

Crystallite Size Effects of Carbon-Supported Platinum on Oxygen Reduction in Liquid Acids

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ABSTRACT

Pt/C catalysts with two different Pt crystallite sizes [as-received (20 weight percent (w/o) Pt/C powder from E-TEK) and heat-treated (900°C in inert atmosphere)] were analyzed for the reduction of oxygen in half-cells using rotating disk electrodes. Measurements in HF (1.17 M) show that the specific activity of the catalysts increases with the Pt crystallite size. In contrast, measurements in H₂SO₄ (1.17 M) indicate that the specific activity is nearly independent of the Pt crystallite size. One of the reasons for the difference in behavior observed between these acids is the difference in specific adsorption of anions on the Pt sites from H₂SO₄ (adsorbing) and HF (nonadsorbing) solutions. This study indicates that both the oxygen reduction reaction and anion adsorption on the Pt sites are crystallite-size sensitive in H₂SO₄ solution. In solid polymer fuel cells (SPFCs), the anions are anchored on the backbone of the polymer matrix, and hence only a minimal anion adsorption is expected on the Pt sites of gas diffusion electrodes. From results of the present study, it is believed that the Pt/membrane interface in SPFCs could be better mimicked by the Pt/HF interface rather than the Pt/H₂SO₄ interface.

Introduction

Solid polymer fuel cells (SPFCs) are promising power sources, especially for the electric vehicle applications, because of their high power densities and rapid cold start-up.¹⁻⁴ The direct evaluation of various catalysts for their activity in the gas diffusion electrodes (GDEs) of SPFCs is, however, time consuming and expensive; hence it would be useful to devise a simple half-cell technique which could mimic the complete solid polymer fuel cell. Our group recently carried out a correlative study between a simple rotating disk electrode in sulfuric acid (half-cell) and a complete SPFC for the oxygen reduction reaction on the carbon-supported cobalt catalysts (obtained from pyrolyzed cobalt phthalocyanine).⁵ This study indicated that the relative activity of the Co-based catalysts obtained in half-cell measurements in H₂SO₄ were in agreement with the measurements made in the complete SPFC. Based on the results obtained in that study, it was concluded that RDEs could be used to prescreen the relative activity of various Co-based catalysts and to select potential candidates for the evaluations in SPFCs. In most of the developmental SPFC studies, carbon-supported Pt crystallites have been used as the catalysts for the oxygen reduction reaction. Since platinum crystallite size increases as cell operation time increases, it is important to study the crystallite size effects on the oxygen reduction reaction in half-cells and to determine if the conclusion drawn from the work on Co-based catalysts still holds true for the Pt-based catalysts.

The crystallite size effects of carbon-supported platinum catalysts have been widely studied for the oxygen reduction reaction in liquid acid (*e.g.*, sulfuric and phosphoric acids) electrolytes. Different and sometimes contradictory observations have been reported on these effects. The observations and views of the different research groups on the crystallite size effects can be summarized as follows: (i) mass activity [mA/mg Pt at 0.9 V vs. reversible hydrogen electrode (RHE)] decreases as the Pt particle size increases,⁶⁻⁸ (ii) mass activity increases, reaches a maximum, and then decreases as the crystallite size increases,⁹⁻¹¹ (iii) specific activity (mA/real cm² Pt at 0.9 V vs. RHE) increases as the particle size increases,^{6,9-13} and (iv) specific activity is independent of the crystallite size.^{7,8} Kinoshita¹⁴ attributes the mass activity and specific activity dependencies, described in (ii) and (iii), to the changes in the surface fraction of Pt atoms on the (100) and (111) crystal faces. On the other hand, Watanabe *et al.*⁸ attribute the activity dependencies, described in (i) and (iv), to the changes in the intercrystallite distances. In solid polymer fuel cells, the anions are anchored on the backbone of the

polymer matrix, and only a minimal anion adsorption is expected on the Pt sites of SPFC electrodes. Therefore, in order to reasonably mimic the Pt/membrane interface in a SPFC by Pt/liquid-acid interface in a half-cell, it is important to establish the noninterference of the liquid electrolytic species on the oxygen reduction activity of carbon-supported Pt catalysts. In this paper, we present results which show that the specific activity, for the Pt-based catalysts, in a nonadsorbing electrolyte, such as HF, is increasing with the crystallite size, but it is nearly independent of the crystallite size in anion adsorbing electrolyte such as H₂SO₄.

Experimental

Preparation of rotating disk electrodes.—The as-received (E-TEK, Natick, MA) and heat-treated (900°C for 2 h under flowing Ar atmosphere) 20 w/o carbon-supported Pt catalysts were used in the active layers of RDEs. The Pt particle sizes of the as-received and heat-treated catalysts, as determined by x-ray diffraction (XRD), were 27 and 56 Å, respectively. The active layers on the RDEs were prepared using a method similar to the one described in our previous publication.⁵ The electrode preparation procedure is briefly explained here. A mixture containing 12.9 mg of Pt/C powder (as-received or heat-treated), 0.1 ml of 5 w/o Nafion solution (Aldrich Chemicals), and 0.7 ml of water was ultrasonically blended in a glass vial for 60 min to obtain a thick catalyst paint. A volume of 10 µl of this thick paint was spread on the surface of a vitreous carbon RDE (0.196 cm²) using a micropipette and dried in an air oven at 80°C for about 10 min to obtain a thin active layer. The volume of 10 µl paint corresponds to a loading of 0.823 mg/cm² Pt/C or 0.165 mg/cm² Pt metal. To obtain reproducible results using this sensitive technique, it is important to maintain a constant Pt/C powder loading on the RDE surface. Hence, it is important to note that the paint should be made very uniform (by extensive ultrasonic blending) and the volumetric withdrawals of this viscous paint using a micropipette must be constant. To confirm the reproducibility of the results, three electrodes, as a minimum, were prepared and tested for each catalyst.

Measurements in liquid electrolytes.—RDEs were used to record cyclic voltammograms in oxygen or argon saturated liquid electrolytes. Argon saturated electrolytes were used to obtain the electrochemical active area of the Pt particles. The liquid electrolytes were H₂SO₄ (1.17 M or 0.02 M) and HF (1.17 M). The electrolytes were used as-received from the following suppliers: H₂SO₄, electronic grade from Baker, and HF, from Fisher Scientific. A saturated calomel electrode (SCE) and a reversible hydrogen electrode (RHE) were used as reference electrodes in

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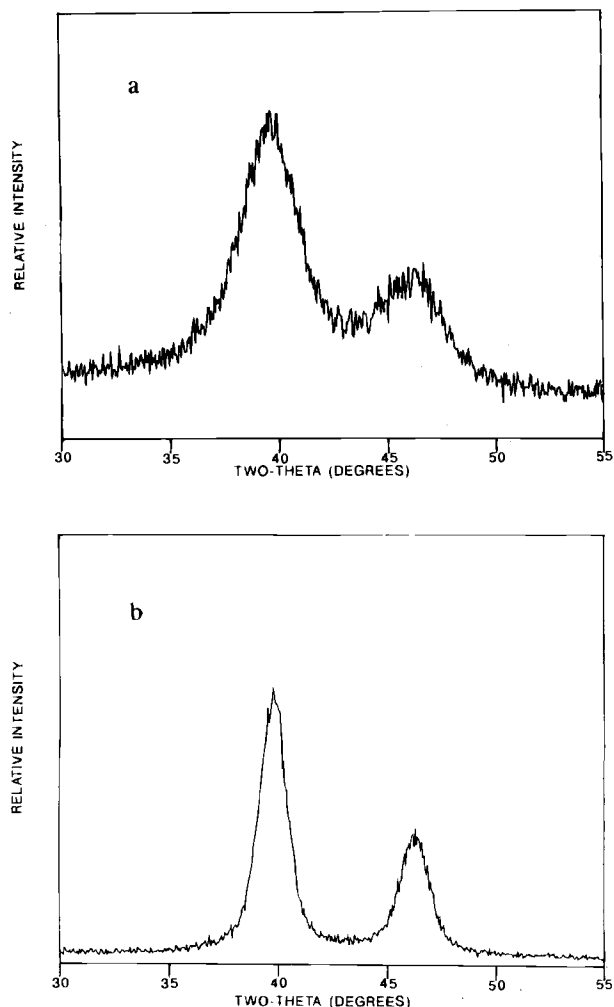


Fig. 1. X-ray diffractograms for the as-received (a) and heat-treated (900°C for 2 h under flowing Ar) and (b) Pt/C catalysts.

H₂SO₄ and HF, respectively. A platinum foil served as the counterelectrode in both acids. A Teflon made cell was used for the measurements in HF acid and the design of this cell will be reported in a future publication. All the measurements, unless otherwise noted, were carried out in argon and oxygen saturated electrolytes on stationary and rotating (1500 rpm) electrodes, respectively. A scan rate of 10 mV/s was maintained for all the measurements on RDEs. Measurements are referenced to SCE. All the measurements of this study were carried out with a model AFRDE-4 bipotentiostat and an AFMMSRX rotating speed control from Pine Instruments Company.

X-ray diffraction analysis.—The diffractograms were recorded using a Siemens D500 diffractometer with a copper source. The diffractometer was operated in the step scan mode with a 0.05° step and 12 s fixed time in the range of 30 to 55° (2θ).

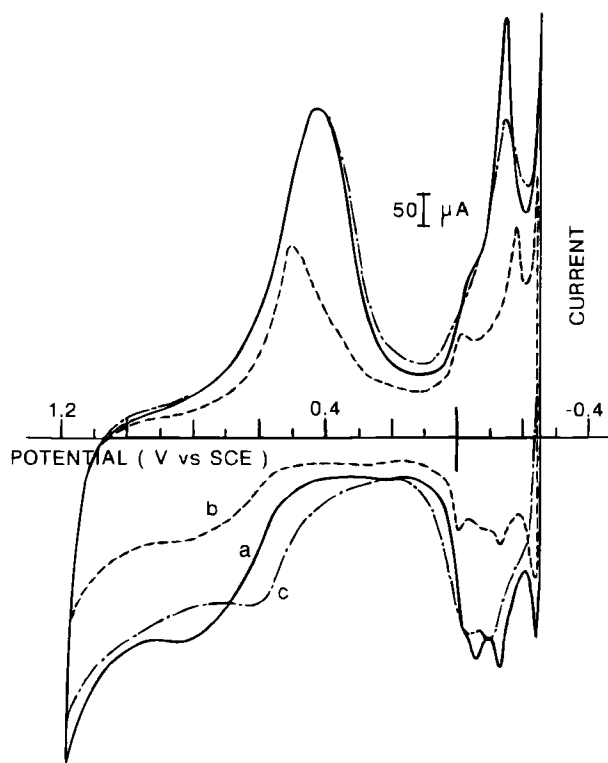


Fig. 2. Cyclic voltammograms for the as-received, a, and the heat-treated, b, Pt/C catalysts in H₂SO₄ (1.17 M). The curve c is the voltammogram obtained for the as-received catalyst in HF (1.17 M) solution. These voltammograms were recorded on a stationary RDE in Ar saturated solutions at the scan rate of 10 mV/s.

Results and Discussion

Heat-treatment effect on the crystallite size and the electrochemical active area.—Typical x-ray diffractograms for the as-received and heat-treated Pt/C catalysts are shown in Fig. 1a and b, respectively. The crystallite sizes for these catalysts were calculated from the full width at half-maximum (FWHM) of the (111) peak at 39.8° (2θ) and are noted in Table I. As expected, there is an increase in the Pt crystallite size of the heat-treated Pt/C catalysts (56 Å) compared to the as-received Pt/C catalyst (27 Å). The specific surface area *S* (m²/g) for the Pt crystallites was calculated using the following equation¹⁵

$$S = \frac{6 \times 10^4}{\rho d} \quad [1]$$

where *d* is the diameter of the particle in Å and ρ is the density of platinum metal (21.4 g/cm³). There is a 50% drop in the surface area of the Pt crystallites due to heat-treatment (Table I). The positions of the Pt peaks are not shifted due to heat-treatment. This indicates the absence of alloying of the Pt metal with the carbon support.

Table I. Effect of heat-treatment on the platinum particle size and the roughness factor of the electrode.

Catalyst	Size from XRD ^a (Å)	Area from XRD ^a (m ² /g)	Area from CV ^b (m ² /g)	Pt utilization efficiency for RDE (%) ^c	Roughness factor for RDE ^d
As-received Pt/C	27	104	87	84	144
Heat-treated Pt/C	56	50	44	88	73

^a Calculated from x-ray diffraction studies.

^b Calculated from cyclic voltammetry studies.

^c Calculated by: area from CV × 100/area from XRD.

^d Calculated by: area from CV/geometric area.

The cyclic voltammograms (CVs) obtained for the as-received and the heat-treated Pt/C catalysts (Nafion impregnated RDEs) are shown in Fig. 2 (curves a and b). These voltammograms were obtained in argon saturated H_2SO_4 (1.17 M) using RDEs. The electrochemical specific surface areas of the as-received and the heat-treated Pt crystallites were calculated by integrating the areas under the adsorption peaks of hydrogen (from -0.2 to 0.1 V vs. SCE).¹⁶ These values are reported in Table I. They were obtained by assuming a charge of $210 \mu\text{C}/\text{cm}^2$ for the Pt surface and by taking into account the Pt loading on the electrode. In agreement with the XRD results, the CV results indicate that there is a 50% decrease in the surface area of the Pt crystallites due to heat-treatment. The platinum utilization efficiencies calculated from the surface areas obtained from the XRD and RDE studies are also reported in Table I. A loss of 12 to 16% surface area is observed on the Nafion impregnated RDEs, as compared to the surface area calculated from the XRD. This loss is similar to the 20% surface area loss reported by other research groups for the recast or solution-processed Nafion coated planar Pt disk electrodes.^{17,18} This loss of surface area on the Nafion impregnated Pt/C catalysts may be attributed to the anchoring (blocking) of the recast Nafion on the surface of the Pt sites and to the inaccessibility of the protons to the Pt surfaces which are present in between the Pt crystallites and the carbon support. The coverage by organic impurities from the recast film may also contribute, in part, to the loss of surface area. However, the Pt utilization efficiencies evaluated in this work (84 to 88%) is considerably higher than the values reported by Perez *et al.* (about 10%).¹⁹ Perez *et al.* have utilized PTFE incorporated Pt/C electrodes whereas the present work utilizes Nafion incorporated Pt/C electrodes. The improved Pt utilization efficiency may be attributed to the enhanced contact area between the electrolyte and the Pt sites due to the proton conducting nature of the Nafion electrolyte.

Investigations in HF.—Hydrofluoric acid is known to be a nonadsorbing electrolyte. This is confirmed in the present work by the cyclic voltammogram obtained in 1.17 M HF (Fig. 2, curve C). It is known, indeed, that the adsorbed anions inhibit the formation of oxygenated species on the surface of Pt.²⁰ In 1.17 M HF, the oxide formation occurs at less positive potentials than in 1.17 M H_2SO_4 . In the absence of anion penetration from H_2SO_4 through the recast Nafion, one would expect similar cyclic voltammograms for both H_2SO_4 and HF as the anions in the recast Nafion are anchored on the backbone of the polymer matrix. Obviously, this is not the case as evidenced from curve A and curve C in Fig. 2, for H_2SO_4 and HF, respectively.

The cathodic scans for oxygen reduction reaction in HF (1.17 M) for the as-received and heat-treated catalysts are

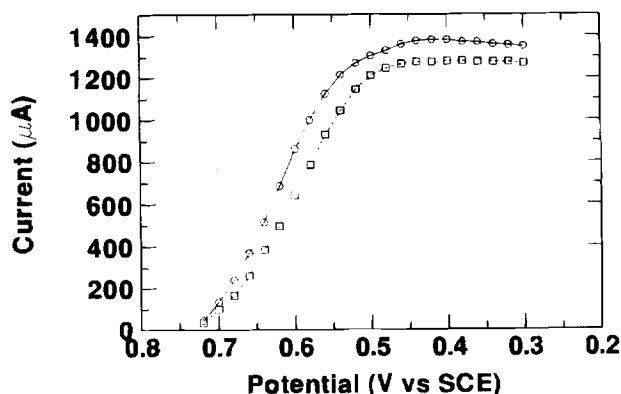


Fig. 3. RDE cathodic scan measurements for the as-received (○) and heat-treated (□) Pt/C catalysts in O_2 saturated 1.17 M H_2SO_4 solution.

shown in Fig. 3. These curves were obtained at 1500 rpm in 1.17 M HF for the Nafion impregnated Pt/C catalyst layer spread on vitreous-carbon RDE. To calculate the mass and specific activity values at 0.9 V vs. RHE (0.66 V vs. SCE), the reduction currents were corrected for mass-transport limitations for all RDE measurements. The mass-transport corrected current or the net kinetic current (i_{kin}) was obtained using the following equation

$$i_{\text{kin}} = \frac{i_{\text{lim}} \cdot i_{\text{obs}}}{(i_{\text{lim}} - i_{\text{obs}})} \quad [2]$$

where i_{lim} and i_{obs} are the limiting and observed currents, respectively. The mass and specific activity values at 0.9 V vs. RHE for the as-received and heat-treated Pt/C catalysts are shown in Table IIA.

The specific activity [calculated by: mass-activity (in mA/mg Pt) ÷ specific area (in $\text{cm}^2/\text{mg Pt}$)] is 1.3 times higher for the heat-treated catalysts as compared to the as-received catalysts. This indicates that the specific activity increases as the crystallite size increases from 27 to 56 Å.

The increase of the specific activity of Pt crystallites in hot ($\sim 180^\circ\text{C}$) phosphoric acid has been reported for heat-treated Pt/C catalysts (900°C) as compared to the as-received Pt/C catalysts by Jalan *et al.*²¹ and Beard and Ross.²² Jalan *et al.* attributed the improved specific activity to the Pt-C alloy formation. However, our XRD studies on the heat-treated Pt/C catalysts do not indicate the Pt-C alloy formation. Beard and Ross attributed the improved activity to the structural changes with the crystallite size [*i.e.*, the (100) surfaces on the large crystallites are more active than the dominating (111) surfaces on the small crystallites]. Our RDE results in HF are better interpreted in terms of the structural changes of the Pt crystallite size on the electrocatalytic activity.

Theoretical analysis of Kinoshita¹⁴ indicates the following: (i) the mass-averaged distribution (representative of the mass activity) of the atoms on the (111) and (100) surfaces steeply increases as the particle size increases, reaches a maximum at about 35 Å and decreases slowly as the particle size increases above 35 Å, and (ii) the surface-averaged distribution (representative of the specific activity) of the atoms on the (111) and (100) surfaces increases as the particle size increases up to about 60 Å and then reaches a near-saturation value. The mass-averaged and surface-averaged distributions of the atoms on the edge and corner sites continuously decrease as the crystallite size increases. Thus, Kinoshita attributes the improved activity of the large crystallites to the increase in the surface fraction of Pt atoms on the (111) and (100) crystal faces with a corresponding decrease on the edge and corner sites. The experimental evidence to support this theoretical analysis was obtained from the hydrogen oxidation current-potential profiles.²³ It has been experimentally shown that the third anodic peak (corresponding to the

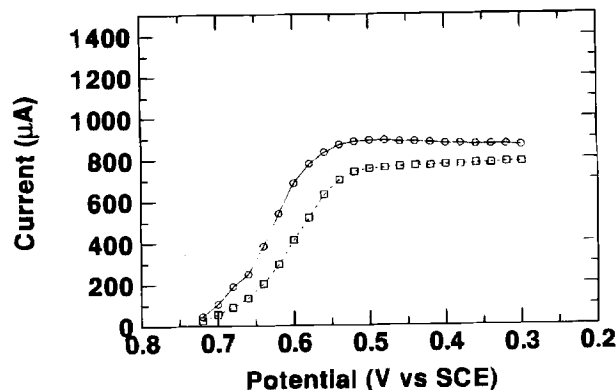


Fig. 4. RDE cathodic scan measurements for the as-received (○) and heat-treated (□) Pt/C catalysts in O_2 saturated 1.17 M H_2SO_4 solution.

Table II. Mass and specific activities comparisons between the as-received and heat-treated Pt/C electrocatalysts for the oxygen reduction reaction.

A: in 1.17 M hydrofluoric acid at room temperature.				
Catalyst	Mass activity at 0.9 V vs. RHE (mA/mg Pt)		Specific activity at 0.9 V vs. RHE (mA/cm ²) ^a	
	Individual electrode	Average	Individual electrode	Average
As-received Pt/C	15.1	15.9	0.0145	0.0152
	15.8		0.0152	
	16.6		0.0160	
Heat-treated Pt/C	9.2	9.7	0.0184	0.0193
	9.7		0.0194	
	10.1		0.0202	
B: in 1.17 M sulfuric acid at room temperature.				
Catalyst	Mass activity at 0.9 V vs. RHE (mA/mg Pt)		Specific activity at 0.9 V vs. RHE (mA/cm ²) ^a	
	Individual electrode	Average	Individual electrode	Average
As-received Pt/C	10.7	11.0	0.0103	0.0107
	10.8		0.0105	
	10.9		0.0105	
	11.7		0.0113	
Heat-treated Pt/C	3.9	4.9	0.0078	0.0098
	4.4		0.0088	
	5.1		0.0100	
	6.3		0.0126	

^aCalculated by: mass-activity (in mA/mg Pt) ÷ specific area in cm²/mg Pt) from XRD.

desorption of the hydrogen atoms adsorbed on the edge and corner sites) becomes more apparent as the crystallite size decreases.²³ An apparent correlation exists between the profiles of the hydrogen oxidation curves shown in Fig. 2 and the profiles reported by Kinoshita,²³ where the third anodic peak (the middle hydrogen-oxidation peak in Fig. 2) becomes well defined for the as-received Pt/C catalysts (curve a; Pt size 27 Å) as compared to the heat-treated catalysts (curve b; Pt size 56 Å). These studies indicate that the electrocatalytic activity is crystallite-size sensitive.

Investigations in H₂SO₄.—The cathodic scans of the potentiodynamic potential-current curves for the as-received and heat-treated Pt/C catalysts are shown in Fig. 4. The results shown in Table IIB indicate a 50% drop in the mass activity and no improvement in the specific activity due to the heat-treatment of the Pt/C catalyst. These results are consistent with the reported^{7,8,10} values in H₂SO₄ when they are compared for the crystallite sizes used in this study, *i.e.*, ~27 and ~56 Å. But the activities obtained in H₂SO₄ are not consistent with the results obtained in HF: the specific activity for the heat-treated Pt/C catalysts in HF increases (and is therefore size dependent) whereas in H₂SO₄ it remains nearly the same (and is

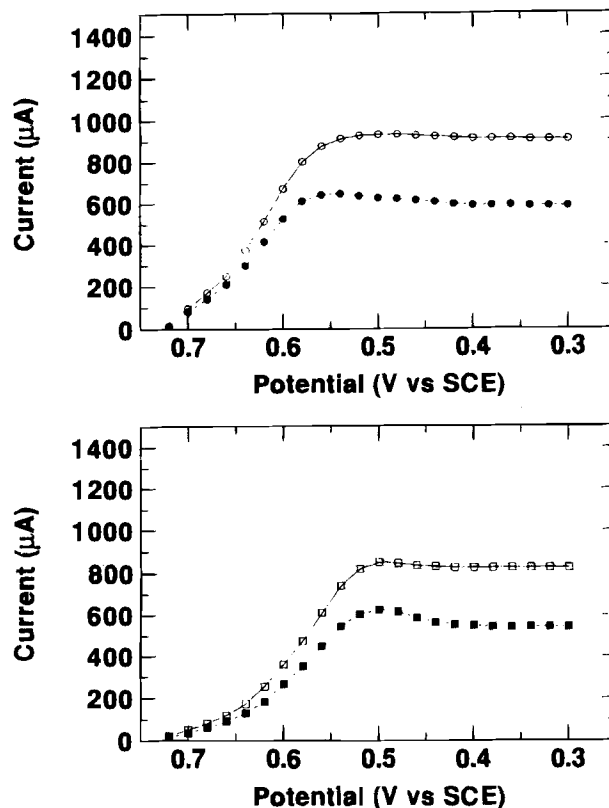


Fig. 5. RDE cathodic scan measurements in O₂ saturated 1.17 M H₂SO₄. (a, top) As-received Pt/C catalyst without (○) and with (●) added Na₂SO₄ to the solution. (b, bottom) Heat-treated Pt/C catalyst without (□) and with (■) added Na₂SO₄ to the solution.

therefore size independent). This inconsistency of the activity between the RDE measurements in H₂SO₄ and HF could possibly arise from the nature of the electrolyte. It is well known²⁴⁻²⁶ that the anions in H₂SO₄ are strongly adsorbed on the Pt sites at room temperature, whereas anions in HF are not. Thus it is possible that the anions in H₂SO₄ are also, along with oxygen, competing for the Pt sites. If anion adsorption is also crystallite-size sensitive, then the independence of the specific activity for oxygen reduction in sulfuric acid between the as-received and heat-treated Pt/C catalysts could be possible. Therefore, it is important to further confirm that the anion adsorption in H₂SO₄ competes with the oxygen adsorption for the Pt sites.

Confirmation of competition between anion adsorption and oxygen reduction.—An increase of sulfate ion concentration in the electrolyte was obtained by the addition of Na₂SO₄ (0.5 M) to sulfuric acid (1.17 M). In such conditions, there was a decrease in the activity for both as-received and heat-treated Pt/C catalysts as shown in Fig. 5a and b, respectively. This is expected since sulfate ion adsorption is known to block (111) and (100) faces of Pt.²⁴⁻²⁶ Since the surface fraction of Pt atoms on (100) and (111) faces increases with the catalyst particle size,¹⁴ the effect of sulfate ion adsorption on heat-treated Pt/C is

Table III. Mass and specific activities comparisons between the as-received and heat-treated Pt/C electrocatalysts for the oxygen reduction reaction on RDE (at room temperature; 1.17 M sulfuric acid) with and without the addition of Na₂SO₄.

Catalyst	Without Na ₂ SO ₄ addition		With Na ₂ SO ₄ addition	
	Mass activity at 0.9 V vs. RHE (mA/mg Pt)	Specific activity at 0.9 V vs. RHE (mA/cm ²)	Mass activity at 0.9 V vs. RHE (mA/mg Pt)	Specific activity at 0.9 V vs. RHE (mA/cm ²)
As-received Pt/C	10.7	0.0103	9.7	0.0093
Heat-treated Pt/C	4.4	0.0088	3.3	0.0066

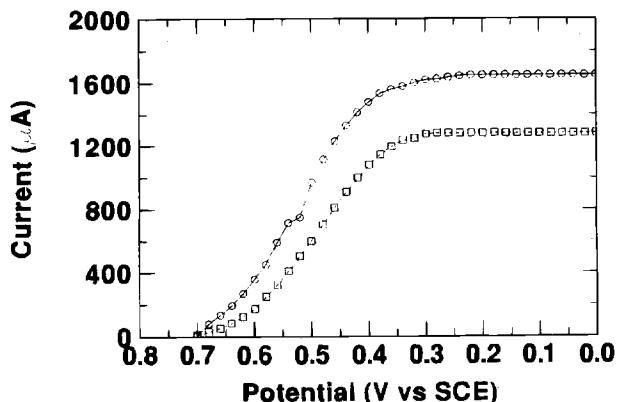


Fig. 6. RDE cathodic scan measurements for the as-received (○) and heat-treated (□) Pt/C catalysts in O_2 saturated $0.02 M H_2SO_4$ solution at the scan rate of $10 mV/s$.

expected to be larger than for the as-received catalyst. This is indeed observed for the mass or specific activity values as reported in Table III.

The electrocatalytic reduction of oxygen was also carried out in dilute H_2SO_4 ($0.02 M$) in order to decrease the influence of anion effects. The cathodic scans of potential-current curves for the as-received and heat-treated catalysts in dilute sulfuric acid are shown in Fig. 6. The mass and specific activities (at $0.58 V vs. SCE$ or $0.9 V vs. RHE$) in these dilute acids for both as-received and heat-treated Pt/C catalysts are noted in Table IV. The comparison of the activity results in dilute sulfuric acid (Table IV) with the RDE activity results in concentrated sulfuric acid (Table IIB) indicates a 1.8 times enhancement in dilute acid. This enhancement of activity in dilute sulfuric acid could be attributed to a lower anion adsorption on the catalytic sites and higher solubility of oxygen. But the specific activity remains independent of crystallite size irrespective of sulfuric acid concentration.

Mass transport effects on the RDE activity measurements.—Since the electrode roughness factors are very high (Table I), there is a possibility that the activity values reported in this work may have an influence of the mass-transport limitation. It is important to ensure that the independence of the specific activity in sulfuric acid exists also on low surface area electrodes. Hence the electrodes with very low electrochemical surface area (referred as “spot electrodes”) were prepared by reducing the amount of Pt/C loading, *i.e.*, catalyst paint, on the RDE surface. Instead of spreading $10 \mu l$ of the catalyst paint on the RDE surface (see the Experimental section), only a little speck of the paint was placed at the center of the disk surface and dried. This kind of electrode was prepared for both the as-received and heat-treated Pt/C catalysts. The areas under the hydrogen adsorption/desorption curves for the as-received and heat-treated Pt/C catalysts in dilute sulfuric acid, shown in Fig. 7, indicate the availability of very low electrochemical surface areas (ESA). Since the areas under the hydrogen adsorption/desorption curves for the as-received and heat-treated Pt/C catalysts on these two electrodes are nearly the same, they can be considered to have the same ESA. The ESA values on these electrodes

Table IV. Mass and specific activities comparisons between the as-received and heat-treated Pt/C electrocatalysts on RDE at room temperature for the oxygen reduction reaction in $0.02 M$ sulfuric acid.

Catalyst	Mass activity at $0.9 V vs. RHE$ (mA/mg Pt)	Specific activity at $0.9 V vs. RHE$ (mA/cm ²)
As-received Pt/C	19.3	0.0186
Heat-treated Pt/C	9.7	0.0194

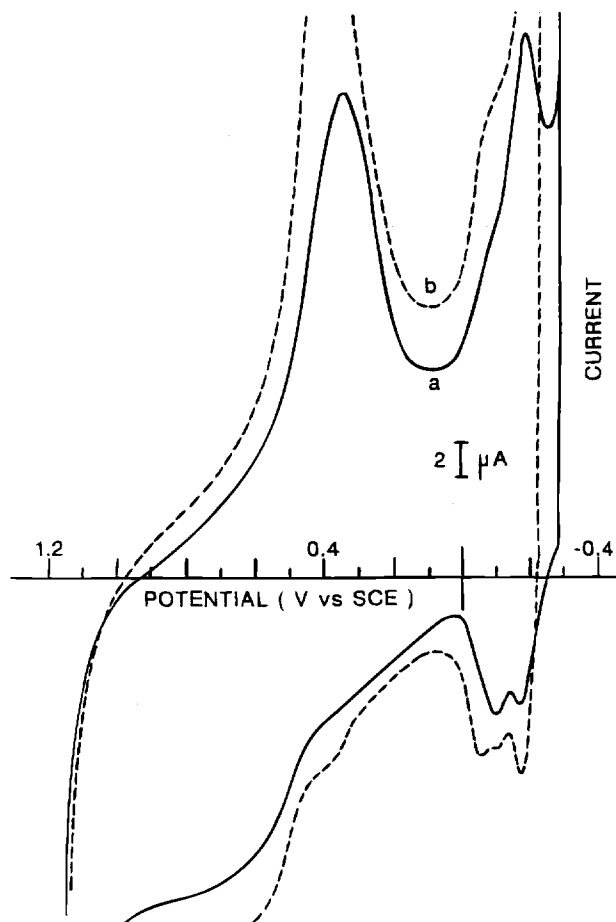


Fig. 7. Cyclic voltammograms obtained with the spot electrodes for the as-received, a, and heat-treated, b, Pt/C catalysts in argon saturated $0.02 M H_2SO_4$ solution at the scan rate of $10 mV/s$.

are very low (about $1.4 cm^2$) as compared to the ESA obtained from $10 \mu l$ paint (10 to $28 cm^2$). The cathodic and anodic scans for the oxygen reduction of these electrodes are shown in Fig. 8. The currents at the low current region are nearly the same for both as-received and heat-treated Pt/C catalysts. Thus the studies on the spot electrodes also indicate a behavior similar to that of the electrodes prepared from $10 \mu l$ of the catalyst paint, *i.e.*, the specific activity remains independent of crystallite size. These results in H_2SO_4 are in contradiction, irrespective of electrolyte concentration and electrode surface area, with the results obtained in HF. A nonadsorbing liquid electrolyte

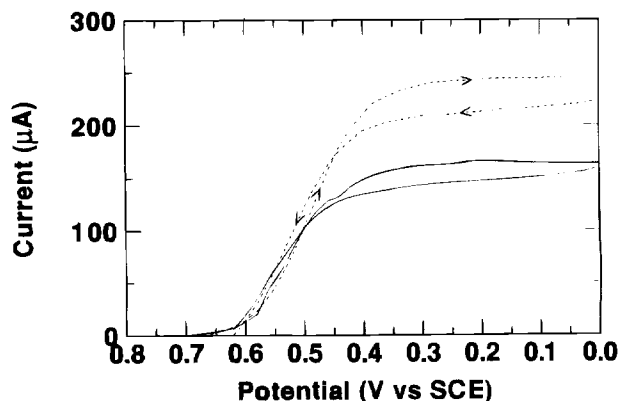


Fig. 8. RDE cathodic and anodic scan measurements for the spot electrode in O_2 saturated $0.02 M H_2SO_4$ solution for the as-received (solid line) and heat-treated (dashed line) Pt/C catalysts.

is therefore required for Pt-based catalysts in order to possibly mimic the GDE results by the RDE results.

It is interesting to note that the current values in the cathodic scan at high anodic potentials, in Fig. 8, are lower than in the anodic scan. This behavior has been observed on a few electrodes. The lower current in the cathodic scan as compared to the anodic scan is due to the blocking effect of the surface oxide formed during the anodic scan.^{27,28}

Conclusion

In a previous work on the Co-based catalysts,⁵ we demonstrated that a parallel of relative mass activity existed between RDE (in H₂SO₄) and GDE (in SPFCs) measurements. It was proposed that RDEs could be used to prescreen the relative activity of the Co-based catalysts. In the present work, we show that this may not be valid for the Pt-based catalysts. In HF (1.17 M), the specific activity of the Pt-based catalysts increases with the size of the Pt crystallite. In contrast, the specific activity obtained by the RDE measurements is nearly independent of the crystallite size when these measurements are performed in H₂SO₄ solution (1.17 M). The difference in behavior observed between the results in HF and H₂SO₄ acids is partly attributed to the crystallite size sensitive adsorption of anions on the Pt sites from H₂SO₄ solution. From the results obtained in the present study, it is believed that, in order to reasonably correlate the RDE results with the GDE results obtained in SPFCs, it is important to isolate the influence of anion adsorption on the Pt sites. Results obtained in a correlative study between RDE and GDE on Pt/C and Pt-alloy/C catalysts will be presented in a future publication.

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