiometric 1 : 1 ratio but greater than about 20 per cent, as below this concentration the alloy became too ductile for powdering. Skeleton powder and Raney alloy were mixed in the ratio of 1 : 1 v/v and compacted into discs under high pressures with the incorporation of two platinum screens to increase their mechanical strength. The aluminium was dissolved out first by dilute, then by concentrated, caustic potash solutions at temperatures up to 80°C. Complete removal of aluminium is not possible, but further dissolution of this metal was obtained anodically.

The electrodes were evaluated using caustic potash, potassium carbonate and sulphuric acid as electrolytes. Hydrogen and methanol were employed as fuels, and the noble metal electrode performances were compared with those of copper, cobalt and nickel.

With hydrogen in KOH electrolyte, all electrodes reached the reversible hydrogen potential on open circuit, with platinum giving the least polarisation. With platinum, palladium and rhodium electrodes current densities obtainable exceeded 500 mA/cm² and 300 mA/cm² respectively, when using hydrogen and methanol as fuels, and limiting current densities were not determined. Since

the results obtained with nickel electrodes were found to be inferior to those reported in earlier work, it was concluded that all electrodes investigated might have been improved by the use of better powder metallurgical techniques.

With methanol in KOH electrolyte, palladium provided the best results, platinum and rhodium following in decreasing order of performance. With methanol in acid solution platinum was found to be most active. In all cases, activity was considerably reduced when potassium carbonate solutions were employed as electrolyte. Copper and cobalt were not considered to be satisfactory catalysts for methanol or hydrogen electrodes. It was also found that sintering the noble metal electrodes destroys their activity with methanol and seriously affects it for use with hydrogen.

A laboratory-scale fuel cell using a palladium fuel electrode, a silver oxygen electrode and a 5N solution of KOH as electrolyte, was employed to examine the degree of conversion of methanol. The conclusion was formed that even at room temperature methanol oxidation proceeds almost completely to carbonate or carbon dioxide.

When formaldehyde and formic acid were investigated as possible fuels, large current densities were obtained with polarisations comparable with those observed for methanol. Similar results were found in alkaline and acid electrolytes, although somewhat higher fuel conversion efficiencies were obtained in the latter. No appreciable electrochemical oxidation was found under the experimental conditions employed when hexane or methylcyclohexane were tried as fuels. H. C.

Oxides of Iridium and Ruthenium

NEW VALUES FOR OXYGEN PRESSURES OF FORMATION

In his review of the thermodynamics of the gaseous oxides of the platinum metals, C. B. Alcock (*Platinum Metals Rev.*, 1961, 5, 134) referred to the work of Schäfer and his collaborators on the oxides of iridium and ruthenium. Some further experimental work has now been reported by G. Schneidereith in the course of a dissertation from the Harald Schäfer Institute of Münster, Westphalia.

Schäfer and his co-workers had previously found that coarse crystals of IrO_2 and RuO_2 were produced by heating the metals in a stream of oxygen (760 torr) to 1150 and 1270°C respectively. Both metals form volatile trioxides which, in contact with the colder walls of the quartz vessel, decompose to rough single crystals of blue-black IrO_2 and black RuO_2 . The oxygen pressures of formation of these dioxides have been determined by Schneidereith by different methods and compared with the numerical values given by Alcock. Some of the values reported are set out in the table.

Solid IrO_2 dissolves less than 5 atomic per cent of iridium. The enthalphy of formation $\Delta H(298)$ —calculated from the elements—amounts to -52.42 Kcal for

Oxygen-pressures p in torr for reactions $\text{IrO}_2 \rightarrow \text{Ir} + \text{O}_2$ and $\text{RuO}_2 \rightarrow \text{Ru} + \text{O}_2$ at temperatures t in °C		
t	p for IrO_2	p for RuO_2
900	34	—
950	76	—
1000	154	—
1050	316	—
1100	572	1.5..4.5
1124	760	~2
1150	1020	3.3..6.9
1200	—	6.7..12
1250	—	13.2..23
1300	—	~25

IrO_2 and to -68.1 Kcal for RuO_2 . The resistivities of single crystals of IrO_2 and RuO_2 at 22°C were found to be 48 microhm-cm and 50 microhm-cm respectively. The temperature coefficients between -78 and $+22^\circ\text{C}$ were approximately $+0.0008$ for IrO_2 and $+0.00075$ for RuO_2 .

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