Platinum Metals in the Fuel Cell

THEIR FUNCTION AND APPLICATIONS IN ELECTRODE STRUCTURES

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The high catalytic activity exhibited by some of the platinum group metals, together with their excellent resistance to corrosion, form the basis of their applications in fuel cells. In this article the author describes the use of these metals in cells fuelled by hydrogen/oxygen, ammonia, hydrazine and hydrocarbons. The kinetics of the electrochemical oxidation of hydrocarbons are examined, a mechanism of electrode poisoning is discussed, and finally the author comments on the likely usage of platinum metals in fuel cell technology.

In the postscript of a communication to the Philosophical Magazine in 1838, Grove (1) described a significant observation – the electrochemical recombination of hydrogen and oxygen. Grove not only foresaw the possibility of obtaining useful electrical energy from such a system, but stated, "I hope by repeating this experiment in series to effect decomposition of water by means of its composition", and thus indicated the possibility of regenerating such a device electrically. In these experiments Grove used platinum for both anode and cathode, an element still used extensively in present fuel cell technology.

Since this first disclosure of Grove many studies (2) have been conducted on different electrolytes and electrode materials. Most significant among these was the work of F. T. Bacon (3) (which has been largely responsible for stimulating the present technology) based on the concept of using a cheap material—nickel—to construct both anode and cathode. However, the platinum metals are still widely used in fuel cell electrodes because of their unique properties:

(1) They have the advantage of being more active catalysts at lower temperatures than other known catalytic materials and for low temperature hydrogen- or oxygen-depolarised electrodes such metals as platinum are outstanding in their ability to sustain high reaction rates at ambient temperatures.

(2) The high nobility of these metals provides them with good resistance to corrosion in concentrated electrolytes and up to moderate temperatures.

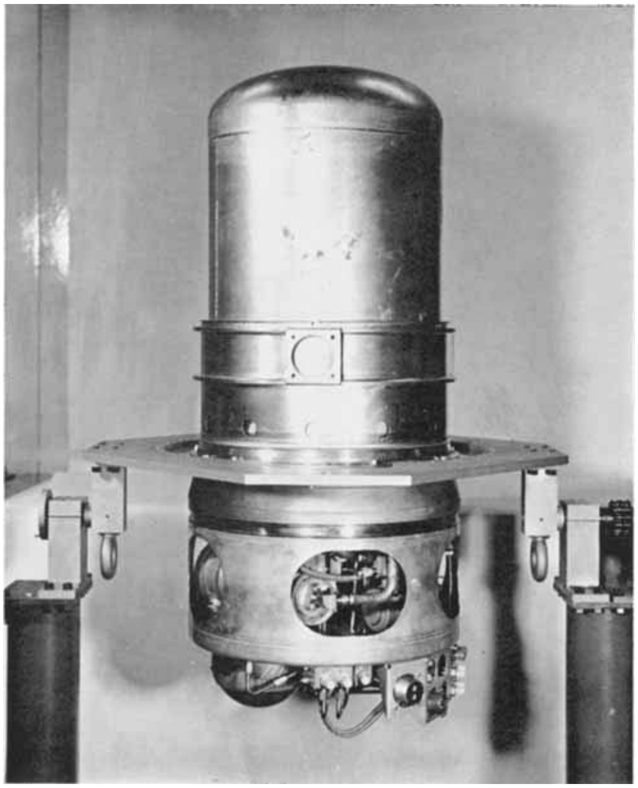
(3) They have the ability to catalyse the direct oxidation of saturated aliphatic hydrocarbons at temperatures below 200°C. This is because of the capacity of platinum, iridium and rhodium to chemisorb hydrocarbons dissociatively at low temperatures.

Some of the unique advantages of the platinum metals are best demonstrated by examples of their applications today.

Low Temperature Hydrogen/Oxygen Cells

Many investigators (2, 4) have published data on this type of cell using platinum as both anodic and cathodic catalyst. In both cases the high performance of such systems is

The first fuel cell system to be fully engineered as an independent source of power. It has been developed for the U.S. "Apollo" space project by the Pratt & Whitney Aircraft Fuel Cell Production Facility at East Hartford, Connecticut, and uses platinum group metal electrodes



attributable to the large exchange currents that platinum can sustain in both the essential electrode processes:

$$\left.\begin{array}{ll} H_2 \longrightarrow 2H^+ + 2e^- & \text{acid} \\ \text{or } H_2 + 2OH^- \longrightarrow 2H_2O + 2e^- & \text{base} \end{array}\right. \quad \text{(i)}$$

$$\left.\begin{array}{ll} 2e^- + O_2 + 2H^+ \longrightarrow H_2O_2 & \text{acid} \\ 2e^- + O_2 + H_2O \longrightarrow HO_2^- + OH^- & \text{base} \end{array}\right. \quad \text{(ii)}$$

The high values of i_0 are associated with the low heat of chemisorption of hydrogen and oxygen on platinum metals.

Impure Hydrogen Fuel Cells

Recently an electrode (5) has been developed specifically to utilise impure hydrogen sources. The electrode was designed to be used with gas streams obtained by reforming cheap hydrocarbon fuels such as diesel oil, gasoline or natural gas, the reformate containing H_2, CO_2, CO, H_2O and, of course, residual hydrocarbons. Similarly, anhydrous ammonia can be cracked forming a stream of hydrogen, nitrogen and ammonia.

Obviously, in such a system the hydrogen must be oxidised in such a manner that the electrolyte is not contaminated by inert or soluble impurities. This is achieved by using a palladium alloy membrane to extract the hydrogen from the gas phase. The hydrogen diffuses through the metal and is ionised at the electrolyte interface. This is shown schematically in the diagram on page 44. This electrode has the advantage of being able to sustain hydrogen oxidation at current densities of the order of 150 to 200 amp/ft^2 down to a very low H_2 partial pressure (less than 1 psia) and thus permits high utilisation of the reformed fuel. Since the palladium alloy membrance is maintained at potentials close to RHE*, the electrode is quite stable in alkaline or acid electrolytes.

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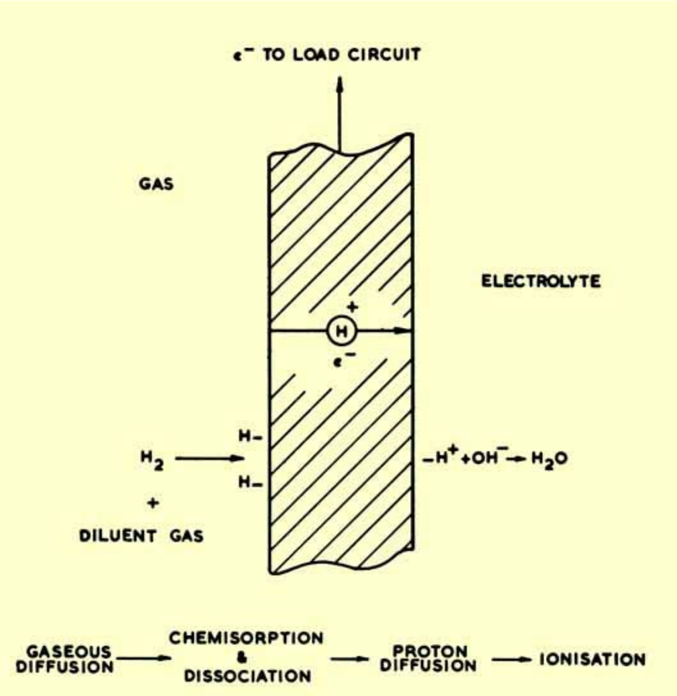
*Reversible hydrogen electrode in same electrolyte

Ammonia Fuel Cells

Anhydrous ammonia is a common commodity in the U.S.A., and there have been many attempts to develop fuel cells which will directly oxidise ammonia to nitrogen and water. It has been found (6, 7) that the oxidation can only proceed at acceptable rates in alkaline electrolytes and in the presence of noble metal catalysts. A recent kinetic study of Pt/NH_3 electrodes (7) indicates that the rate-limiting electrochemical step involves the breaking of N-H bonds on the surface. It appears that the ammonia undergoes a step-wise dehydrogenation (the hydrogen being oxidised electrochemically) and that various chemisorbed intermediates are involved. The final rate-limiting step appears to be the recombination of nitrogen atoms, which is not an electrochemical process and, therefore, results in a limiting current condition. The usefulness of the ammonia electrode is rather limited by the fact that slow corrosion occurs even with the noble metals at quite moderate temperatures. This can be attributed to the fact that the ammonia electrode shows considerable polarisation and must, therefore, operate in potential regions where the formation of metal-ammonia complexes is favoured, resulting in solution of the noble metal and consequently, gross changes in the electrode structure and surface area.

Hydrazine Fuel Cells

Hydrazine cells have been developed (8) since hydrazine is an extremely active fuel, comparable with hydrogen. In fact, hydrazine is oxidised on platinum metals at potentials and current densities similar to that obtained with hydrogen. At open circuit conditions in the presence of dilute solutions of hydrazine in KOH, potentials slightly negative to RHE can be attained. If the hydrazine concentration exceeds 1 per cent by weight, hydrogen and nitrogen are evolved on platinum black surfaces. It has not been demonstrated whether this involves anodic oxidation of the hydrazine coupled with the cathodic generation of hydrogen or whether the process is a non-electrochemical surface decomposition; the negative potentials would indicate the former. Analysis of the kinetic data for the oxidation of hydrazine contrasts with the case of ammonia, in that no limiting current is observed, implying that nitrogen atom recombination does not take place and that the nitrogen-nitrogen bond is never broken.

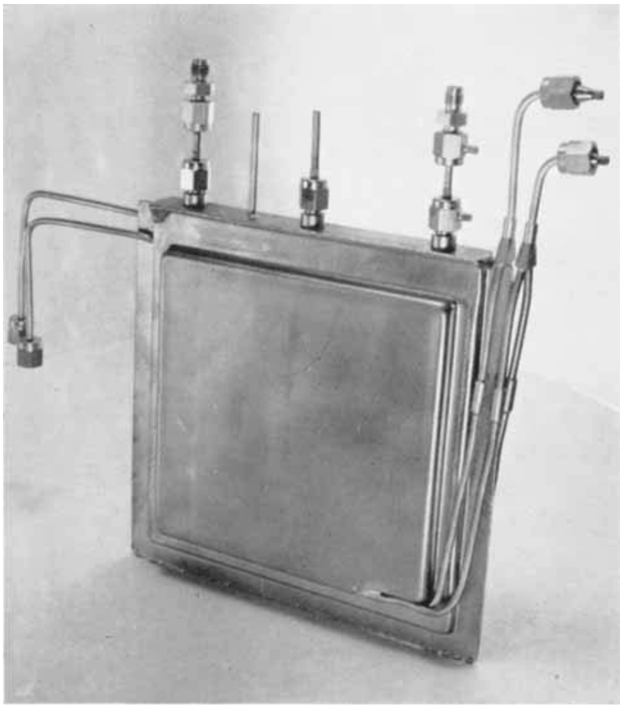


The sequence of mechanisms involved at a non-porous anode

Oxygen Depolarised Cathodes

The noble metals have been used extensively as catalysts for oxygen cathodes in both

A Leesona Moos Laboratories experimental two-cell Carbox module, also employing a noble metal electrode system



acidic and alkaline electrolytes. The table below compares the catalytic activity of platinum, palladium, and silver in alkaline electrolyte. These data (9) were obtained using polished flat plates of these metals having approximately the same surface area, the solution being saturated with oxygen gas. Data obtained at different temperatures indicate different activation energies for the rate-limiting electrochemical process on each metal decreasing in the order silver > platinum > palladium. It has been amply proved (9, 10) that reduction of oxygen on metals involves the formation of peroxide species in both alkaline and acidic electrolytes. Detailed kinetic analysis of this system is extremely difficult and at O_2 diffusion electrodes involving mass transfer through a meniscus, polarisation analysis is virtually impossible because of the many interacting parameters. However, at lower temperatures heterogeneous decomposition of peroxide species is extremely important in determining operating potentials of electrodes and the platinum metals are well-known hydrogen peroxide decomposition catalysts. The relative polarisation-contributions of i_0 (i.e. rate constant) for the reduction process (ii) and the rate constant for peroxide decomposition are difficult to assess.

Oxygen Reduction Current in 1N KOH at 40°C

	μA cms^{-2} at 850 mV vs. R H E
Silver	<30
Platinum	94
Palladium	335

For cathodes in acid electrolytes the noble metals appear to be far superior catalysts. This is partly attributable to the fact that at anodic potentials in acid electrolytes they are the only materials which form stable, insoluble, conducting oxides.

Hydrocarbon Fuel Cells

The successful oxidation of saturated hydrocarbons to CO_2 and H_2O at low temperatures is perhaps the most intriguing application of noble metal catalysts (11). Useful current densities can be generated on noble metal surfaces above 70°C. The reaction rates at fixed polarisation increase with temperature and oxidation can occur in any strong acid which does not interfere with catalytic activity. However, above 100°C, few acids are sufficiently stable for fuel cell operation.

Different polarisations are observed at porous, diffusion-type electrodes with various hydrocarbon species and generally speaking the rate of oxidation at a given potential decreases in the order ethylene > propane > ethane > butane. However, with the exception of methane this does not appear to be attributable to different values of i_0; rather the differences appear to lie in the mass-transfer mechanism involving solubility and diffusion coefficients of different hydrocarbons.

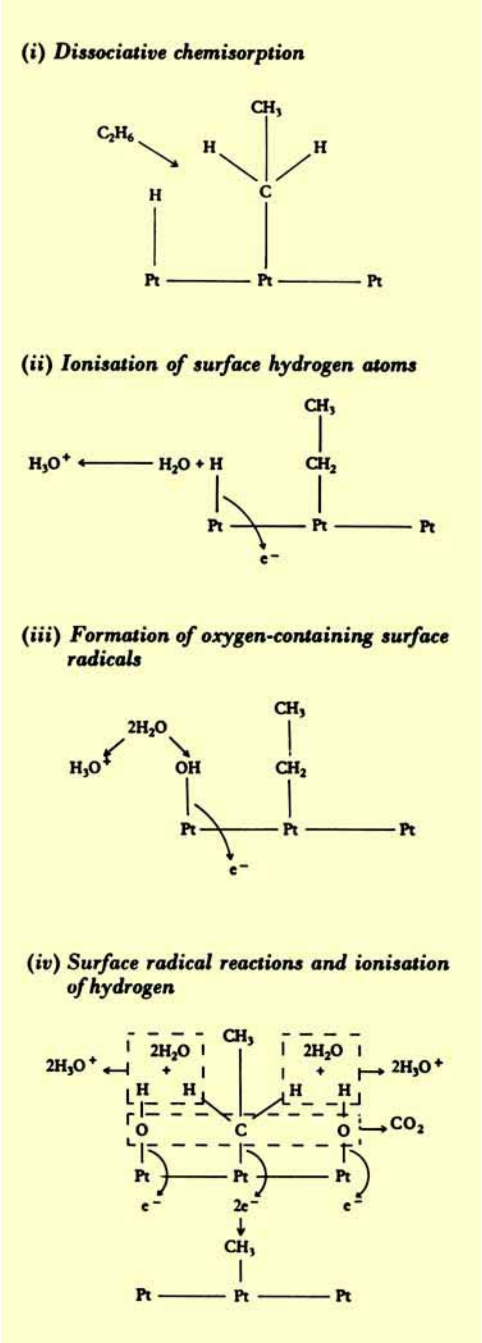
It is interesting to consider what electrode reactions are involved in the oxidation of hydrocarbons to CO_2 and water, the preponderant oxidation products (11). Obviously, oxidation of a C-C-C skeleton to a CO_2 molecule involves addition of oxygen atoms to the carbon atom. This must involve the transfer of oxygen from either anions or water. The most likely sequence is:

1. Dissociative chemisorption of the hydrocarbon followed by:
2. Anodic oxidation of the dissociated hydrogen atoms;
3. Anodic oxidation of Pt sites with oxygen-containing radicals;
4. Reaction between the carbon skeletons chemisorbed on the platinum and oxygen-containing radicals on neighbouring Pt surface sites.

Since at a temperature of 100°C reasonable rates can be measured for the oxidation of hydrocarbon to CO_2 at potentials of the order of 0.3 to 0.4 volts vs. RHE, it is likely that the oxygen-containing radical is OH. (The Pt-OH bond strength should be much lower than that of Pt=O or Pt-O-Pt) thus, there is in effect a surface radical reaction between adjacent OH radicals and the carbon skeleton to form CO_2 while the other products of the reaction are protons formed by the dissociation of water on the surface. This is shown in the schematic diagram.

Stage (4) is very difficult to define in detailed sequence and in terms of electron-transfer processes since nothing is known about the Pt-C bond type and its statistical mechanical properties. Much will depend on the vibrational, rocking, and rotational frequencies of this complex.

Ionisation of hydrogen at 0.3V RHE is very rapid and cannot be rate limiting; $\theta_H \rightarrow 0$.



(i) Dissociative chemisorption

(ii) Ionisation of surface hydrogen atoms

(iii) Formation of oxygen-containing surface radicals

(iv) Surface radical reactions and ionisation of hydrogen

The poisoning of electrodes used for the oxidation of carbonaceous fuels is well-known (12); a species is formed which contaminates the surface and restricts the oxidation rate of the carbonaceous material. Recently, J. Giner (13) made a significant observation that in sulphuric acid on platinum CO_2 can be reduced at potentials within 200 mV of RHE forming a poisoning product which he calls "reduced CO_2". Giner has shown that this species is re-oxidised at a more positive potential and removed from the surface. This is undoubtedly a major electrode poisoning phenomenon. The Sabatier reaction (18) above 250°C can reduce CO_2 with $H_2 \rightarrow CH_4 + H_2O$. Giner's preliminary data do not indicate however that CH_4 is the product in the electrochemical system.

It seems most likely that this species is, in fact, a form of chemisorbed CO resulting from the reaction between CO_2 molecules and hydrogen atoms present on the platinum surface. It is well known that carbon monoxide, at temperatures below 200°C, is strongly chemisorbed on noble metals such as platinum and that there is considerable heat of chemisorption; hence the ability of platinum metals selectively to oxidise CO in the presence of H_2 (14). If the heat of chemisorption of carbon monoxide is sufficiently high, reduction of CO_2 by hydrogen atoms will occur (although not thermodynamically favoured in the gas phase) since it will result in a species of carbon monoxide having a low thermodynamic activity.

Energy States ↑

$H_2O + CO + Pt$

$2Pt\text{-}H + CO_2$

$H_2O + Pt{=}CO$ (or Pt-CO-Pt)

The form of this chemisorbed CO remains to be demonstrated: almost certainly it is oxidised by the mechanism described above for hydrocarbons. The large heat of chemisorption of CO on platinum may result in a large activation energy barrier for the recombination step with Pt-OH.

Platinum is probably unique in that it can chemisorb hydrocarbons while at the same time possessing the property that oxygen radicals can be deposited on its surface reversibly at potentials close to RHE. The rate of oxidation will be:

$R = f(\theta_{OH})^n . (1\text{-}\theta_{OH})$, since

$\theta_{CH} = f(1\text{-}\theta_{OH})$ and $\theta_H \rightarrow O$ at 300 mV RHE

where θ_{OH} and θ_{CH} are the coverages respective to OH and the chemisorbed

The platinum metals will be used in most fuel cell designs in diffusion-type electrodes in the form of high surface area "blacks" in order to achieve the highest possible activity per gram of metal. This electronphotomicrograph of a platinum black electrode surface of high catalytic activity demonstrates the very complex structure of platinum black itself (x 20,000) carbon radicals. θ_{OH} is, of course, potential-dependent and will govern the potential dependence of R. Thus, the rate of formation of Pt-OH would be the rate-determining electrochemical step in the overall process. However, at very anodic potentials (0.80V vs. RHE) θ_O or θ_{OH} increases rapidly and will cause θ_{CH} to decrease significantly resulting in the well-known "peak oxidation current" observed in this region. The rate of dissociative chemisorption of the hydrocarbon is probably rate-limiting at potentials positive to this "peak potential".

Incorporation of Platinum in Fuel Cell Electrodes

Noble metals in most cases are used in diffusion-type electrodes in the form of high area blacks in order to obtain the highest possible area and activity per gram of metal. There are, however, many ways of supporting these blacks on different types of substrate, for example:

(1) Dispersion on porous carbon (3);
(2) Dispersion in porous metals such as nickel (15);
(3) Dispersions with P.T.F.E. supported on grids of porous metals (4b, 11);
(4) Dispersion on porous plastics (16);
(5) Raney-type metal matrices (17).

The blacks can be prepared electrolytically or by chemical reactions; the techniques are amply described in the literature. The electronmicrograph of a platinum black electrode surface shown here demonstrates the very complex nature of platinum black itself.

Future Usage of the Platinum Metals

Undoubtedly the extent to which the platinum metals will be used in fuel cells will depend primarily on the cost which will, of course, depend on future supplies of the metals and the amount of metal required to provide 1 kW of electrical generating capacity. If metal usage can be brought down to the level of approximately $10 of platinum per kW of generating capacity and adequate supplies of platinum are available, we can expect to see a multitude of fuel cell systems based on noble metal catalysts. At $100 of platinum/kW, these catalysts will still find many applications because of their unique properties.

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