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PREPARATION AND EVALUATION OF ELECTROCATALYSTS FOR PHOSPHORIC ACID FUEL CELLS.

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ABSTRACT

Highly dispersed platinum has been placed on carbon supports that were developed under the EPRI RP 1200-2 program so that they may be used as phosphoric acid fuel cell electrocatalysts. These catalysts were characterized for both the platinum surface areas and crystallite sizes. For a given carbon impregnation technique with the noble metal salt, a definite correlation between the specific surface area of the derived platinum crystallites to the BET surface area of the carbon support was found.

I. Objective and Scope of Work

The overall objective of this electrocatalysis program is to define the feasibility of lowering the electrocatalyst cost and increasing the activity in phosphoric acid fuel cells, as a way to increase the commercial viability of fuel cells for producing electrical power.

The specific objective of the present task is the preparation of a series of well characterized electrocatalysts for evaluation in phosphoric acid fuel cells. They should be comprised of platinum crystallites supported on carbon substrates. Variations in the type of carbon substrate and the platinum crystallite size on the carbon substrate are needed. Carbons with well defined properties will be selected from materials characterized under the EPRI Carbon Substrate Program, RP 1200-2.

II. Introduction

Cost is a critical factor in the application of phosphoric acid fuel cell systems for producing electrical power. In turn, efficiency of the electrocatalysts must be high for fuel cell systems to become commercially viable. Present phosphoric acid fuel cells use platinum as the catalyst on both the anode and cathode. As a result of considerable research in the last ten years, the combined platinum loading of the anode and cathode is less than 1 mg/cm^2. This was accomplished principally by supporting platinum on a high surface area conductive carbon black. This meant that the platinum surface area could be increased for a given platinum loading at the electrodes.

It can be reasoned that, since there are so few atoms in small crystallites, the metallurgical and chemical properties of the bulk material do not hold when very small particles are obtained. Recently, it has been claimed that the catalytic activity of platinum decreases as the surface area of the catalyst is increased. Even if this is so, since a decrease in Tafel slope is associated with the increased catalyst surface area, small crystallites are more efficient in the current density range of practical interest (see Appendix A).

The preparation of high surface area electrocatalysts is, therefore, an important aspect of fuel cell technology. Highly dispersed electrocatalytic materials have been recently reviewed by Kinoshita and Stonehart (1). They have discussed details of various catalyst preparation techniques. Among these, impregnation of metal salt on suitable inert support has been widely accepted as an industrial process.

As discussed later, the process used in this program involves controlled impregnation of the carbon support with a solution of chloroplatinic acid -- the least expensive salt of platinum -- followed by careful heating to dryness and subsequent gas phase reduction to platinum metal.

III. Technical Progress

a. Carbon Selection: Many carbons have been identified and characterized under the EPRI RP 1200-2 program. From these, eight carbons were selected to represent a cross section of presently viable electrocatalyst support.

They are:	Vulcan XC-72R	as received
	Vulcan XC-72R	1200 HT
		1400 HT
		1800 HT
		2500 HT
	Shawinigan Acetylene Black	as received
	Shawinigan	1200 HT
	Shawinigan	2500 HT

b. Catalyst Preparation: Typically, 10 w/o platinum supported on carbon electrocatalysts were prepared from chloroplatinic acid by the following procedure. Carbon black samples (1 - 2 g) were wetted by pouring the appropriate amount of aqueous solution of H_2PtCl_6 (10 mg Pt/ml of solution) onto the powder. After a brief ultrasonic agitation the solution was completely impregnated into the porous carbon black and no free solution observed. The mixture was air dried in an oven at about 60°C. This dried catalyst was ground in a mortar and placed in a tube furnace. After purging with helium for about 2 hours, pure hydrogen was introduced and the temperature increased rapidly to 200°C. The hydrogen reduction was carried out for 1 hour. The reduced or "activated" catalyst was then cooled to room temperature in pure helium.

c. Catalyst Characterization: CO Chemisorption: A slug flow CO chemisorption method (2) was used to determine the specific platinum surface area of the supported electrocatalysts prepared in this program. A stream of helium was passed over the reduced or "activated" catalyst sample and a known amount of CO injected into the helium stream. The amount of CO not adsorbed and therefore remaining in the helium stream was measured by a thermal conductivity bridge detector. The amount of CO adsorbed on the Pt surface was obtained by difference. The amount of CO adsorbed per gram of catalyst is a measure of metal dispersion and is directly converted to specific surface area of platinum crystallites. The results are presented in Table I.

Table I.

Properties of selected carbons and electrocatalysts.

Carbon	Heat Treatment temperature °C	BET surface area. m^2/g.	Carbon weight loss % at 100 min., 1.0V, 210°C	Platinum cryst. surface area. m^2/g.
Vulcan XC-72R	None	254	3.7	153
Vulcan XC-72R	1200	174	2.0	154
Vulcan XC-72R	1400	140	---	107
Vulcan XC-72R	1800	95	---	81
Vulcan XC-72R	2500	65	.62	62
Shawinigan AC Blk.	None	65	1.5	82
Shawinigan AC Blk.	1200	62	2.1	92
Shawinigan AC Blk.	2500	45	.9	58

Transmission Electron Microscopy: To substantiate the surface area measurements and to identify the Pt-C sites high resolution transmission electron microscopy of catalyzed Vulcan XC-72R as received and Vulcan XC-72R 2500 HT -- two carbon surface extremes of this carbon black were examined. Typical electron micrographs of 10 w/o Pt on Vulcan XC-72R as received and 10 w/o Pt on graphitized Vulcan XC-72R are shown in Figures 1 and 2. Mean particle sizes of platinum crystallites were measured. Assuming a spherical geometry, the following equation is used to calculate the specific surface area S in m^2/g of platinum:

$$S = \frac{6}{\rho d} \times 10^4$$

where d is the mean particle diameter in Å, and $\rho = 21.4\ g/cm^3$ is the density of platinum. In addition, to confirm the surface area measurements by other methods, this technique reveals the particle size distribution, the spatial dispersion, and the morphology of the support material.

Electrochemical Surface Area: Surface area measurements are also being made using an electrochemical technique (3, 4) in 50 w/o H_3PO_4 at room temperature. The electrocatalyst was formed into an electrode and was repeatedly cycled between 0 mv (RHE) and 1500 mv (RHE) to remove adsorbed impurities. The electrode was then held at 400 mv (RHE) for 2 minutes. Following this period a voltammetric sweep at 10 mv/sec between 0 mv (RHE) and 1400 mv was recorded. A typical voltammetric sweep representing hydrogen adsorption (reduction) and desorption or removal (oxidation) is shown in Figure 3 for a Teflon bonded platinum black electrode structure. The platinum surface areas are calculated from the coulombic charge required to oxidize adsorbed hydrogen.

d. Discussion of Results: Analytical data for selected carbons and electrocatalysts containing 10 w/o platinum are presented in Table I. The heat treated carbons have improved corrosion resistance from the point of view of carbon loss under operating fuel cell conditions. It should be noted, however, that the diminished surface areas of the carbons as a consequence of the heat treatments, causes the derived platinum crystallite surface areas to be lower during the catalyzation process. Figure 4 shows that for our catalyzation process, the specific surface areas of the platinum crystallites deposited on the carbon supports are related to the BET surface areas of the carbons. The transmission

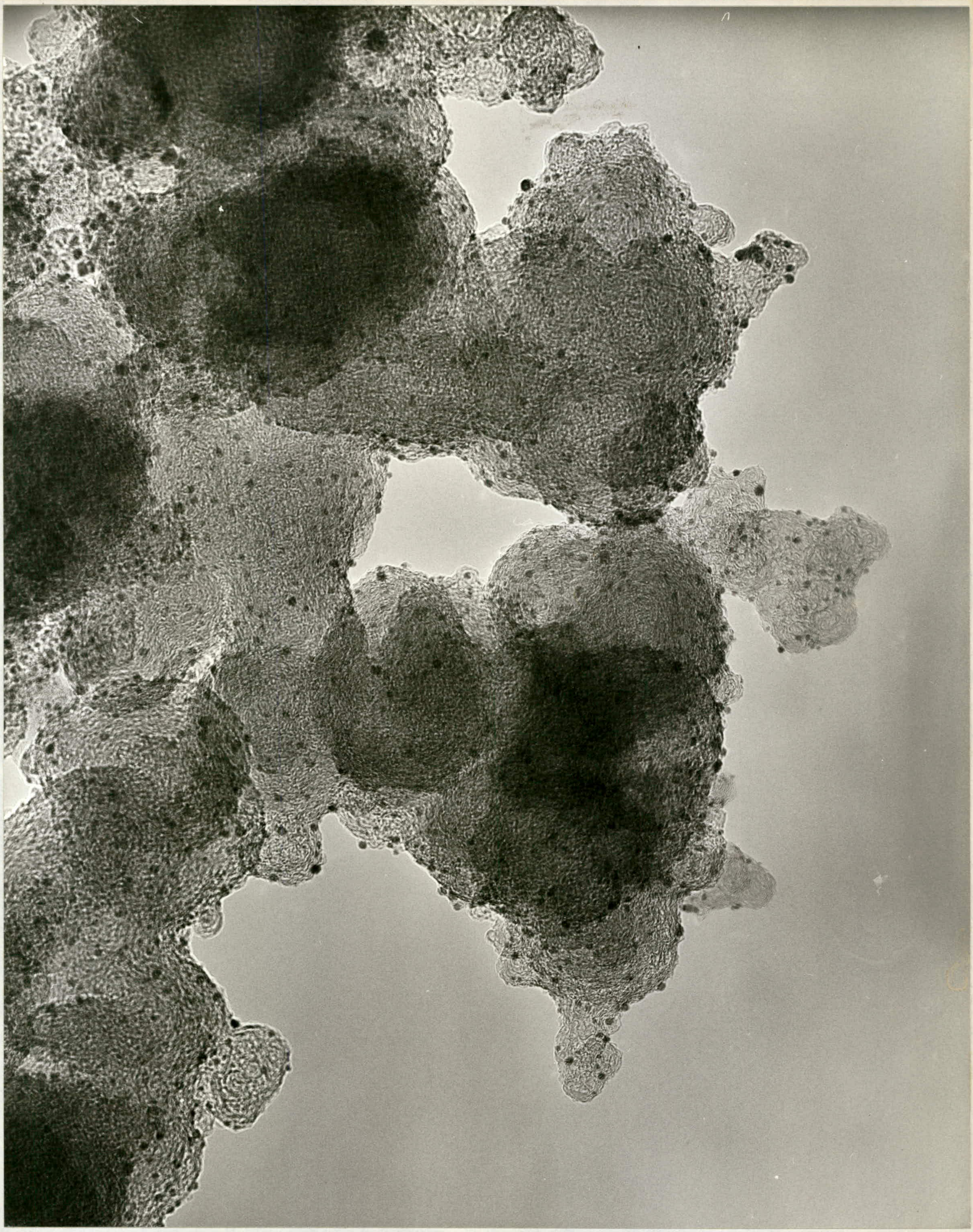

Figure 1. Electron Micrograph of 10 w/o platinum supported on Vulcan XC-72R
Magnification X830,000 (1mm = 12 Å)

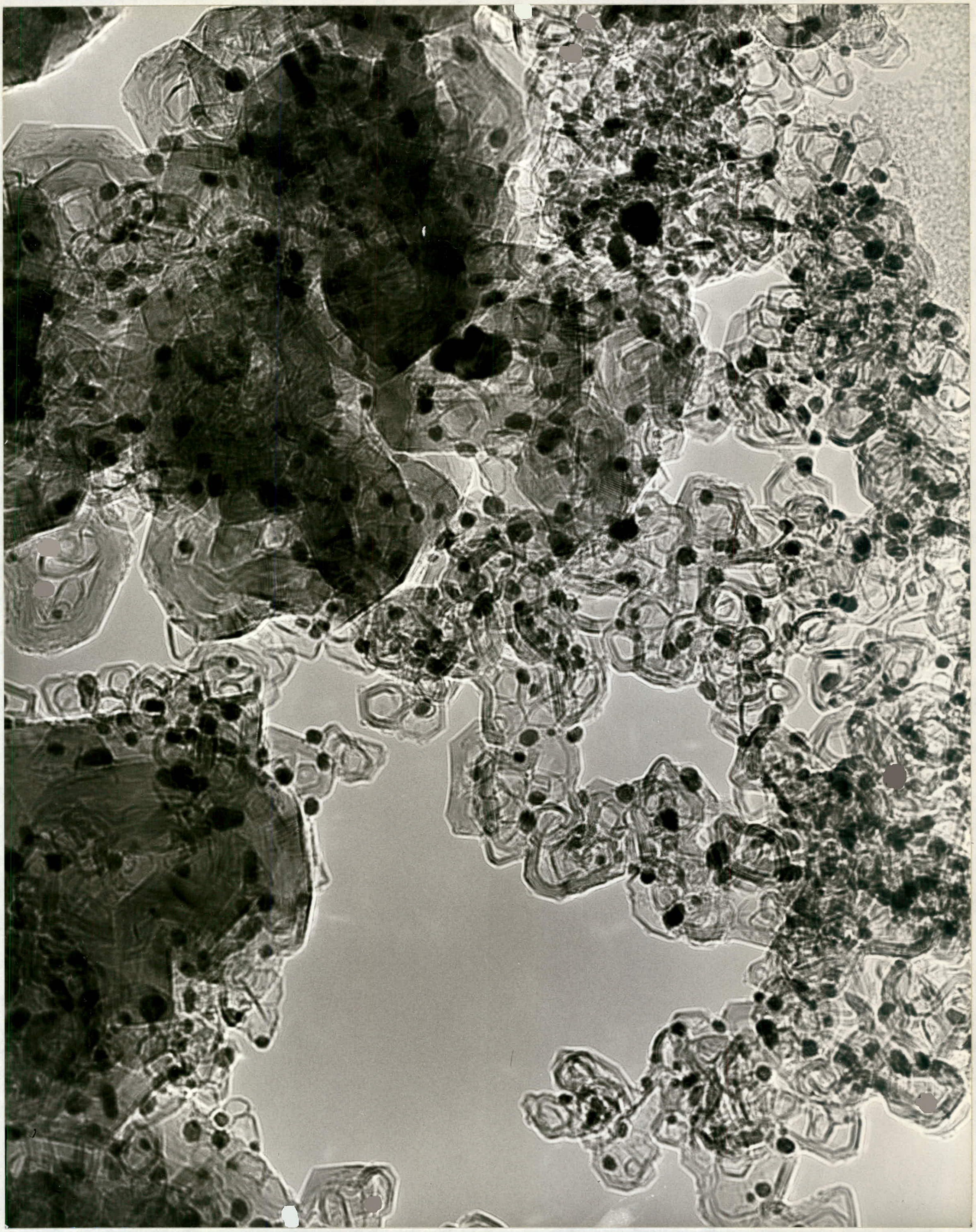

Figure 2. Electron micrograph of 10 w/o platinum on graphitized Vulcan XC-72R.
Magnification X830,000 (1mm = 12 Å)

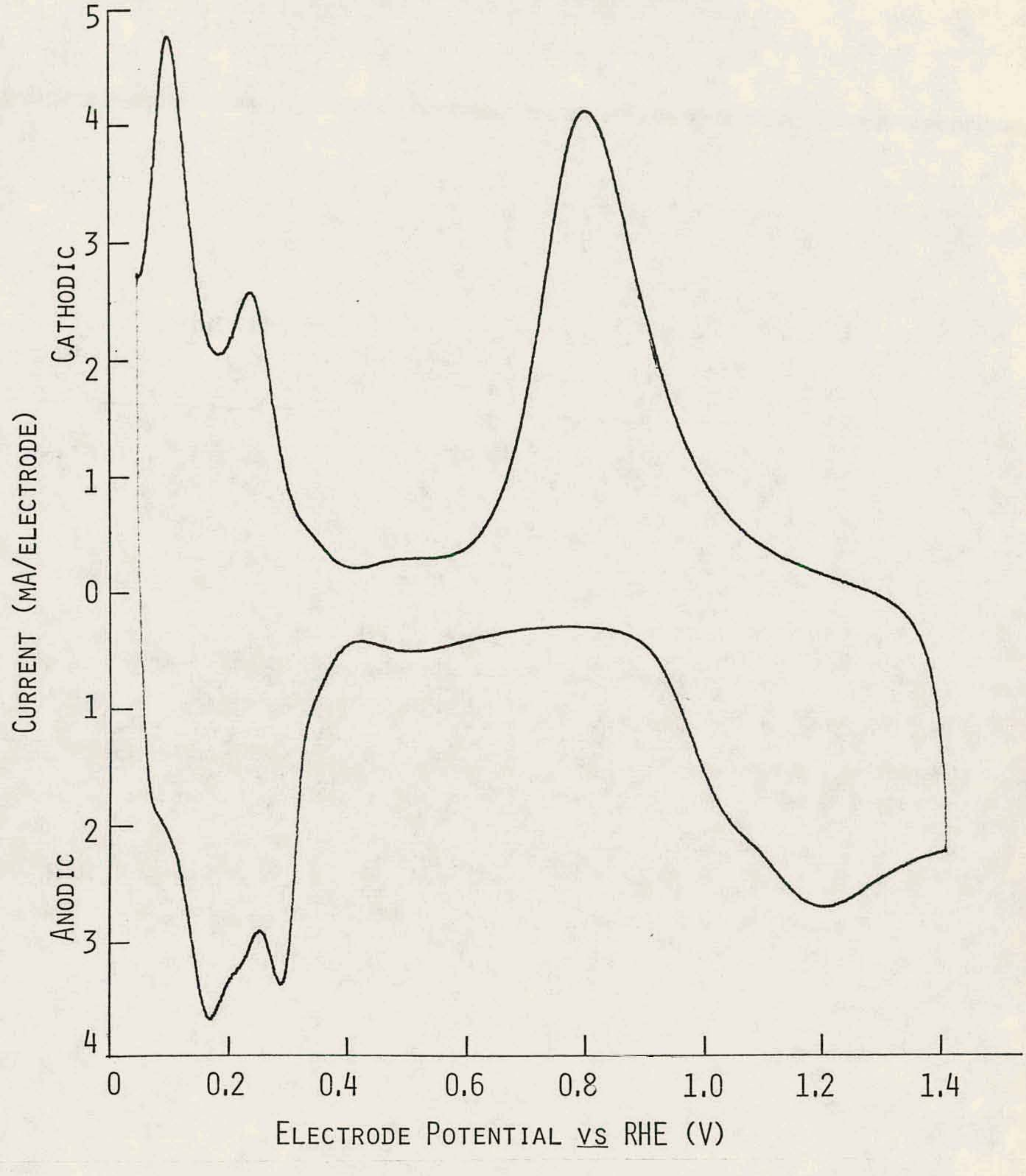

Figure 3. Potentiodynamic current/potential profile for Pt-black in 50 w/o H_3PO_4 at 23° C; sweep rate - .010 V/s.

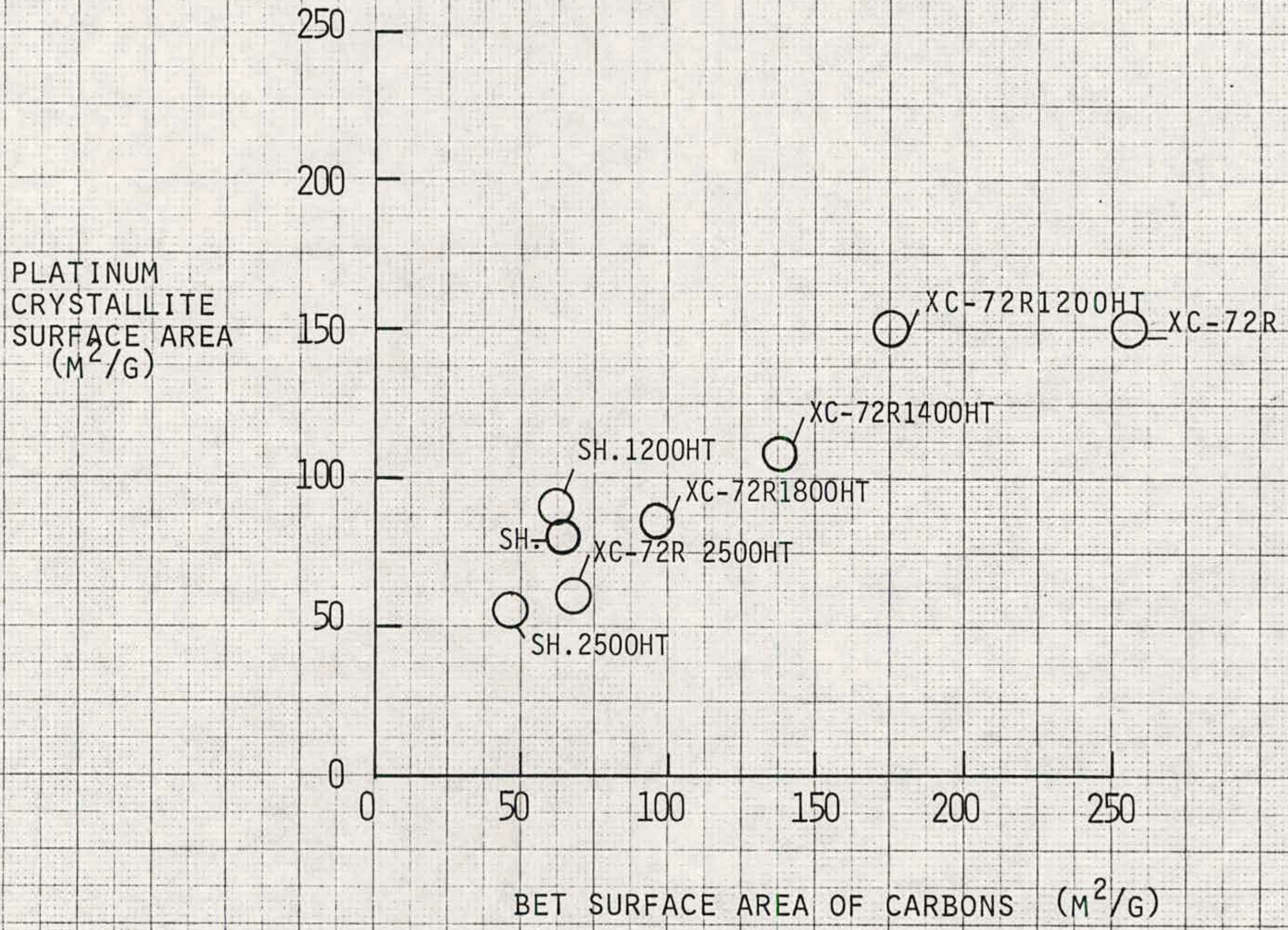

Figure 4. Platinum crystallite surface areas at 10w/o Pt loading as a function of the carbon support surface areas.

electron micrographs in Figure 1 and Figure 2 show that the platinum particles on the as-received Vulcan XC-72R (BET surface area = 254 m^2/g) are much smaller than the platinum particles deposited on the graphitized Vulcan XC-72R (BET surface area = 62 m^2g).

The fact that platinum crystallites deposited on as-received Shawinigan acetylene black have much lower surface area than platinum on as-received Vulcan XC-72R indicates that the observed effect is not due to heat treatment, but indeed is related to the surface areas of carbon support.

Further justification of this observation is found in Exxon's work for EPRI (5). For their "Catalyst Sintering Studies" they selected carbon supports with large differences in crystal structure (amorphous to graphitic) and surface properties (as measured by volatile contents and pH) for catalyzation. Using their data for nominally 10 w/o Pt deposited by an impregnation technique, Figure 5 is a plot of platinum crystallite surface area against the BET surface area of carbons. Note that due to the overall lower platinum dispersion and higher surface areas of carbons used by Exxon, the scale in Figure 5 is different from that used in Figure 4. Although there is some scatter, a definite increase of platinum surface area with increased surface area of carbon support can be seen to be present. Part of the scatter is believed to be due to inadequacy of the N_2 adsorption BET method to distinguish between true and available surface areas for microporous materials (6).

There can be a number of reasons for the observed behavior; the simplest of them being that there are a constant number of active or trap sites for platinum crystallites and that graphitic carbons have fewer defect sites than turbostratic carbon blacks. Carbons with lower surface area, therefore, will have relatively fewer crystallites and defects; hence for a given platinum loading the platinum crystallites will be larger than those on high surface area carbons.

Electrocatalysts with <u>only</u> 1 w/o platinum were prepared on as-received Vulcan XC-72R (BET surface area 254 m^2/g) and Vulcan XC-72R 3000 HT (BET surface area 60 m^2/g). As seen in the electron micrographs in Figures 6 and 7, even for 1 w/o platinum loading the size of the platinum crystallites on the graphitized carbon black is much larger than that on the high surface area carbon black. As a matter

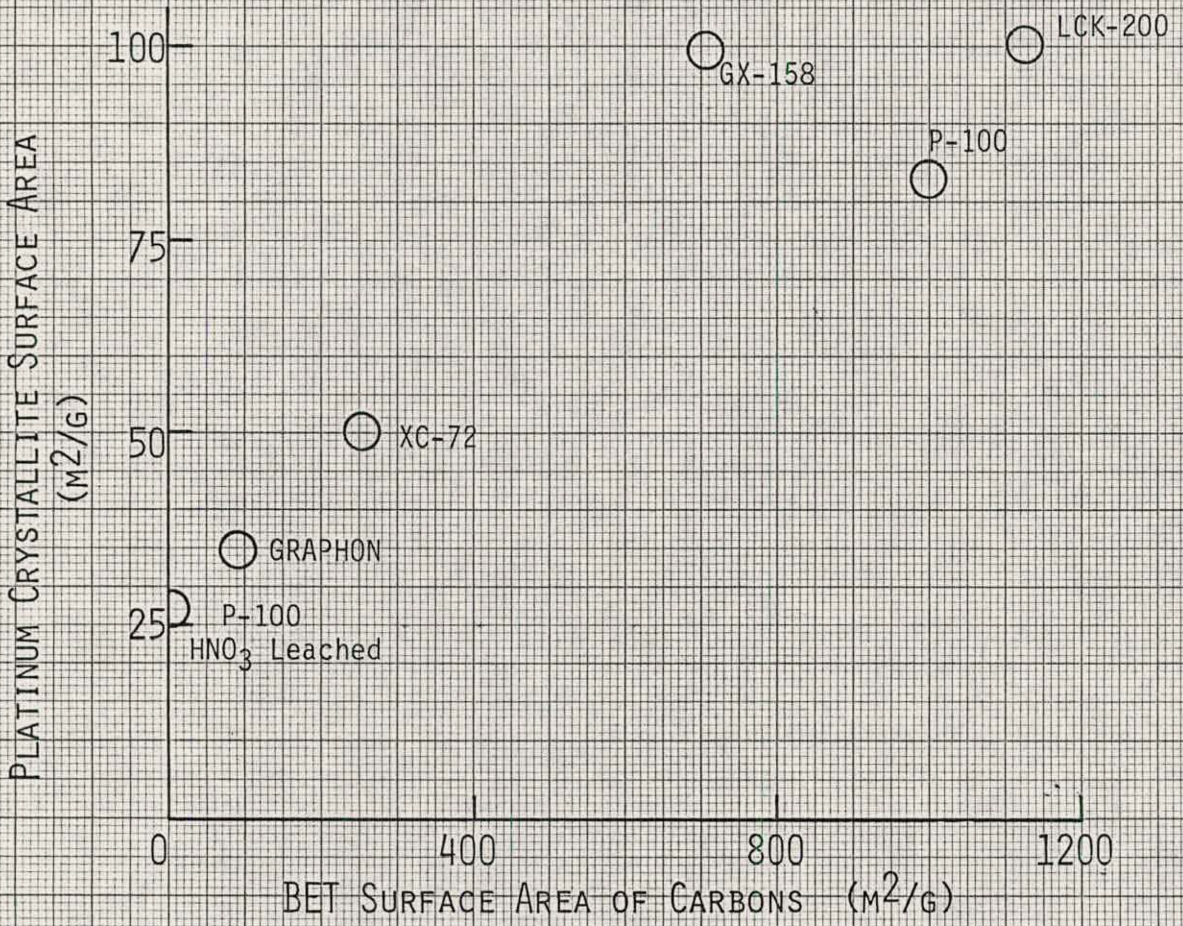

Figure 5. Platinum crystallite surface areas at 10 w/o Pt loading as a function of the carbon support surface areas.

Figure 6. Electron micrograph of 1 w/o platinum on Vulcan XC-72 R.
Magnification X830,000 (1mm = 12 Å)

Figure 7. Electron micrograph of 1 w/o platinum on graphitized Vulcan XC-72 R. Magnification X830,000 (1mm = 12 Å)

of fact, for a given carbon support the platinum crystallite size is about the same for 10 w/o Pt and 1 w/o Pt loading. Clearly, the simple hypothesis presented above does not hold and other related factors such as wettability and microporosity of the support material will influence the catalyzation.

It should be noted that with 100% dispersion of the platinum (every platinum atom being used), the platinum crystallite surface area will approach 250 m^2/g. Clearly, there is considerable scope of catalyst dispersion improvement. Improved catalyzation techniques will increase the platinum metal utilization and in turn reduce the cost, provided that the electrocatalysts can be formed into high utilization electrode structures.

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APPENDIX A

Recently, it was reported [1] that the true or specific activity of Pt approximately doubled and the Tafel slope increased from 90 mv/decade to 110 mv/decade as the surface area of Pt was decreased from 80 to 10 m^2/g. It was concluded that this is of importance for fuel cell applications since this phenomenon reduces the decay of a cell to a value which is less than would be predicted from a surface area loss at constant activity. Unfortunately, this conclusion ignored the effect of the increase in Tafel slope at practical operating current density and misled Christner and Ross [2] to state that no net gain in performance is realized as Pt crystallite size is reduced.

A simple calculation, using Equation 1 would show that loss of platinum surface area, in fact, causes a practical fuel cell to decay more than one would expect with constant activity and slope. The potential, E, of a fuel cell cathode operating at a current density of I ma/cm^2 on air is given by

$$E = 900 - b_m \log \frac{i}{I} - b_m \log 0.21 \qquad (1)$$

where b_m is the measured Tafel slope, and 0.21 in the Nernst term is O_2 partial pressure in air. The current density, i, on O_2 at 900 mv is given by

$$i = Ao\ Sg\ W_{pt} \qquad (2)$$

where, as defined in (1) Ao is the activity per unit surface area of Pt, Sg is the surface area per unit pass of Pt and W_{pt} is the mass of Pt per unit geometric area of the electrode.

For a typical 0.5 mg/cm^2 platinum loaded cathode, the results of such calculations for the two cases are compared in Figure 1A. Curves A and B represent activation controlled performance curve for reduction of pure oxygen and of oxygen in air, respectively, for a catalyst with 80 m^2/gm initial platinum surface area, 40 $\mu A/cm^2$ activity, and -90 mv/decade Tafel slope. The curve C represents performance of a cathode operating on air when the platinum surface area has reduced to 10 m^2/gm at constant activity and slope. As reported, however, a catalyst with 10 m^2/gm platinum surface area has 80μ A/cm^2 activity and -110 mv/decade Tafel slope; curve D is an air performance curve for such a case.

Since an ambient pressure, state of the art, practical fuel cell operates at 215-265 mA/cm^2 (Reference 3: Figures 16 and 11), the phenomena observed in Ref. 1 clearly increase the decay of a cell. Any reduction in average oxygen partial pressure due to oxygen utilization at the cathode would increase the magnitude of the Nernst term in Equation 1 and make the situation worse.

Furthermore, only the electrochemically active surface area of the platinum -- that includes dry, active and any dissolved platinum -- is taken into account, and hence any relationship between surface area and crystallite size becomes dubious.

Bregoli's work, quite the contrary to his conclusion, emphasizes the need for continuing efforts to reduce or to stop recrystallization (surface area loss) of platinum catalyst.

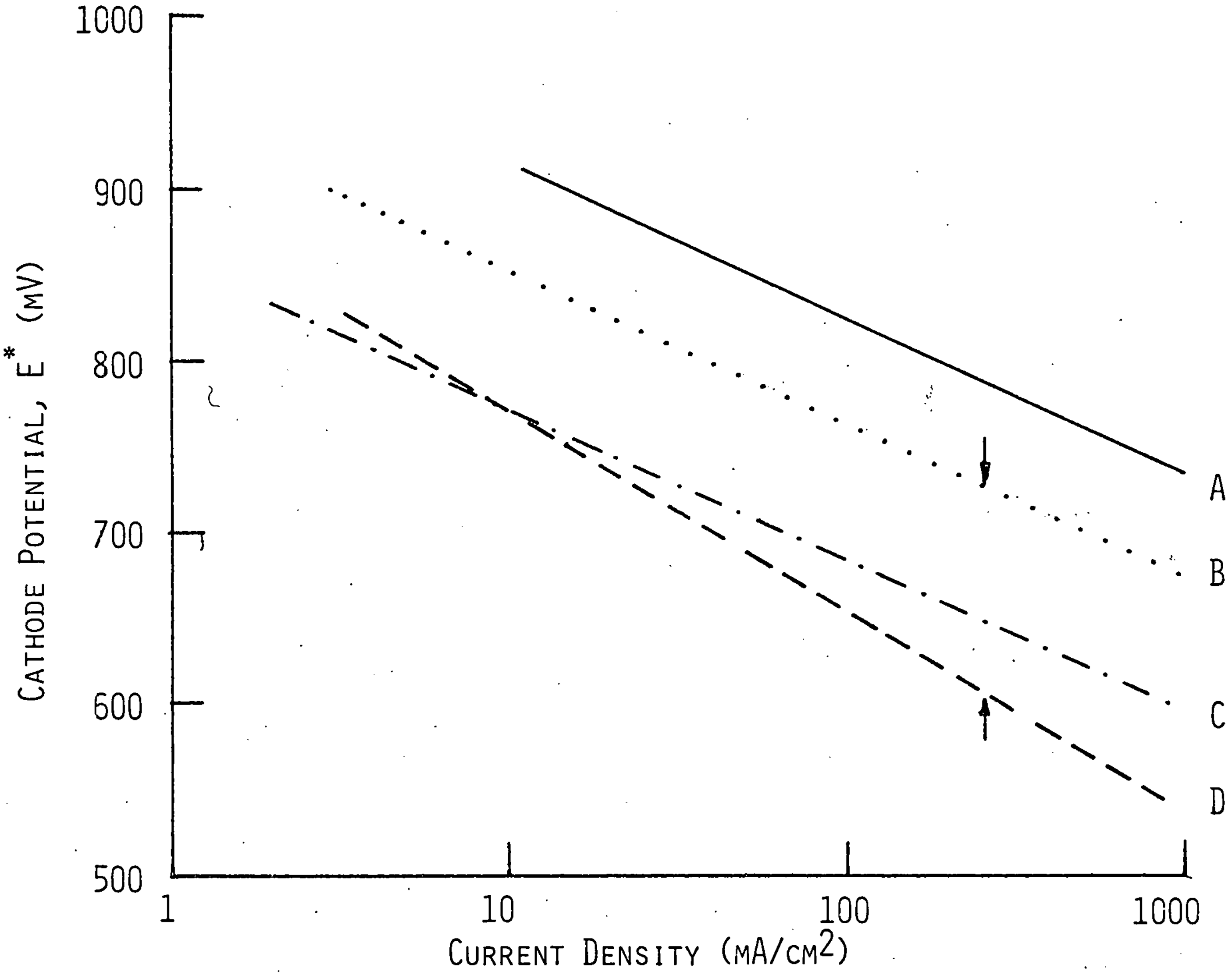

Figure 1A. Comparison of cathode potentials at 177° C in 99 w/o H_3PO_4 for 0.5 mg Pt/cm^2 loading.
A: 80 m^2/g Pt, 40 μA/cm^2, -90 mV/decade, on 1 atm. O_2.
B: 80 m^2/g Pt, 40 μA/cm^2, -90 mV/decade, on 1 atm. air.
C: 10 m^2/g Pt, 40 μA/cm^2, -90 mV/decade, on 1 atm. air.
D: 10 m^2/g Pt, 80 μA/cm^2, -110 mV/decade, on 1 atm. air.

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