

# Development of alloy electrocatalysts for phosphoric acid fuel cells (PAFC)\*

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One of the great scientific achievements for electrocatalysis in the past ten years has been the ability to reproducibly form microparticles of platinum metals in conductive supports. The dimensions of these crystallites are such that up to 50% of the atom content is at the crystallite surface; they are single crystals, and have metallurgical properties that are unlike bulk metals. These have found application as electrocatalysts in hot phosphoric acid fuel cells (PAFC) for oxygen reduction and hydrogen oxidation. Much of the recent work has been involved with developing various binary and ternary alloy combinations while at the same time, maintaining the crystallite microdimensions. Pt-Co-Cr alloys are one of the most favoured combinations for oxygen reduction and the Pt-Pd alloys are favoured for hydrogen oxidation, especially in the presence of trace poisons such as carbon monoxide and hydrogen sulphide. Operation of these electrocatalysts is the subject of much investigation, with the present conclusion that the apparent mode of catalytic enhancement with the binary and ternary platinum alloys for oxygen reduction, resides in the leaching of the non-platinum elements from the alloy crystallite surfaces to give a microroughening, and thereby an increased reaction surface area.

## 1. Introduction

A previous keynote address by this author on a related topic [1] considered the status for preparing and characterizing highly dispersed platinum electrocatalysts, particularly when the metal particles approached such small dimensions that over 50% of the atom content resided at the particle surface. The operation of these materials, when applied to phosphoric acid fuel cells as electrocatalysts is, of course, critical. In that paper, detailed consideration was given to an understanding of the unusual properties of these very small noble-metal particles.

Subsequent to that period, there has been increased emphasis on preparing *alloys* of metals with platinum in order to increase the kinetic rate of reaction for both the oxygen reduction, and hydrogen oxidation in the presence of electrocatalyst poisons, specifically carbon monoxide and hydrogen sulphide. Much of the relevant information resides within the patent literature, and it is the intent of this paper to draw heavily upon this valuable resource since it is often overlooked by many academic research workers.

## 2. A rational basis for surface area terms

To prepare highly dispersed metal catalysts, an inert support is mandatory in order to separate the metal crystallites and thereby produce a very high surface to volume ratio in the metal crystallites. In any dis-

cussion of high surface area materials, one comes to a point of describing surfaces in terms of a 'BET surface area', which is expressed as  $\text{m}^2 \text{g}^{-1}$  of material. This was the format originally set out by Brunauer, Emmett and Teller [28] in their pioneering work of nitrogen adsorption on solid surfaces at the boiling point of nitrogen.

In a comparison of surface areas for dissimilar materials such as carbon, silica, platinum, palladium and nickel the BET values do not easily translate into a ready comparison of the relative surface areas or sizes for small metal particles. The situation is even more difficult when binary and then ternary alloys are discussed. In electrochemical applications in acid electrolytes, metal electrocatalyst particles are supported on a variety of carbons, many of which have different surface properties, and different degrees of graphitization. In alkaline systems, metal supports (e.g. Ni and Co) and metal oxide (e.g. doped  $\text{TiO}_2$ ) are possible. In gas phase catalysis, silica and alumina are common supports, each of which has a characteristic surface area given in terms of  $\text{m}^2 \text{g}^{-1}$ .

Assuming that small metal particles approaching atomic dimensions are spherical (i.e. Kelvin forces are operating so that there is a minimisation in the surface energy of the metal, hence it becomes liquid-like), then the specific surface area  $S$  ( $\text{m}^2 \text{g}^{-1}$ ) is calculated using the equation:

$$S = \frac{6 \times 10^3}{\rho d}$$

\* This paper is based on an address given before the 40th International Society of Electrochemistry meeting, Kyoto, Japan (1989).

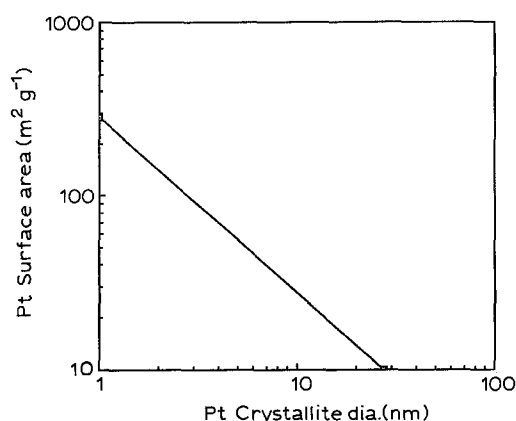


Fig. 1. Relationship between platinum crystallite size and the specific surface area.

where  $d$  is the mean particle diameter in nanometres and  $\rho$  is the density of the metal. In the case of platinum,  $\rho = 21.4 \text{ g cm}^{-3}$ , leading to Fig. 1, which demonstrates the relationship between surface area and crystallite size for platinum. If other metals are considered, then each has a new relation between surface area and crystallite size. It is clear that in order to obtain a surface area comparison, one must utilise the atomic weight of the material to normalise the surface area.

In the case where all the atoms in the crystallite are at the surface, then 100% dispersion of the metal has been achieved, and we would expect unusual properties of the metal due to the lack of bulk metallurgical properties. The crystallite size at which all of the atoms are located in the surface is about 0.7 nm. It is of considerable interest that with present chemistry commercial platinum electrocatalysts can be prepared reproducibly in kilogram quantities on stabilised carbon surfaces with the platinum having 180 to 200  $\text{m}^2 \text{g}^{-1}$  giving metal particles of 1.4 to 1.5 nm in diameter.

Table 1 is generated by normalising for the atomic weight for a number of metals and supports. This lists

the carbons that have been used as supports for the noble metals in PAFC. It can be seen that the normalised surface areas and dimensions for the highly dispersed metal crystallites are amazingly comparable to the dimensions of the highest surface area carbons, especially when one considers that a large part of the carbon surface area is contained in micropores. The 'chainy' Denka acetylene black has a significantly lower surface area, and a greater crystallite size, but is included in the table for reference. The metals chosen in the table are also representative of those elements that have been promoted for alloying with platinum to be used as PAFC electrocatalysts.

From Table 1 we can see that with 10 wt % Pt on carbon (Consel I) then in 100 g of electrocatalyst the platinum concentration is 0.051 25 mol and the carbon concentration is 7.5 mol. This translates into 1 896  $\text{m}^2$  and 22 500  $\text{m}^2$ , respectively, for 1.4 nm platinum particles. Quite remarkably, this means that over 8.4% of the total surface in the electrocatalyst is due to the platinum.

### 3. Development of alloy oxygen reduction electrocatalysts

Early work at United Technologies (now IFC) considered refractory metal combinations with platinum as oxygen reduction electrocatalysts. The preferred non-platinum alloying metal was vanadium [2]. These alloys exhibited apparently higher reaction rates than platinum alone. This led to a search for other binary alloy combinations, as well as improved methods for making these alloys. It was found that over a period of time at oxygen reduction potentials in hot phosphoric acid, the vanadium was leached out from the alloy, and a search was instigated for more stable alloys that not only exhibited higher reactivity for the oxygen reduction reaction, but also resisted surface area loss ('sintering') of the metal particles.

Table 1. Comparison of crystallite sizes and surface areas

Material	Crystallite size (nm)	BET Surface A. ( $\text{m}^2 \text{g}^{-1}$ )	Atomic Wt. ( $\text{g mol}^{-1}$ )	Normalized S.A. ( $\text{cm}^2 \text{mol}^{-1}$ )
Fumed silica	7-14	200-400	60	1.2
<i>Carbons</i>				
Denka Black	-	65	12	0.0780
Vulcan XC-72	-	250	12	0.3
Consel I	-	250	12	0.3
Black Pearls 2000	-	1475	12	1.77
Black Pearls 2000 (HT 2700°)	-	220	12	0.2640
<i>Metals</i>				
Platinum	0.7	275	195.1	5.36
Platinum	1.4	190	195.1	3.7
Silver	0.7	497	107.9	5.36
Palladium	0.7	504	106.4	5.36
Copper	0.7	845	63.5	5.36
Cobalt	0.7	910	58.9	5.36
Iron	0.7	961	55.8	5.36
Chromium	0.7	1032	52	5.36

This led to the development of platinum–chromium alloys [3]. Here, it was disclosed that whereas in the case of the platinum–vanadium alloy in 99% phosphoric acid at 350° F (194° C) and at a potential of 0.9 V/RHE, over 67% by weight of the vanadium had dissolved; in the chromium case, only 37% had dissolved under comparable conditions. This does not necessarily mean that these alloys of the noble metal are unstable, since there is insufficient evidence to judge whether all of the non-noble metal is contained in an alloy with the noble metal, or that it is formed into a preferred alloy composition. Clearly unreacted non-noble metal will be expected to leach out of the electrode structure under these fuel cell operating conditions. In an effort to further increase the reaction rate, it was found that the addition of cobalt [4] to the platinum–chromium alloy forming the first ternary alloy, boosted the oxygen reduction rate, although there was no indication of the lifetime for the catalyst system. This was then followed by a new patent [5] using the same metal composition but describing a specific ordering of the ternary alloy. From the performance data in that patent, it was not apparent that any increase in the kinetic rate for the oxygen reduction reaction was achieved using an ordered material. It did emphasise the truism that the *method* of making the catalyst is critical to the catalyst performance, since catalysts prepared from the same elements but with different preparation technologies give significantly different performances.

Other binary alloy combinations have been disclosed, platinum–iron having a Pt<sub>3</sub>Fe superlattice structure [6], and an unusual binary alloy of platinum–copper [7], which is reported to have a high reaction rate with low performance loss over several thousands of hours in the hot fuel cell environment. This latter catalyst is troubling, since any loss of copper from the cathode electrocatalyst is expected to migrate to the anode, on which it will be reduced to the metal.

Underpotential deposition of copper on platinum is known to occur at anode potentials, and since the rate determining step for the hydrogen electrode is known [1] to be the dual-site dissociation of the hydrogen molecule on uncovered platinum sites, copper monolayers are then site specific poisons. Nevertheless, it remains to be seen whether this concern is valid.

More recently, Tsurumi *et al.* [8] presented a summary of platinum alloy catalyst performances for oxygen reduction, comparing the oxygen reduction potentials in 190° C phosphoric acid at 200 mA cm<sup>-2</sup> and with 0.5 mg Pt cm<sup>-2</sup> of the electrode. This is shown in Fig. 2. It is seen that over a period of time, there has been a progressive increase in performance due to electrocatalyst development. The ternary alloy disclosed by TKK was not described in detail, but it can be anticipated that further catalyst developments will be achieved as the theories for the structure and operation of these alloys becomes better understood.

One attempt at an understanding of the binary alloys was presented by Jalan and Taylor [9]. They proposed that the reaction rate for oxygen reduction

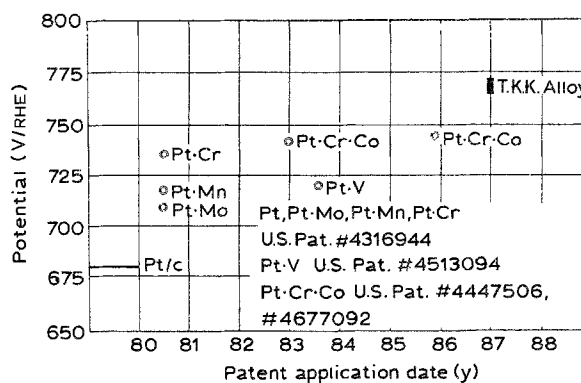


Fig. 2. Comparisons of oxygen reduction performance with the published patent literature. Electrodes contain 0.5 mg Pt cm<sup>-2</sup> at 190° C and 200 mA cm<sup>-2</sup> current density. [\*\*TKK is Tanaka Kikin-zoku Kogyo K.K. of Japan.]

was increased with a decrease in the interatomic (nearest neighbour) spacing of the elements in the alloy. It was predicted that platinum–vanadium and platinum–chromium were the best combinations.

In reality, bulk measurements of the properties of alloy particles with dimensions under discussion here do not reflect the surface atomic distributions; since it is well known that surface segregation of the alloy occurs. In this way, the surface of the alloy particle will be enriched in that alloy component that provides the lowest surface energy, given the proviso of the reaction environment. In the case of platinum–gold alloys (preferred cathode electrocatalysts for high temperature alkaline fuel cells in US space missions) the surface of the electrocatalyst particle is enriched with a gold phase and, as a consequence, the sub-surface in the particle must then become enriched with the platinum phase.

The operation of advanced alloys of these metals as electrocatalysts is far more complex than the simplistic approach given by Jalan and Taylor [9]. It is expected that new theories will evolve, although competitive business considerations will probably keep the best predictive theories hidden for the preparation and operation of electrocatalysts, at least for a time.

In an attempt to clarify the claims for electrocatalytic enhancement of the oxygen reaction, studies have been made to analyse the surface properties of these particular alloy combinations. In the case of the platinum–vanadium alloys, it was found [10] that the vanadium was completely depleted from the alloy under operating fuel cell conditions, leaving behind only platinum. In the case of the platinum–chromium alloys [11–14] the catalytic enhancement was attributed to a roughening of the platinum crystallite surface caused by the leaching of the non-platinum element. Slow surface diffusion of the platinum allowed the surface roughness to be maintained for many hours under test conditions.

This view was reinforced by the work of Ross [15] who gave a recent overview of his relevant work. Most recently, Beard and Ross [16] extended their work from low surface area alloys to high surface area materials emphasizing the platinum–cobalt binary alloy system. Here again, the only effect that could be seen

was that of a surface area enhancement for the alloy crystallite due to leaching of the Co from the surface. The works of Ross have been directed for many years towards the formation of discrete intermetallic compounds, and in this latest work he showed that the loss of cobalt was lowest in those alloys that were most ordered with  $\text{Pt}_3\text{Co}$ .

At present the evidence for an electrocatalytic enhancement of the oxygen reduction reaction is meagre, both with low surface area alloys and high surface area crystallites. Only surface roughening is observed as a contribution to the higher reaction rate.

The operating phosphoric acid fuel cell undoubtedly does show catalytic performance enhancements well above those performances shown by pure platinum. It remains to be seen for how long this performance enhancement is achieved, since lifetime of the electrocatalyst in the fuel cell environment is the other important feature.

#### 4. Development of alloy hydrogen oxidation electrocatalysts

Research into development of advanced alloys for the anode has not had so much attention as the cathode, simply because the anode has not been perceived as having significant electrocatalytic problems.

In practice and to a great extent, the PAFC has been operated to overcome many of the problems that exist with the fuel supply to the anode. Phosphoric acid is not a particularly good electrolyte, save the virtue that it can be operated at high temperatures — a necessary requirement to flash evaporate the product water from the fuel cell.

An ability to operate at high temperature is also required to minimise the carbon monoxide poisoning problem. Fuel sources for the hydrogen require some sort of fuel processing, either steam reforming or other fuel conditioning. These conventional processes produce both carbon monoxide and carbon dioxide in the gas stream. The choice of an acid electrolyte allows the carbon dioxide to be rejected, but the small quantity

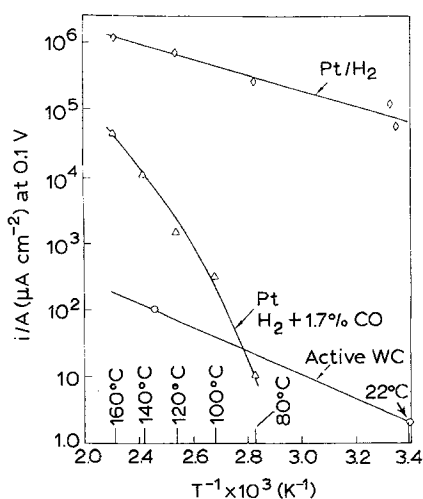


Fig. 3. Specific oxidation rate for hydrogen molecules in phosphoric acid at 0.1 V/RHE [17].

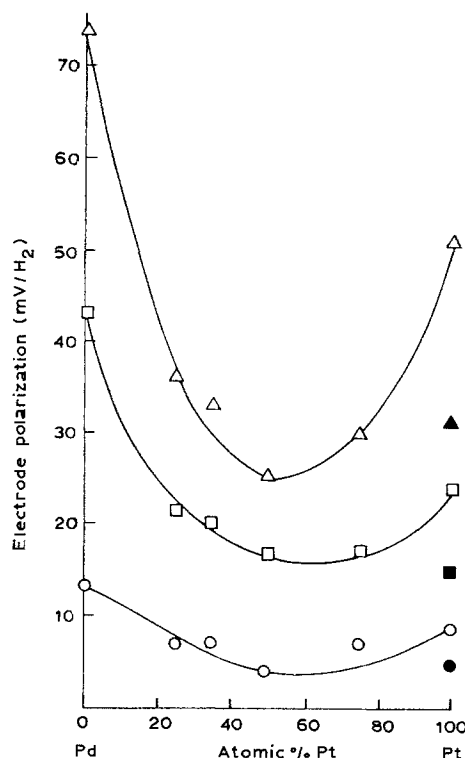


Fig. 4. Hydrogen polarization at  $200 \text{ mA cm}^{-2}$  with various fuel gases. The catalysts are 4 wt % PGM (Platinum Group Metals)/Consel I with a loading of  $0.2 \text{ mg PGM/cm}^2$ . 100%  $\text{H}_3\text{PO}_4$  at  $180^\circ\text{C}$ . Catalysts were heat treated to  $700^\circ\text{C}$  (○) 4 wt % Pt/Consel I catalyst, (●) pure hydrogen, (■) 10% CO/bal. hydrogen, (▲) 30% CO/bal. hydrogen, (△) 30% CO/bal.  $\text{H}_2$ , (□) 10% CO/bal.  $\text{H}_2$ , and (○) pure  $\text{H}_2$ .

of carbon monoxide is a site selective poison for the platinum, and hence lowers the reaction rate for hydrogen dissociation.

The dramatic influence of temperature on the oxidation rate of hydrogen containing 1.7% CO is shown in the Arrhenius plot of Fig. 3, taken from [17]. It can be seen that as the temperature increases, the apparent reaction rate for hydrogen oxidation in the presence of carbon monoxide increases more rapidly on platinum than that for pure hydrogen on the same platinum surface. This is caused by the change in the adsorption isotherm for carbon monoxide on the platinum, rapidly attaining a surface equilibrium that favours the uncovered platinum surface as temperature increases. The challenge was to provide an electrocatalyst that had more poison tolerance than platinum alone, and was capable of retarding surface area loss.

Platinum-palladium alloys were found [18, 19] to be more tolerant than platinum alone, and were resistant to 'sintering'. In addition, they could be prepared with a very high surface area. Results of a detailed study are shown in Fig. 4, where the ratio of platinum to palladium in the alloy was systematically varied, and the hydrogen polarization examined with various fuel gas mixtures. It is significant that there is a decided minimum in the polarization at 50/50 at. % Pt/Pd. In addition, the performance of the heat treated and stabilised alloy catalyst exceeded the performance of the unstabilised platinum catalyst. Platinum-palladium alloy catalysts are now the preferred anode catalyst

compositions for high temperature alkaline fuel cells in the US space program.

Earlier, Stonehart and co-workers had examined [20] a series of binary platinum alloys for carbon monoxide tolerance, and had concluded that ruthenium was beneficial. The degree of poisoning of the alloy surface by carbon monoxide decreased as the ruthenium content increased. Alloys of this type are now [21] utilised in low temperature solid-polymer electrolyte fuel cells where the temperature cannot be increased due to drying out of the polymer membrane.

### 5. Structures of electrocatalysts

The subject of electrocatalyst operation and utilisation in a porous electrode structure has been hotly debated. A paper by Bregoli [22] implied that for oxygen reduction in phosphoric acid, as the platinum crystallites on the carbon surface became smaller (the platinum surface area increased) so the specific activity of the platinum decreased. This was called a 'crystallite size effect' and had the implication that efforts to increase the platinum crystallite surface area were futile, since the gains in performance that could be expected from the increased surface areas were negated by the decreases in the specific activities. The results from Bregoli are shown in Fig. 5.

On examination of Bregoli's data, it appeared that in all of the electrocatalysts studied, the metal loading on the carbon was constant, and the carbon support surface area was not varied. Stonehart repeated an examination of the 'crystallite size effect' using both the Vulcan XC-72 (BET  $250 \text{ m}^2 \text{ g}^{-1}$ ) and Shawinigan acetylene black (BET  $65 \text{ m}^2 \text{ g}^{-1}$ ), and compared those results to Bregoli's. Another relationship for the 'crystallite size effect' was found for the Shawinigan

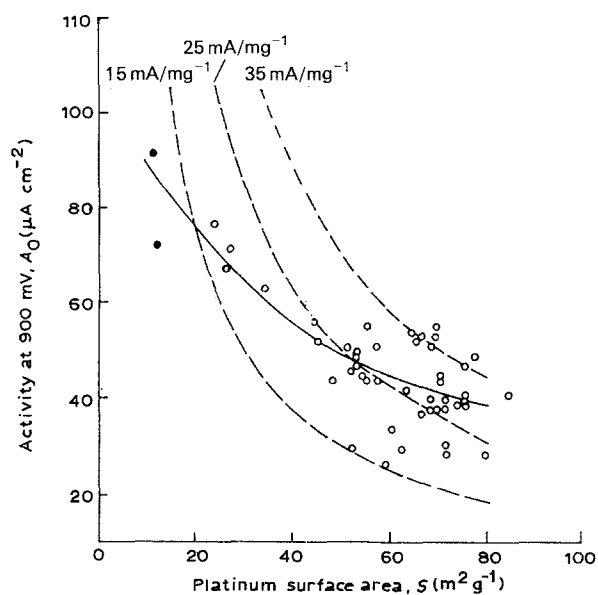


Fig. 5. Specific activity as a function of surface area at  $177^\circ \text{C}$  in 99 wt%  $\text{H}_3\text{PO}_4$ . (○) Platinum supported on Vulcan XC-72; (●) Platinum black blended with Vulcan XC-72. Solid line is a fit of the data; broken lines are for constant activities per unit mass of 15, 25 and  $35 \text{ mA mg}^{-1}$  Pt.

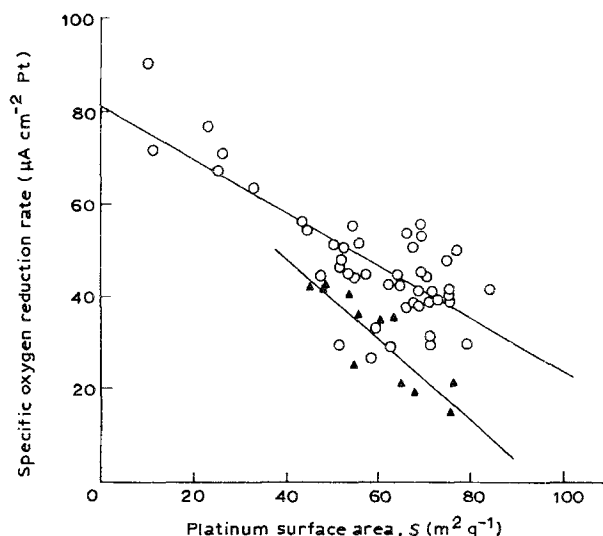


Fig. 6. Specific oxygen reduction rate as a function of surface area at  $180^\circ \text{C}$  in 100%  $\text{H}_3\text{PO}_4$  at 900 mV/RHE. (○) Platinum on Vulcan XC-72 from Bregoli, (▲) Platinum on acetylene black.

acetylene black (similar to Denka Black) supported catalysts. Those results are shown in Fig. 6, which was shown previously [1]. An analysis of the Bregoli data indicated a straightline fit having the same degree of significance as the curve fit drawn by Bregoli in Fig. 5.

Subsequent to that time, Stonehart and co-workers showed [23], and stated explicitly [24], that the results demonstrated 'the extrapolated lines for the Vulcan XC-72 and the acetylene black supported catalysts gave the same specific oxygen reduction rate of  $80 \text{ mA cm}^{-2} \text{ Pt}$  on the ordinate. More importantly, the two lines describe *specific* electrocatalytic activities for the platinum electrocatalyst crystallites that are *the same* when the crystallite separations on the support are *the same*, irrespective of the differing crystallite sizes. That is, the specific reduction rate with  $70 \text{ m}^2 \text{ g}^{-1}$  Pt on acetylene black is the same as  $100 \text{ m}^2 \text{ g}^{-1}$  Pt on Vulcan XC-72, and for these two electrocatalysts, the average platinum crystallite *separations* are the same.'

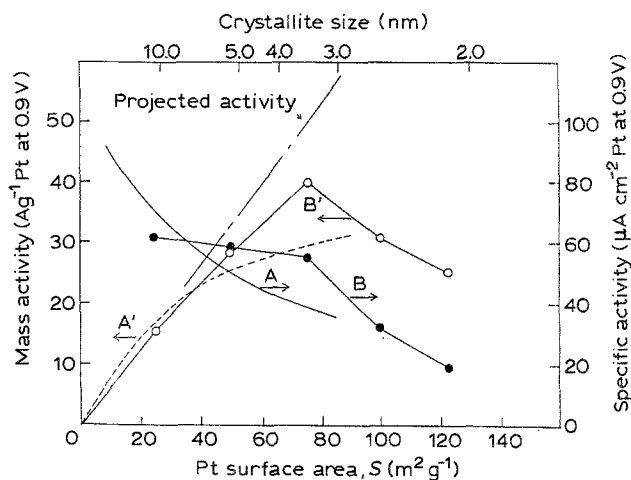


Fig. 7. Relationship between the specific surface area of supported platinum and the specific activity (or the mass activity) for pure oxygen reduction in hot phosphoric acid; cited from Bregoli's data (solid and dashed lines),  $177^\circ \text{C}$  [22], and Sattler and Ross's data (○, ●,  $190^\circ \text{C}$  [25, 26]). Curves A and B relate to the right-hand scale, curves A' and B' relate to the left-hand scale.

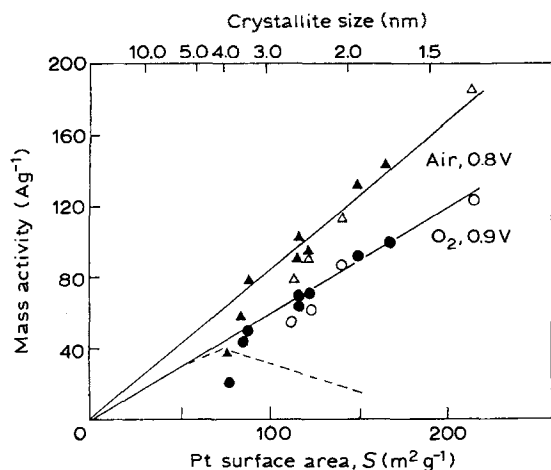


Fig. 8. Variation of the mass activity of platinum for oxygen reduction with specific surface area of the platinum at 190°C in 100%  $\text{H}_3\text{PO}_4$ . Broken line reproduced from Ross's work [18, 19] (see Fig. 7).

Notwithstanding the foregoing, Ross and co-worker [25, 26] lent further credence to the idea that a 'crystallite size effect' existed. Figure 7 is a summary of the Bregoli and Ross data, showing the mass activity and specific activity as functions of the platinum crystallite sizes and surface areas. Ross's data [25, 26] show a maximum in the mass activity at around  $80 \text{ m}^2 \text{ g}^{-1}$  which then decreases as the surface area of the platinum increases. The projected activity is that activity expected if the performance increases linearly with the surface area of the platinum catalysts, which is to be expected if the oxygen reduction reaction is first order in oxygen, and a heterogeneous process is rate controlling.

In order to resolve the situation, Watanabe *et al.* [27] carefully examined a series of platinum catalysts with different loadings, different crystallite sizes, and on different carbon supports; following the directives outlined previously by Stonehart [23, 24]. Those results are shown in Fig. 8 for the phosphoric acid electrolyte. In both sulphuric acid and phosphoric acid electrolytes, it was concluded that platinum *did not* exhibit a 'crystallite size effect' for the reduction of oxygen.

Further analyses of the crystallite separations on the carbon surfaces showed a commonality for all the results, irrespective of the platinum crystallite sizes, the carbon supports, or the metal loadings on the carbon. Those results are shown in Fig. 9, where it can be seen that when the crystallite separations are greater than 1.7 nm the specific activity for the platinum is constant. At crystallite separations less than 1.7 nm the specific activity decreases, producing the apparent 'crystallite size effect' noted by both Bregoli and Ross. So, this effect is not due to the platinum crystallite sizes, but rather to the spatial distributions of the crystallites on the carbon supports.

## 6. Summary

It has been one purpose of this review paper to indicate the importance of information in the patent literature,

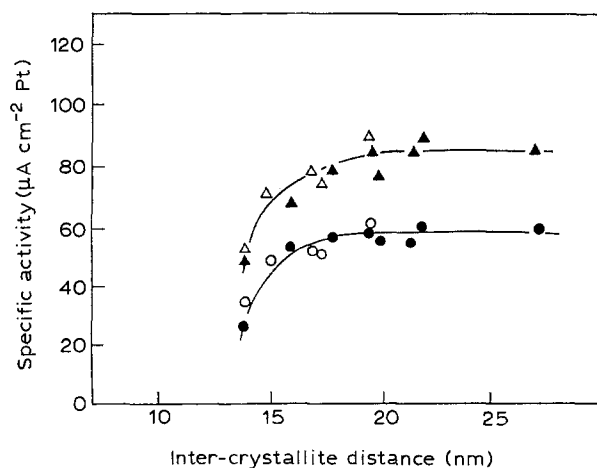


Fig. 9. Specific activity of dispersed platinum crystallites for oxygen reduction at 190°C in 100%  $\text{H}_3\text{PO}_4$  as a function of intercrystallite distance of platinum on the surface of various carbon blacks and various amounts of Pt loading. (●)  $\text{O}_2$  at 0.9 V, (▲) air at 0.8 V.

showing developments within the field of phosphoric acid fuel cells, where significant advances in the preparation and operation of alloy electrocatalysts have been made, both for oxygen reduction and hydrogen oxidation in the presence of site specific poisons. In addition, advancements in our understanding of electrocatalyst structures as opposed to electrode structures (yet another story) is demonstrated.

Clearly, space does not allow for an exhaustive analysis of all the work in this field, but the preparation of alloys with atomic dimensions, operating in the hot phosphoric acid environment shows stimulating progress. In any field, progress does not stop, but builds upon previous knowledge, so we can look forward to the development of an all-encompassing theory for those surface processes that lead to electrocatalysis, preparation of electrocatalysts, and further refinements in electrocatalyst structure theories.

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