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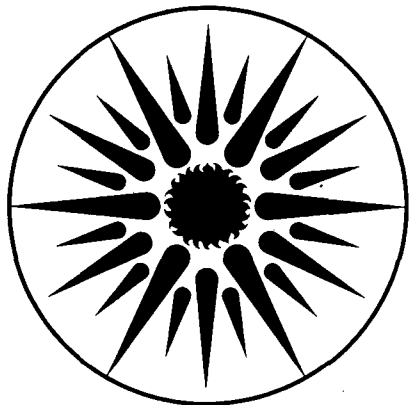
### Particle Size Effects for Oxygen Reduction on Highly Dispersed Platinum in Acid Electrolytes

K. Kinoshita

January 1989

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**PARTICLE SIZE EFFECTS FOR OXYGEN REDUCTION  
ON HIGHLY DISPERSED PLATINUM  
IN ACID ELECTROLYTES**

by

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January 1989

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**Particle Size Effects for Oxygen Reduction  
on Highly Dispersed Platinum  
in Acid Electrolytes**

by

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**Abstract**

The particle size effects for oxygen reduction kinetics on highly dispersed Pt particles in acid electrolytes are discussed. It is suggested that the change in the fraction of surface atoms on the (100) crystal face of Pt particles, which are assumed to be cubo-octahedral structures, can be correlated to the mass activity (A/g Pt) and specific activity ( $\mu\text{A}/\text{cm}^2$  Pt) of highly dispersed Pt electrocatalysts. The reduction of oxygen on supported Pt particles in acid electrolytes is classified as a "demanding" or "structure-sensitive" reaction; the specific activity increases with an increase in particle size.

## List of Symbols

c	corner sites
d	average particle size (nm)
$d_{\text{at}}$	diameter of a Pt atom (0.276 nm)
e	edge sites
N(s)	number of Pt surface atoms
N(t)	total number of Pt atoms in the particle
N(100)	number of Pt atoms on the (100) crystal face
N(111)	number of Pt atoms on the (111) crystal face
N(e+c)	number of Pt atoms on the corner and edge sites
MA	mass activity (A/g Pt)
MAD	mass-averaged distribution
MAD(100)	$\frac{N(100)}{N(t)}$
MAD(111)	$\frac{N(111)}{N(t)}$
MAD(e+c)	$\frac{N(e+c)}{N(t)}$
SA	specific activity ( $\mu\text{A}/\text{cm}^2$ )
SAD	surface-averaged distribution
SAD(100)	$\frac{N(100)}{N(s)}$
SAD(111)	$\frac{N(111)}{N(s)}$
SAD(e+c)	$\frac{N(e+c)}{N(s)}$

## Introduction

Platinum is probably the best electrocatalyst for oxygen reduction in acid fuel cells. To obtain the optimum utilization of platinum, it is generally dispersed as small particles on a conductive support such as high-surface-area carbon powders. Numerous studies (1-9) have reported on the kinetics of oxygen reduction on supported platinum electrocatalysts in acid electrolytes (i.e.,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ). However, there still remains some debate on the effects of platinum particle size on electrocatalytic activity for oxygen reduction. As we shall summarize below, different conclusions were reached concerning the effects of particle size on the rate of oxygen reduction.

Boudart (10) suggested that heterogeneous catalysis on supported metal particles can be classified into various categories according to the relationship between the particle size of the metal and its catalytic activity ("particle size effect"). "Facile" or "structure-insensitive" reactions exhibit a specific rate that does not depend on particle size (i.e., all metal atoms on the particle have comparable activity). "Demanding" or "structure-sensitive" reactions exhibit a specific rate that depends on particle size, and specific sites with special geometric arrangements are involved as so-called "active sites." Because supported catalysts usually contain a wide distribution of particle sizes, experimental evidence for a particle size effect is often difficult to obtain.

The purpose of this paper is twofold: (i) to examine the effect of Pt crystallite size on the kinetics of oxygen reduction in acid electrolytes, and (ii) to provide an interpretation for experimental data reported in the literature on oxygen reduction on highly dispersed Pt electrocatalysts. Two major assumptions are used in this analysis: (i) the Pt particles have a well-defined structure amenable to mathematical analysis of the surface concentration of atoms, and (ii) the surface structure plays an important role in the kinetics of oxygen reduction.

## Oxygen Reduction on Supported Platinum Electrocatalysts

The electrocatalytic activity of supported platinum electrocatalysts is reported in the literature as a mass activity (MA) or a specific activity (SA), and these results are obtained as a function of surface area or particle size (d). In other words, the rate of oxygen reduction on supported Pt

electrocatalysts at a given electrode potential in the Tafel region is normalized to the mass of Pt (mass activity) or the surface area of Pt (specific activity) in the electrode. The mass activity has practical implications because the cost of an electrode depends on the amount of Pt used.

Examples that illustrate the effects of particle size on the electrocatalytic active of highly dispersed platinum for oxygen reduction are summarized in Table 1. Analysis of the data suggests the following contradictory trends:

- mass activity reaches a maximum at about 3-5 nm (1-4)
- mass activity increases as the Pt particle size decreases (5-8)
- specific activity decreases as the Pt particle size decreases (1-4,7)
- specific activity is constant, independent of the the Pt particle size (5,6,8)

In this paper, we will present an argument to rationalize some of the trends observed in Table 1. The decrease in the mass activity observed with smaller Pt particles (1-4) is referred to as "lost activity." The lost activity is detrimental because it counteracts the use of highly dispersed Pt to obtain maximum utilization of the expensive electrocatalyst.

### **Platinum Particle Structure**

Platinum has a face-centered cubic structure. The analysis by Romanowski (11), using the concept of localized metal bonds (i.e., only nearest-neighbor interactions are considered), suggests that a minimum surface energy is obtained for Pt particles that have a cubo-octahedral structure.<sup>a</sup> The cubo-octahedral particles consist of eight octahedral (111) crystal faces and six cubic (100) crystal faces bounded by edge and corner atoms (see Figure 1). If we assume that the cubo-octahedral structure is the stable form of Pt particle, then the relationship between the Pt particle size and number of atoms associated with the (111) and (100) crystal faces and the edge and corner sites can be predicted by the analysis of Van Hardeveld and co-workers (12-14).

<sup>a</sup> High-resolution transmission electron microscopy of Pt supported on carbon showed evidence that Pt particles have a cubo-octahedral structure (2).



In this paper, the Pt particle diameter is defined (13) as the diameter of a sphere (d) with a volume equal to  $N_t$  times the volume occupied by an atom in the unit cell, i.e.,

$$d = \left[ \frac{6 (d_{at} \sqrt{2})^3}{\pi 4} N(t) \right]^{1/3} = 1.11 d_{at} \sqrt[3]{N(t)} \quad (1)$$

where  $d_{at}$  is the diameter of a Pt atom (0.276 nm) and  $N(t)$  is the total number of Pt atoms in the particle. If we further assume that the edges of both the octahedral and cubic faces of the cubo-octahedral structure contain the same number of atoms, then the distributions of surface atoms on the (111) and (100) crystal faces and the edge and corner sites shown in Figure 2 are obtained.<sup>b</sup> In this figure the distribution of surface atoms is normalized to the total number of atoms in the particle (MAD) and on the surface of the particle (SAD). The interesting feature in Figure 2a is the maximum in the mass-averaged distribution that is observed for the (111) and (100) crystal faces. For a cubo-octahedral Pt particle, maxima in MAD(100) and MAD(111) are observed at a particle size of ~3.5 nm for the (100) crystal face and ~2 nm for the (111) crystal face, respectively. For the edge and corner sites, MAD(e+c) decreases rapidly as the particle size increases. The surface-averaged distribution for the (100) and (111) crystal faces and the edge and corner sites are plotted in Figure 2b. Both SAD(111) and SAD(100) increase as the particle size increases. On the other hand, SAD(e+c) decreases rapidly with an increase in particle size. For d larger than about 10 nm, SAD (e+c) decreases to less than 10%.

Supported platinum electrocatalysts are generally prepared by a variety of techniques (i.e., impregnating the carbon powder with a platinum salt solution, adsorbing colloidal Pt on the carbon, adsorbing a platinum salt on the powder surface, etc.). Regardless of the preparative procedure, "structurally incomplete" particles are formed because the exact number of Pt atoms which are necessary to form a complete structure (i.e., particle consisting of only (111) and (100) crystal faces) is unlikely to nucleate to produce Pt particles. This means that crystal faces besides the (111) and (100)

<sup>b</sup> Van Hardeveld and co-workers (12-14) also obtained distributions for particles with different number of atoms on the edges of the octahedral and cubic faces.

orientations are formed on cubo-octahedral structures, and they are created by the addition of atoms to existing crystal faces. The surface sites that are associated with  $B_5$  sites<sup>c</sup> (12,13), for example (110) and (113) crystal faces, are likely to form on particles that do not contain the exact number of atoms to produce complete cubo-octahedral structures. The analysis by Van Hardeveld and co-workers (12-14) indicates that  $B_5$  sites represent only a small fraction of the total atoms in Pt particles that are less than about 1.5 nm and larger than about 8 nm. However, for particles between these two particle diameters, the mass-averaged distribution of  $B_5$  sites could reach a maximum of about 15%. In the discussion that follows,  $B_5$  sites are not considered as active sites because they are similar to the sites on the (110) crystal face, which is presumed to be of low electrocatalytic activity.

The implications of the surface structure of small Pt particles on electrocatalytic activity for oxygen reduction can be discussed in terms of geometric models reported in the literature. A commercial software program (Cricketgraph, Version 1.2, Cricket Software, Malvern, PA) was used on a Macintosh II (Apple Computer Co., Cupertino, CA) to manipulate the data that was analyzed.

## Discussion

Establishing a correlation between the rate of oxygen reduction and a structural property of small Pt particles requires *a priori* knowledge of the electrocatalytic activity of specific atom sites. Currently, we have no direct experimental evidence that crystal-face sites are present on highly dispersed Pt particles which exhibit preferential electrocatalytic activity that differs significantly from that of edge and/or corner sites. In fact, studies by Ross (15) indicate that the rate of oxygen reduction in 1 N HClO<sub>4</sub> or 1 N H<sub>2</sub>SO<sub>4</sub> is similar on (111), (100) and stepped surfaces on well-oriented Pt surfaces. However, Ross (1,2) concluded from studies with Pt supported on carbon in 98% H<sub>3</sub>PO<sub>4</sub> that the (111) and (110) crystal faces are less active for oxygen reduction than the (100) crystal face. Bett et al. (8) concluded that atoms at edges or corners are not more active than those on the crystal faces, and that oxygen reduction on highly dispersed Pt electrocatalysts in 1 N H<sub>2</sub>SO<sub>4</sub> occurs

<sup>c</sup>  $B_5$  sites are sites on Pt particles where an adsorbed entity makes a point-contact to five Pt atoms. On the (111) and (100) crystal faces there are only  $B_3$  and  $B_4$  sites, respectively.

primarily on the crystal faces. The lack of agreement between the electrocatalytic activity of single-crystal Pt surfaces and the corresponding crystal faces associated with supported Pt particles suggests that studies of "ideal" surfaces cannot be easily applied to understanding electrocatalysis at small particles.

It seems reasonable to expect that if the (100) crystal face of small Pt particles is the dominant electrocatalytically active site for oxygen reduction, as Ross suggests (1,2), then MAD(100) should show the same trend as MA with particle size. For a cubo-octahedral Pt structure, MAD (100) has a maximum at  $d$  of about 3.5 nm (see Figure 2a). Measurements of the kinetics of oxygen reduction on highly dispersed Pt particles by Ross (1-3) and Peuckert et al. (4) indicate that a maximum in MA is obtained at an average Pt particle size of between 3.5 and 5.5 nm. If one accepts the conclusion by Ross (1,2) that the (100) crystal face of highly dispersed Pt particles is the active site for oxygen reduction, then the kinetic data showing a maximum MA can be rationalized with the change in MAD with  $d$ . This correlation is illustrated in Figure 3 which shows superimposed plots of MA and MAD(100) as a function of  $d$  for the data reported by Ross and Peuckert et al. The close agreement in the trend of the data, especially those of Peuckert et al., is coincidental because we know that highly dispersed electrocatalysts contain a distribution of particle sizes, and only the average particle size is considered in our analysis. In general, highly dispersed electrocatalysts with a small  $d$  tend to have a narrower particle-size distribution than that of electrocatalysts with a larger  $d$ . According to Luss (16), changes in the observed specific activity may be less than changes in the true specific activity when comparisons are made of catalysts with small  $d$  (narrow particle size distribution) and with large  $d$  (wide particle size distribution).

The dependence of SA and SAD(100) on  $d$  is illustrated in Figure 4. The results, which were reported by Ross (1-3) and Peuckert et al. (4), both show the same trend, increasing with an increase in Pt particle size. Here again, a remarkably close agreement in the trend of SA and SAD(100) is observed. This close relationship suggests that oxygen reduction on highly dispersed Pt in acid electrolytes is a structure-sensitive reaction, according to the classification suggested by Boudart (10).

The results reported by Watanabe et al. (5,6), Bregoli (7), Bett et al. (8), and Blurton et al. (9) show no clear evidence of a maximum in MA. The scatter in the data presented by Blurton et al. precludes further analysis in this paper. However, some of the other results can be rationalized by the above argument. Plots of MAD superimposed on MA data obtained by Bregoli, Watanabe et al., and Bett et al. are shown in Figure 5. Although a maximum in MA is not observed in the results of Bregoli and Bett et al., one can speculate that if the measurements were extended to highly dispersed Pt particles of smaller particle size, perhaps a maximum in MA, as observed by Ross (1-3) and Peuckert et al. (4), would be obtained. It would appear that the data indicate the dependence of MA on  $d$  that corresponds to the decreasing branch (i.e., MA decreases as  $d$  increases). Ross (1) reported that the maximum in MA shifted to  $d$  of 1.5-2 nm in different acid electrolytes at room temperature. Thus it does not seem unreasonable to suggest that a maximum in MA might exist at a smaller  $d$ . Analysis of the data reported by Watanabe et al. (5,6) shows that MA decreases with an increase in  $d$  (see Figure 5c, for example), but any argument that a maximum in MA should be present at smaller  $d$  is tenuous. This is because the measurements were reported for  $d$  as small as about 1.5 nm, and to expect a maximum in MA at even smaller  $d$  does not seem reasonable. Particles that are much less than 1 nm would consist of edge and corner sites (e.g., cubo-octahedron of 13 atoms contains 12 atoms at the edge and corner sites,  $d = 0.7$  nm), and no (100) crystal faces would be present in these small particles to serve as active sites. At this time, we cannot present a clear rationalization for the results of Watanabe et al. in terms of a correlation with the surface concentration of active sites on the (100) crystal face. It should be noted that a similar trend between  $d$  and MA or  $N(e+c)$  exists, as shown in Figure 5d. However, there does not appear to be any basis for suggesting that edge and corner sites are active sites for oxygen reduction on the electrocatalysts prepared by Watanabe et al.

The SA data reported by Watanabe et al. (5,6), Bregoli (7), and Bett et al. (8) are shown in Figure 6. The results obtained by Bregoli show a similar trend between SA and SAD(100). However, no conclusive trend is evident in the results from the other two research groups. A specific activity that is constant, independent of  $d$ , is difficult to rationalize by the above argument. If the electrocatalytically active sites are associated with the (100) crystal face, then SA should increase with an increase

in d (see Figure 2b). Watanabe et al. suggest that SA is constant when the mean interparticle separation distance between Pt particles on the carbon surface is  $\geq 20$  nm, which they calculated for their supported electrocatalysts. Thus in the case of the results of Watanabe et al., the interparticle separation distance is introduced to explain the constant specific activity of highly dispersed Pt particles. A similar rationalization to explain the constant SA reported by Bett et al. may be possible but the interparticle separation distance cannot be determined from the published data. Analysis of the data from Watanabe et al. (see Figure 6d) shows a correlation between SA and  $N(e+c)$ , but the significance of this relationship is unclear at this time.

The SAD(111) and SAD(100), as well as MAD(111) and MAD(100), show similar trends as a function of Pt particle size (see Figure 2). Thus it is appropriate to suggest that the (111) crystal face is also an active site for oxygen reduction. If both the (100) and (111) crystal faces are electrocatalytically active sites, the same conclusion is possible to explain the change in MA and SA with a change in particle size. However, as assumed above, we developed our argument on the basis of the (100) crystal face as the active sites, following the conclusion of Ross (2).

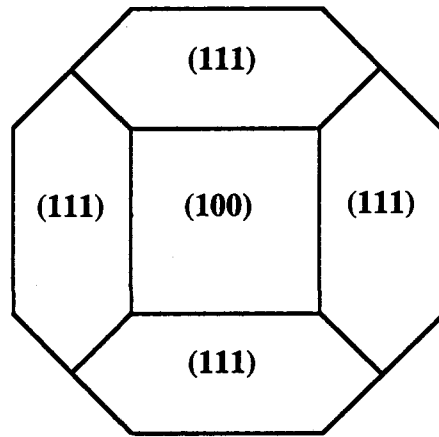
A rigorous argument for particle size effects in electrocatalysis involving oxygen reduction would require intimate knowledge of the specific activity of different sites on the particle surface. In addition, the role of the substrate, which could be involved in metal-support interactions that affect electrocatalysis, must be considered. At this time, insufficient experimental evidence is available to extend our argument further to develop a mechanistic model of the reaction pathway of oxygen molecules on the Pt (100) crystal surface. However, it should be noted that mechanisms have been proposed in the literature (17-20) to explain the reaction pathway for oxygen reduction on specific electrocatalytic sites.

In summary, a simplistic argument is presented to interpret results on the effects of Pt particle size on the kinetics of oxygen reduction. It is proposed that the similar trends of MA and MAD(100), and SA and SAD(100), as a function of particle size indicate a relationship which can explain the effects of particle size of highly dispersed Pt particles on their electrocatalytic activity for oxygen reduction in acid electrolytes. From the above argument, it is concluded that oxygen reduction on

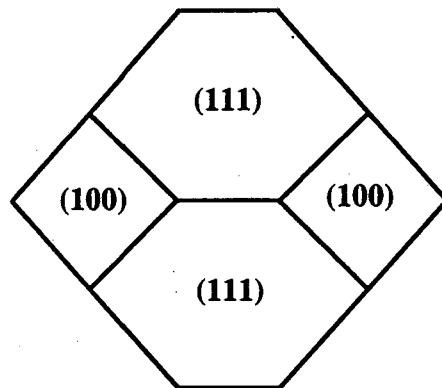
highly dispersed Pt electrocatalysts in acid electrolytes is a demanding or structure-sensitive reaction; the specific activity increases with an increase in particle size.

### **Acknowledgement**

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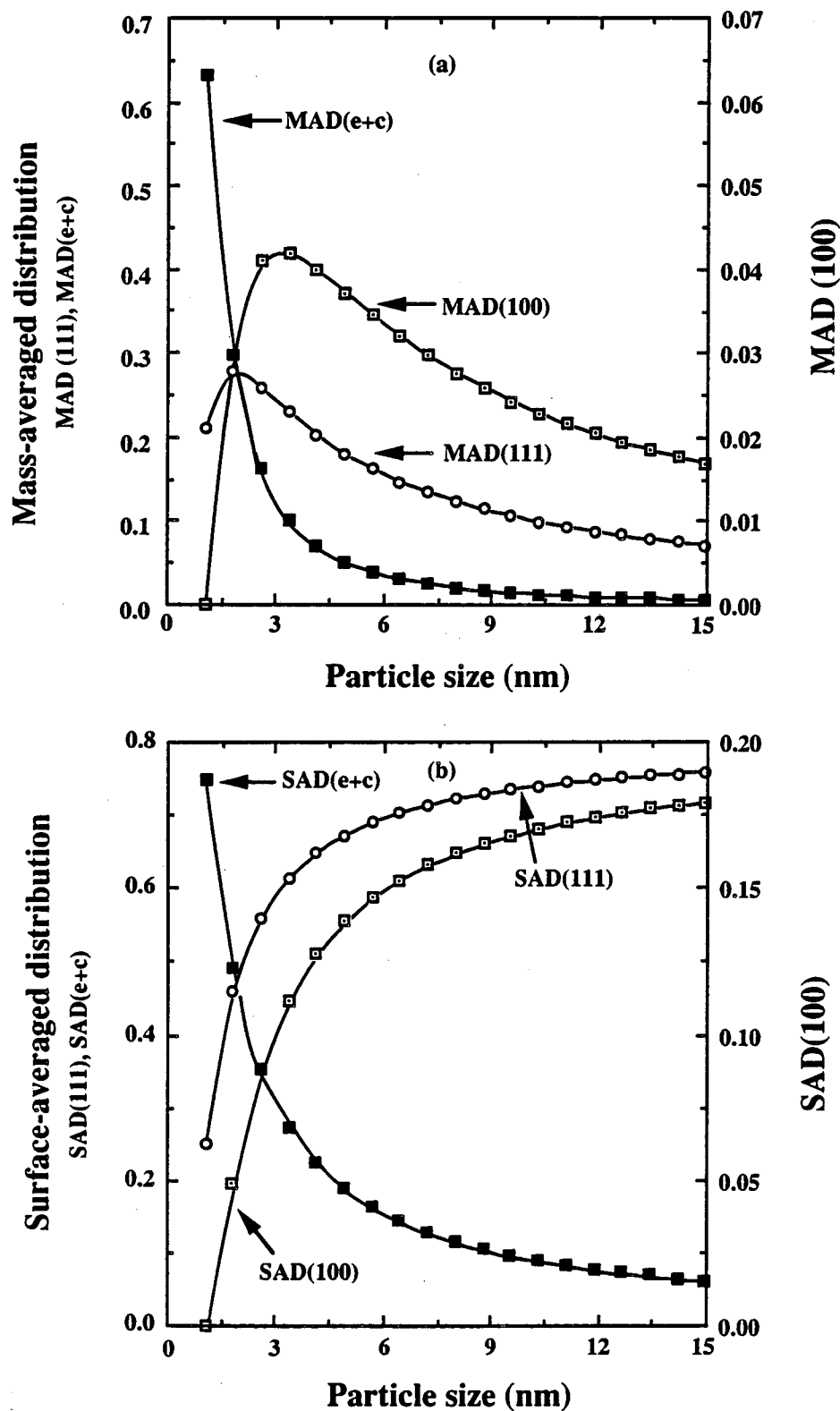


**(100) orientation**



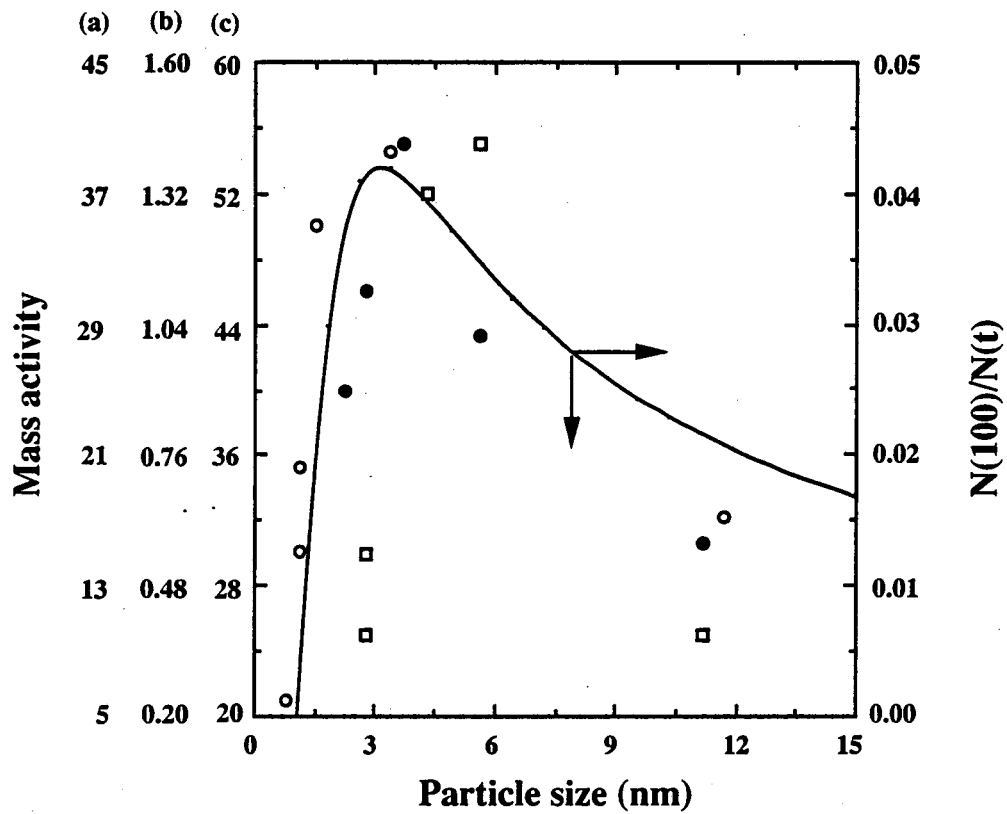
**(110) orientation**

**Figure 1.** Schematic representation of cubo-octahedral particle. (XBL 8812-4138)



**Figure 2.** Mass-averaged distribution and surface-averaged distribution of atoms on the (111) and (100) crystal faces and on the edge and corner sites of a cubo-octahedral. (XBL 8812-4139)  
 (a) MAD;  
 (b) SAD.





**Figure 3.** Superimposed plots of MA for oxygen reduction and MAD (100) as a function of particle size. (solid line) MAD (100). (XBL 8812-4140)

- (a) ●, 98%  $H_3PO_4$ , 180°C (1,2);
- (b) ○, 0.5 M  $H_2SO_4$ , 25°C (4);
- (c) □, 97%  $H_3PO_4$ , 177°C (3).

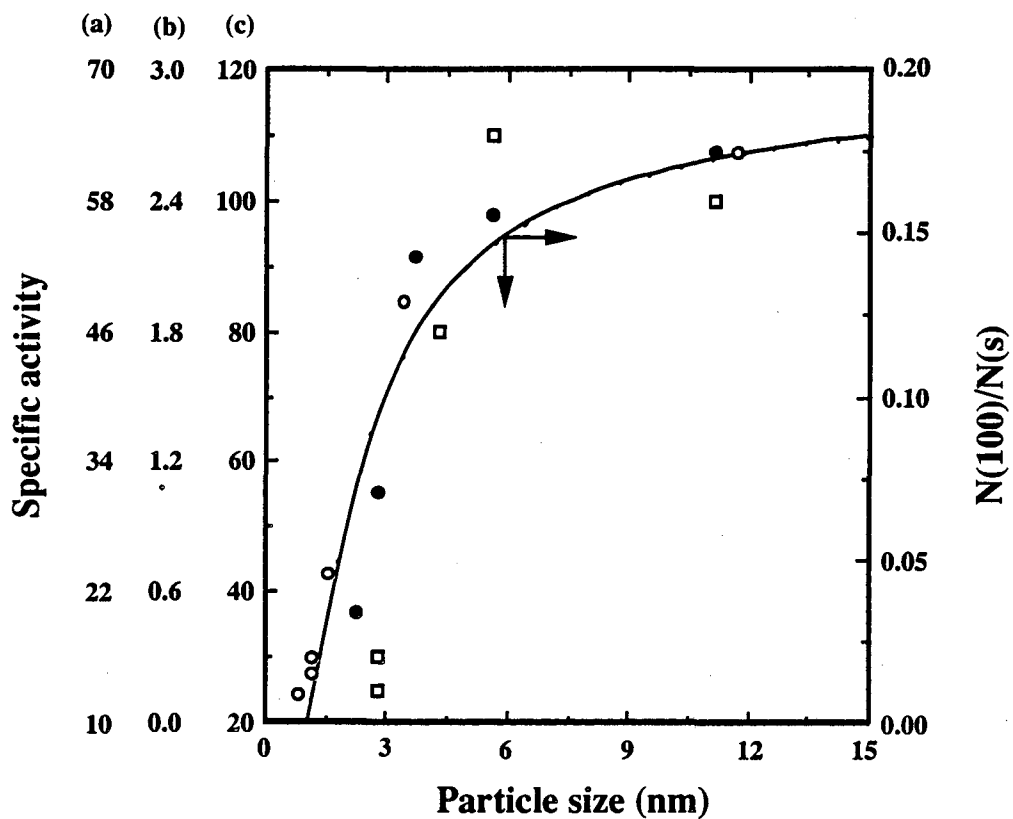
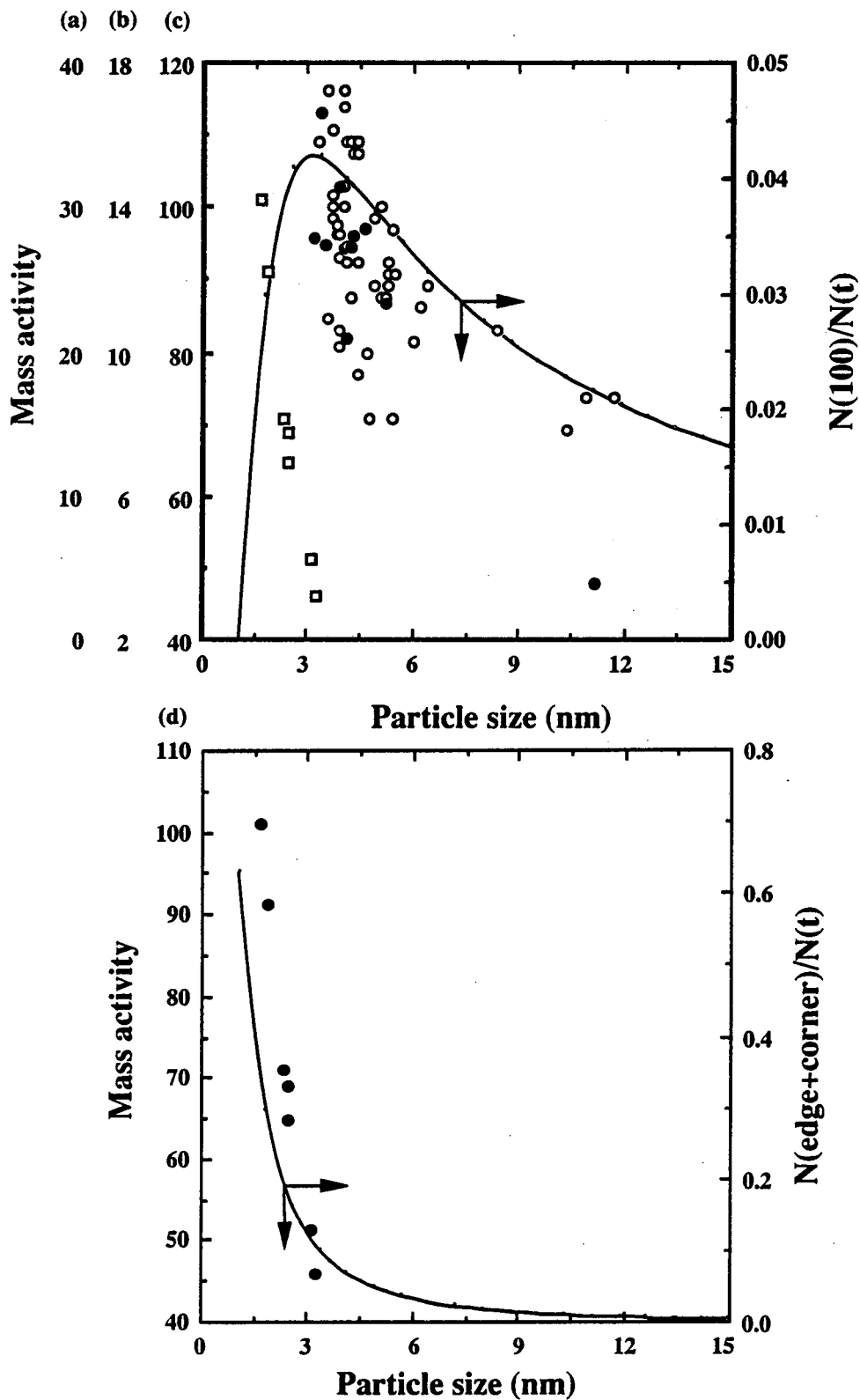
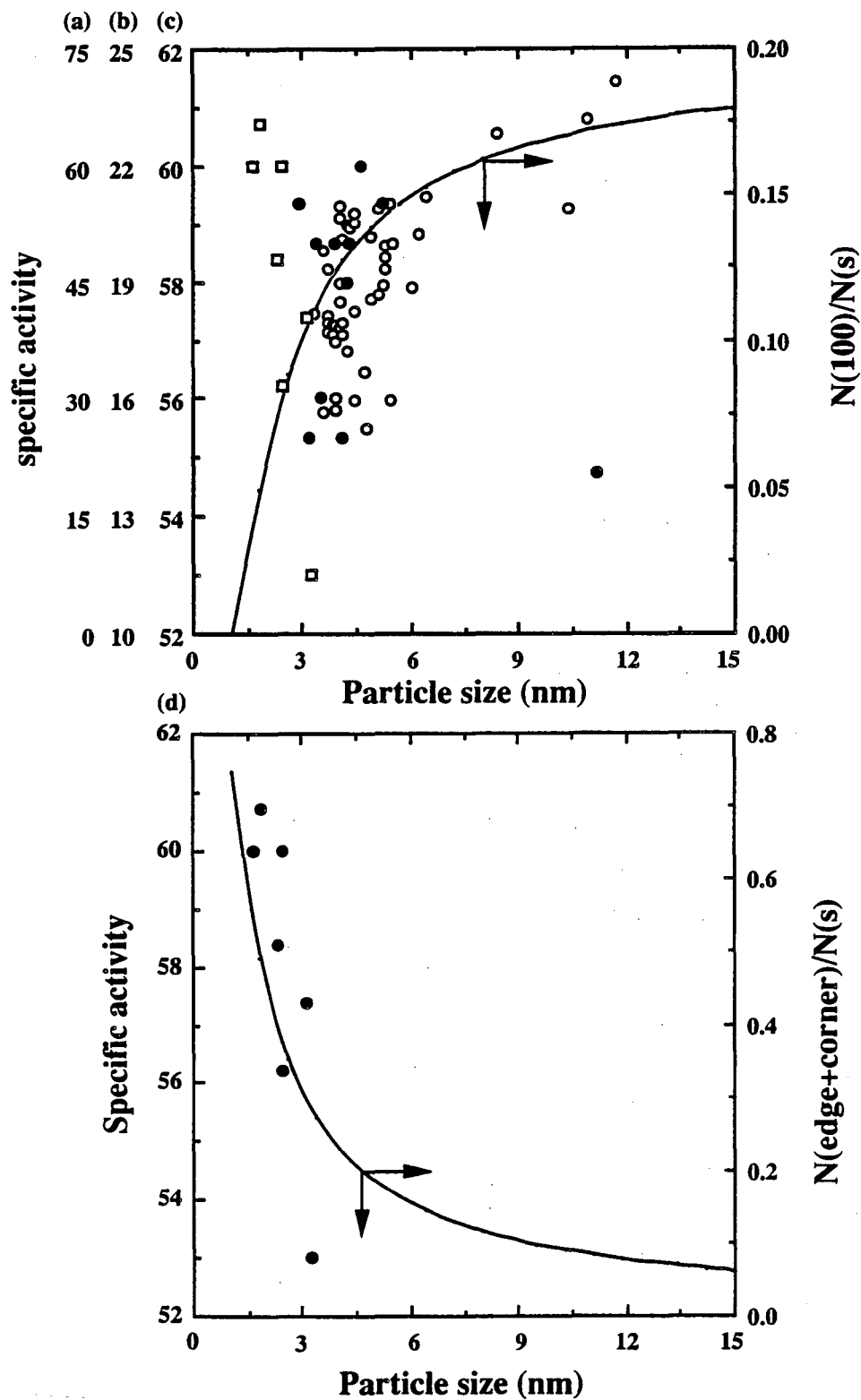


Figure 4. Superimposed plots of SA for oxygen reduction and SAD (100) as a function of particle size. (solid line) SAD (100). (XBL 8812-4141)  
 (a) ●, 98%  $H_3PO_4$ , 180°C (1,2);  
 (b) ○, 0.5 M  $H_2SO_4$ , 25°C (4);  
 (c) □, 97%  $H_3PO_4$ , 177°C (3).



**Figure 5.** Superimposed plots of MA for oxygen reduction, MAD (100), and MAD(e+c) as a function of particle size. (solid line) MAD (100) and MAD(e+c). (XBL 8812-4142)  
 (a)  $\circ$ , 99%  $\text{H}_3\text{PO}_4$ , 177°C (7); (c)  $\square$ , 100%  $\text{H}_3\text{PO}_4$ , 190°C (6);  
 (b)  $\bullet$ , 1 M  $\text{H}_2\text{SO}_4$ , 50°C (8); (d)  $\bullet$ , 100%  $\text{H}_3\text{PO}_4$ , 190°C (6).



**Figure 6.** Superimposed plots of SA for oxygen reduction, SAD (100), and SAD(e+c) as a function of particle size. (solid line) SAD (100) and SAD(e+c). (XBL 8812-4143)  
 (a)  $\square$ , 99%  $H_3PO_4$ , 177°C (7); (c)  $\square$ , 100%  $H_3PO_4$ , 190°C (6);  
 (b)  $\bullet$ , 1 M  $H_2SO_4$ , 50°C (8); (d)  $\bullet$ , 100%  $H_3PO_4$ , 190°C (6).

**Table 1. Oxygen Reduction on Platinum Electrocatalysts Supported on High-Surface-Area Carbons**

Pt Particle Size (nm)	Experimental Conditions <sup>a</sup> Temp. (°C)	Acid	Observations <sup>b</sup>	Reference
2.24-11.2	180	98% H <sub>3</sub> PO <sub>4</sub>	maximum in MA at ~4 nm SA decreases as d decreases	1,2
2.8-11.2	177	97% H <sub>3</sub> PO <sub>4</sub>	maximum in MA at ~5.5 nm SA decreases as d decreases	3
0.78-11.7	25	0.5 M H <sub>2</sub> SO <sub>4</sub>	maximum in MA at ~4 nm SA decreases as d decreases	4
1.4-4.0 <sup>c</sup>	60	1.5 M H <sub>2</sub> SO <sub>4</sub>	MA increases as d decreases SA independent of d	5
1.6-3.2	190	100% H <sub>3</sub> PO <sub>4</sub>	MA increases as d decreases SA independent of d	6
3.0-40	177	99% H <sub>3</sub> PO <sub>4</sub>	SA decreases as d decreases MA increases as d decreases	7
2.9-11.2	50	1 M H <sub>2</sub> SO <sub>4</sub>	MA increases as d decreases SA independent of d	8
1.4-20	70	20% H <sub>2</sub> SO <sub>4</sub>	dependence of MA and SA on d not determined	9

<sup>a</sup> Oxygen pressure ~0.1 MPa.

<sup>b</sup> Activity measured at 0.9 V unless otherwise noted.

<sup>c</sup> Activity measured at 0.85 V.

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