HYDROGEN PEROXIDE FORMATION DURING OXYGEN REDUCTION ON HIGH SURFACE AREA Pt/C CATALYSTS

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ABSTRACT

Hydrogen peroxide formed during the oxygen reduction reaction (ORR) on high surface area platinum on carbon (Pt/C) catalyst was measured using a rotating ring disk electrode (RRDE) coated with a thin film of catalyst. Catalyst samples with varying Pt content (30%-50%) on the same carbon support and catalysts with varying carbon support surface area (56-950 m²/g) and the same platinum mass ratio (50% Pt) were analyzed. The peroxide generation decreased with increase in the platinum active area on all Pt/C samples. Carbon support sample without platinum showed negligible peroxide generation in the typical fuel cell operating region (0.5-0.75 V). The measured Pt active area increased with the carbon support active area, even for same Pt mass ratio and same sized Pt particles. It is hypothesized that enhanced agglomeration of Pt particles on low surface area carbons might cause the lower active area of platinum on the smoother carbon substrates. This loss in the Pt active area and the subsequent generation of extra, difficult to access edges by the Pt agglomerates on which the oxygen is adsorbed less reversibly, might be causing an increase in peroxide generation on low surface area carbon supports.

INTRODUCTION

Hydrogen peroxide formed as a result of incomplete oxygen reduction is suspected of degrading the performance of polymer electrolyte membrane fuel cells. The objective of this study is to investigate the effects of Pt loading and the type of carbon support on the catalytic activity of oxygen reduction catalysts in acidic solution. A thin-film rotating ring-disk electrode (RRDE) was used to determine the fraction of hydrogen peroxide production [1, 2].

Several studies on peroxide production for high surface area Pt/C catalysts have been conducted recently. Paulus et al. [2] analyzed Pt alloyed with Rh and Fe for peroxide production using RRDE and found no significant differences between alloy catalysts and pure Pt in term of peroxide generation. In their study of Fe based fuel cell catalysts using both RRDE and single membrane electrode assemblies (MEAs) for the cathode, Lefevre and Dodelet [3] found loss of catalytic activity which they interpreted to be due to the detrimental effect of H₂O₂ released during ORR. Antoine and Durand [4] studied the effect of Pt particle size on H₂O₂ formation and found that the fraction of peroxide produced increased as the platinum particle size decreased. However, in their Pt/C samples, the Pt mass ratio decreased along with the Pt particle size, such that both factors, viz. decrease in Pt active area and decrease in Pt particle size, might cause increased peroxide production. In another RRDE study on Pt/C catalysts in alkaline media, Genies
et al. [5] have shown that the two electron pathway is significant on carbon as compared to Pt and that the ORR is predominantly governed by the activity of Pt particles dispersed on the carbon support. Other related studies, which do not address peroxide formation, but discuss Pt agglomeration were presented by Stonehart [6] and Watanabe et. al [7].

In spite of these studies on peroxide formation, it is still unclear as to what are the extent of contributions from the Pt and the C species to the formation and/or decomposition of peroxide during the ORR in the potential range of interest. We present here a systematic study of peroxide production on (i) Pt/C catalysts with varying Pt mass ratio on the same carbon support, keeping the Pt particle sizes constant to reveal the effect of the Pt active area, (ii) Pt/C catalysts with varying carbon support surface area, maintaining the same platinum mass ratio and same Pt particle size in order to characterize the dependence of peroxide formation on the carbon support and (iii) the carbon support by itself in order to measure the peroxide formation on carbon as compared to the Pt/C catalyst. Regarding item (ii) above, it will be subsequently shown that it is difficult to separate the effects due to the carbon support from those due to the Pt active area because both are coupled.

EXPERIMENTAL PROCEDURE

Schmidt et al. [1] first developed the method of attaching finely dispersed catalyst powder on a glassy carbon electrode via a thin Nafion® film for electrochemical characterization using RDE. This method was modified slightly to suit our experimental conditions: 2 mg of Pt/C catalyst (as received; provided by 3M) was ultrasonically blended for 15 minutes with 4 ml of distilled water (Millipore SuperQ System; resistivity: 18 MΩ cm). 25 µl of this solution was pipetted on the glassy carbon disk electrode (5 mm dia.) to obtain a catalyst loading of 44 μgcat/cm². After drying in air, a 25 ml of diluted Nafion® solution (10 μl of Nafion® (5 wt% Fluka) + 90 μl of ethanol + 900 μl of distilled water) ultrasonically blended for 5 minutes, was put over the catalyst layer. The thickness of this Nafion® film was estimated to be around 0.1 – 0.15 μm, which has been shown to offer negligible film mass transfer resistance [1]. This procedure of thin film electrode preparation was kept the same for the experiments performed in this work so that the catalyst loading was kept nearly constant throughout.

After preparation, the electrode was immersed in deaerated (ultra high purity N₂, Praxair) 0.5 M H₂SO₄ solution (Fisher) in a standard three electrode cell. A luggin capillary with platinum gauze over which hydrogen was produced via electrolysis and maintained during the experiment, served as the reference electrode (NHE) and a platinum wire in a glass tube with fritted glass end served as the counter electrode. To eliminate effects due to possible contamination from the Nafion® film, the electrode was cycled several times between 0.05 V and 1.2 V to produce clean surfaces. The electrochemical active area was measured by integrating the charge in the hydrogen desorption region and normalizing it by the hydrogen adsorption-desorption charge on platinum (210 μC/cm²).

In order to perform the ORR experiments, the electrolyte was purged with pure O₂ (ultra high purity, Praxair) for 20 minutes prior to every run to achieve saturation and a
cathodic linear sweep was performed on the disk from 0.9 V to 0.05 V (vs NHE) at a scan rate of 10 mV/s under O₂ atmosphere. The ring was held at 1.15 V during the ORR runs and both the ring and the disk currents were recorded using a bi-potentiostat (Pine Instruments, Model: AFCBP1). The ORR runs were performed at 3 to 5 different speeds between 500 rpm and 3000 rpm. Before every ORR run, the capacitive (or the background) current was obtained for both the disk and the ring by sweeping the disk between the same potential limits at the same scan rate of 10 mV/s in deaerated solution. The background polarization currents obtained in the absence of oxygen were then subtracted from the polarization curves under O₂ to obtain the true faradaic currents.

RESULTS

Typical disk and ring currents for cathodic potential sweeps at different rotation speeds are shown in Fig. 1. The background (or capacitive) currents obtained for both the disk and the ring in deaerated solution are also shown in Figs. 1 (a) and (b). The theoretical collection efficiency (N) for the ring current (N = 0.2395), was used to calculate the % mol H₂O₂ [2 - 4]:

\[
\% \text{mol H}_2\text{O}_2 = \frac{\text{moles(H}_2\text{O}_2)}{\text{moles(H}_2\text{O}_2 + \text{H}_2\text{O})} \times 100 = \frac{2 I_R}{N} \times 100
\]

(1)

I_R and I_D are the ring and disk currents, respectively. Several researchers [2 - 4] have found the actual collection efficiency to be within 5 - 10% of the theoretical collection efficiency value by carrying a Fe(CN)⁶⁴⁻/Fe(CN)⁶³⁻ redox reaction at the glassy carbon disc. Since all catalyst samples were compared here for peroxide production at the same rotation speed of 3000 rpm at the same catalyst and Nafion® loading, the theoretical collection efficiency (N) was considered an adequate estimate.

Pt/C Samples with the Same Carbon Support and Different Pt Loading:

Pt/C samples with the same carbon support (carbon active area = 266 m²/g) and varying Pt content (30, 40 and 50 wt% Pt) were analyzed for peroxide production. The % mol peroxide generated by these electrodes as a function of the disk potential is shown in Fig. 2. For convenience, the % mol H₂O₂ produced in different samples are compared at one potential (0.675 V) mid-way in the potential region of typical fuel cell operation (0.5 V - 0.75 V). Table I provides the details of the platinum active area, the mean Pt particle sizes, % mol peroxide and the total moles of peroxide formed at 0.675 V at the same catalyst loading of 44 µg_cat/cm². The variation in the platinum active area with different Pt mass ratios is shown in Fig. 3. It is observed that peroxide formation in terms of both the total moles formed and % mol H₂O₂ decreases with increase in Pt loading (Fig. 4(a)). The total moles and % mol peroxide values normalized by the platinum active area (cm²) and platinum loading (mgpt/cm²) are plotted in Fig. 4 (b) and (c), respectively. These normalized values, which indicate the extent of H₂O₂ formation at the given platinum
loading, also show an almost linear decrease in \( \text{H}_2\text{O}_2 \) production with increase in Pt loading. Fig. 5 shows the variation of the % mol peroxide generation and the inverse of active area with the platinum mass ratio.

Pt/C Samples with the Same Pt Loading and Different Carbon Support:

Pt/C samples with the same Pt loading (50 wt% Pt) having varying carbon supports providing different carbon surface area (56 - 950 m\(^2\)/g) were analyzed for peroxide generation. The variation in the Pt active area with the carbon support surface area is shown in Fig. 6. The values of % mol peroxide and the total moles of peroxide at a disk potential of 0.675 V are plotted as a function of the surface area of carbon support in Fig. 7(a). Table II provides the details of the carbon surface area, Pt active area, mean Pt particle sizes, % mol peroxide and total moles of peroxide formed at 0.675 V with the same catalyst loading of 44 \( \mu \text{g}_{\text{cat}}/\text{cm}^2 \). The total moles and % mol peroxide values normalized by the platinum active area is plotted in Fig. 7(b). The trends show an increase in Pt active area with increase in carbon support surface area (Fig. 6) and also a corresponding decrease in peroxide production (Fig. 8).

H\(_2\)O\(_2\) Formation on Carbon Support:

Peroxide formation on carbon support with a surface area of 266 m\(^2\)/g was analyzed at different loadings (22 - 66 \( \mu \text{g}_{\text{carbon}}/\text{cm}^2 \)) on the disk. Typical disk and ring currents on cathodic potential sweeps for carbon at different rotation speeds are shown in Fig. 10. No mass transport limited region is noticed since the disk current density curves, as well as the ring current curves do not show a variation based on rotation speeds. The ORR current density is at least an order of magnitude lower than for any of the Pt/C samples. The % mol peroxide for different carbon loadings as a function of disc potential are shown in Fig. 11.

DISCUSSION

The observations based on peroxide production studies on the Pt/C samples can be summarized as follows:

(i) Peroxide production decreases with increase in platinum active area,
(ii) Peroxide production on carbon is negligible compared to that on Pt/C catalyst and
(iii) Platinum active area decreases with a decrease in the carbon support surface area for the same overall Pt weight. This may be due to increased Pt agglomeration which correlates with increased peroxide production.

(i) Decrease in Peroxide Production with Increase in Platinum Active Area:
In our RRDE tests with Pt/C samples we notice that the peroxide generation is inversely proportional to the active area of platinum available for the reaction, under conditions of constant catalyst and Nafion® loading (Fig. 9, also Figs. 5 and 8) and for the same overall electrode area. The active area of Pt, plotted as a function of wt% Pt in Fig. 3, shows an increase with the Pt content in the catalyst. The mol% peroxide production and the inverse of the Pt active area as a function of % wt Pt on same carbon support, plotted in Fig. 5, shows a decrease in peroxide production with increase in active area. In the case of Pt/C samples having same Pt mass ratio but varying carbon support surface area, we observe an increase in Pt active area with increase in carbon support area (Fig. 6). Fig. 8, depicting the inverse of Pt active area and mol % peroxide formed, as a function of the carbon support surface area also shows a similar trend in peroxide production with Pt active area. The original Pt particle sizes for all these Pt/C samples are almost equal (2.2-2.6 nm) [9]. This indicates that the net peroxide generation is less favorable on Pt, on which the ORR reaction proceeds mainly by the 4 electron transfer pathway [1, 2, 4 & 8]. Tests conducted on carbon support without any Pt indicate that peroxide production on carbon is negligible at potentials positive to 0.4 V. This suggests a greater decomposition of peroxide, (which is formed on the Pt particles due to possible end-on non-dissociative oxygen adsorption on the edge atoms), when a greater platinum active area is available for the reaction [4, 8].

(ii) Peroxide production on Carbon is negligible:

Runs with 22 μg_{carbon}/cm^2 and 44 μg_{carbon}/cm^2 produced negligible amount of peroxide at potentials positive to 0.5 V (Fig. 11). At potentials cathodic to 0.3 V, however, there is a large increase in % mol H\textsubscript{2}O\textsubscript{2} production on carbon as compared with Pt/C samples. The ring current I\textsubscript{r}, which indicates the total moles of H\textsubscript{2}O\textsubscript{2} formed on carbon as a function of the disc potential, is lower than that on the corresponding Pt/C samples with the same carbon support (Fig. 12). This indicates that, although peroxide formation during ORR is more favorable on carbon at potentials cathodic to 0.3 V, it is not a significant contributor to the net H\textsubscript{2}O\textsubscript{2} formed in the potential range 0.5 V and 0.75 V where fuel cells are typically operated.

(iii) Decrease in Pt Active Area with Decrease in Carbon Support Surface Area:

Pt/C samples having the same platinum mass ratio (50% Pt) exhibit an increase in platinum active area as the surface area of carbon increases (Fig. 6). In these samples, the catalyst loading, the Pt particle sizes and the Nafion\textsuperscript{®} loading were kept constant. The original Pt particle sizes in all these samples were in the range of 2.2-2.4 nm [9]. However, the active area of Pt plotted as a function of the carbon support surface area in Fig. 6, shows an increase in Pt active area with increase of the carbon support surface area. Thus, although the carbon support may not be generating significant amount of peroxide in the potential range of interest, it has an impact on the net peroxide produced on the Pt/C sample by possibly causing a variation in the Pt active area.
Equivalent Pt particle sizes were calculated based on the active area obtained from the hydrogen adsorption/desorption charge calculations and the known weight of catalyst loaded on the disc, assuming that the particles are individual spheres distributed on the carbon support. These radii were then compared with the sizes provided by the catalyst vendors (Table III and Ref. 9). The calculated sizes are in agreement with the vendor data for only very high surface area carbon support (800-950 m$^2$/g) Pt/C catalysts. For low surface area carbons (56-266 m$^2$/g), the calculated sizes are much larger than those indicated by the vendor. The loss in Pt active sites due to the Nafion® loading was determined experimentally on bare and Nafion® coated polycrystalline platinum disk to be of the order of 30%, and was accounted for in the equivalent Pt particle size determination. The increase in average particle size and loss in Pt active area in low surface area carbon support leads us to the hypothesis that there is enhanced agglomeration of Pt particles on the relatively lower surface area carbon. This can be due to (i) the greater equivalent proximity (based on actual [not projected] carbon area) of Pt particles to each other on low surface area carbons (Table IV), and (ii) the relatively smooth substrate offering low “friction” which promotes lateral particle movement leading to their agglomeration. By contrast, the high surface area more convoluted carbon will tend to “lock” the Pt particles in place. A similar observation has been reported by Stonehart [6] and Watanabe et. al [7], who measured the Pt particle sizes as a function of the carbon surface area using TEM, CO adsorption and H$_2$ adsorption. They report that the specific activity for ORR decreased with the average distance between the agglomerated particles. The authors, however, did not measure or consider peroxide formation.

Considering an agglomerate of $N$ particles formed on the carbon support from $n$ initial particles, $n/N$ such agglomerates are generated. We assume a disk-like agglomerate particle, where only the top area is completely exposed to reaction, while the regions of contact between particles are inaccessible for the ORR. A schematic representation of such an agglomerate is shown in Fig. 13. Let $r$ be the radius of each Pt particle and $R$, the radius of the agglomerate disk.

\[
\pi R^2 \approx N \pi r^2 \tag{2}
\]

\[
R = N^{1/2} r \tag{3}
\]

In Eq. 2 we neglect the area due to voids between the closely packed spheres, since this area is only a small fraction of the total area for closely packed spheres. The actual (non-projected) surface area of the agglomerate disk (consisting of $N$ Pt particles) with radius $R$ is:

\[
\text{Area} = \text{(sum of hemispherical area exposed at top face)} + \text{(area along perimeter)}
\]

\[
\text{Area} = 2N\pi r^2 + 2 \pi N^{1/2} r^2 \tag{4}
\]
The ratio of the total Pt active area corresponding to such agglomerates to the true active area in the event of no agglomeration gives a factor of \( \frac{1}{2} \left( 1 + \frac{1}{\sqrt{N}} \right) \) for the loss of active area of the platinum in the Pt/C catalyst due to agglomeration, i.e.,

\[
\text{Measured Pt area} = \frac{1}{2} \left( 1 + \frac{1}{\sqrt{N}} \right) \times (\text{True Pt area})
\]  

(5)

A more realistic model is to assume that once the number of agglomerated particles increases beyond about 4-8 Pt particles, they are likely to form a multilayer structure, as shown schematically in Fig. 14. The exposed area of such an agglomerate was estimated and compared to the cumulative surface area of the total number of single Pt particles. The area reduction associated with agglomerates for both single layer (disk-like) agglomerates and multilayer structures is shown in Fig. 15. Although, there is a loss in active area of Pt as the average number of particles in an agglomerate is increased, Fig. 15 indicates that the multilayer agglomerate particle model provides a larger loss in the active area and hence a better agreement with the experimental results. Such a spherical model, which is only likely for agglomerates involving a larger number of Pt particles in an agglomerate, seems to be consistent with the TEM studies [10].

The numbers of particles (N) in Pt agglomerates of different carbon supports were estimated by taking a ratio of the measured Pt active area to the true Pt area and obtaining the corresponding value of N indicated in Fig. 15. These values of N when plotted against the carbon support surface area show an increased agglomeration on lower surface area carbon (Fig. 16). It is observed that when the Pt loading on the same carbon substrate (carbon surface area = 266 m\(^2\)/g) is increased, the Pt active area per unit weight of Pt, i.e. (Pt active area)/(Pt wt.) in m\(^2\)/gpt, remains substantially the same (Table I). This may indicate that under those conditions, viz. same carbon support and same Pt particle size, the degree of agglomeration is independent of the Pt mass ratio.

Of particular interest to the peroxide formation issue is the presence of limited accessibility regions, such as grain boundaries formed due to contact between individual Pt particles and between the Pt particles and the carbon support. Previous researchers [4, 8] have suggested that the peroxide formation is due to end-on oxygen adsorption on the platinum edge atoms, leading to production of O\(_2\)H\(^-\) species which are not dissociative. This mechanism of peroxide generation is hypothesized to take place on the low coordination number edge atoms of Pt, since the bulk surface is covered by the oxygenated intermediate species. In order to find out whether Pt agglomeration increased the edge regions, we approximate the relative perimeter regions for agglomerated Pt and compare it to the edge region in non-agglomerated single spherical particles.

We arbitrarily approximated that the radius of the circumference of the contact region formed by a single spherical particle sitting on a high surface area carbon support is of the order of 1/10\(^\circ\) of the radius of the particle (Fig. 17). As depicted in Fig. 14, the stacking or agglomeration of individual Pt particles will give rise to creation of additional edges due to increased contact regions formed between the single particles. Assuming that each inter-particle contact also gives rise to a region of circumference corresponding...
to 1/10th the radius of the particle, the ratio of the edge regions of the disk-like (N < 7) or multilayer agglomerates (N > 7) to the sum of all the single particles was calculated and plotted in Fig. 18. It is observed that agglomerated Pt/C samples provide a greater edge region (where peroxide generation is hypothesized to be favored) as compared to non-agglomerated Pt particles based on the same amount of Pt and the same original (non-agglomerated) Pt particle size. Agglomeration of Pt particles leading to low overall Pt active area accompanied by an increase in the edge regions might be collectively responsible for increased peroxide generation on Pt/C catalysts supported by low surface area carbon (Fig. 8). Thus, although the carbon support might not be generating peroxide in the potential range of interest, it has an impact on the net peroxide produced on the Pt/C sample by varying the Pt active area.

The large variability that is noted in peroxide formation and in the calculated degree of agglomeration for low surface area carbons (left hand side of Figs. 7, 8 and 15) may be due to experimental inaccuracies. However, this variability may also be associated with actual fluctuations in the degree of agglomeration for Pt particles on relatively smooth carbon where agglomeration is expected to be high. This high agglomeration may depend on factors such as the type of carbon support, and the shape of the agglomerate, which was assumed to be a disk but actually may be spheroid.

The degree of faceting in the Pt particles may also somewhat affect the peroxide formation [9, 12]. However, in our study, all the Pt samples were generated similarly and therefore the faceting is likely to remain constant for all tested samples, hence the effects we are reporting should be independent of this factor.

CONCLUSIONS

Peroxide production studies using RRDE for different Pt/C samples revealed an inverse relationship between the Pt active area of catalyst and the peroxide produced. Peroxide production was observed to decrease with increasing Pt active area for the same catalyst loading and the same electrode area. A carbon support material tested for peroxide formation showed negligible peroxide formation in the typical potential range of fuel cell operation (0.5-0.75 V). Pt/C samples with same Pt mass ratio but different carbon support surface areas revealed a dependence of Pt active area on carbon support surface area. It is hypothesized that agglomeration of Pt particles due to greater relative proximity between Pt particles on low surface area carbons might cause a loss in Pt active area, and hence, lead to a corresponding increase in production of peroxide. An approximate model indicating the extent of this agglomeration based on the measured Pt active area supports this hypothesis and reveals the generation of more edge regions by Pt agglomerates, which might bring about an increase in the peroxide production by end-on oxygen adsorption.

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Table I: Pt/C samples with varying Pt content on 266 m²/g carbon support

| % wt Pt in Pt/C | Pt loading (mgPt/cm²) | Active Area (cm²)/ (m²/g) | % mol H₂O₂ at 0.675 V | Total mol H₂O₂ (mol) at 0.675 V | Pt size[nm] |
|-----------------|------------------------|---------------------------|-----------------------|-------------------------------|-------------|
| 30              | 0.0132                 | 1.08/43.5                 | 1.77                  | 5.04 X 10⁻¹¹                  | 2.3         |
| 40              | 0.0176                 | 1.48/44.6                 | 1.54                  | 4.54 X 10⁻¹¹                  | 2.3         |
| 50              | 0.0220                 | 1.80/43.4                 | 0.79                  | 2.25 X 10⁻¹¹                  | 2.4         |

Table II: 50% Pt/C Samples with Varying Carbon Support

| Active Area of Carbon (m²/g) | Pt loading (mgPt/cm²) | Active Area (cm²)/ (m²/g) | % mol H₂O₂ at 0.675 V | Total mol H₂O₂ (mol) at 0.675 V | Pt size[nm] |
|-----------------------------|------------------------|---------------------------|-----------------------|-------------------------------|-------------|
| 56                          | 0.0220                 | 2.78/67.0                 | 0.625                 | 2.26 X 10⁻¹¹                  | 2.3         |
| 125                         | 0.0220                 | 1.73/41.7                 | 2.120                 | 6.71 X 10⁻¹¹                  | 2.2         |
| 133                         | 0.0220                 | 1.78/42.9                 | 0.393                 | 1.32 X 10⁻¹¹                  | 2.4         |
| 220                         | 0.0220                 | 2.81/67.7                 | 1.030                 | 5.33 X 10⁻¹¹                  | 2.4         |
| 266                         | 0.0220                 | 1.80/43.4                 | 0.895                 | 2.25 X 10⁻¹¹                  | 2.4         |
| 800                         | 0.0220                 | 3.45/83.1                 | 0.715                 | 2.83 X 10⁻¹¹                  | 2.4         |
| 800                         | 0.0220                 | 3.8/91.6                  | 0.715                 | 2.83 X 10⁻¹¹                  | 2.4         |
| 950                         | 0.0220                 | 4.66/112.3                | 0.461                 | 1.97 X 10⁻¹¹                  | 2.6         |

Table III: Particle Size Calculation for 50% Pt/C Samples with Varying Carbon Support

| Active Area of Carbon (m²/g) | Pt loading (mgPt/cm²) | Active Area (cm²)/ (m²/g) | Pt size {calculated} (nm) | Pt size {given} [9] (nm) |
|-----------------------------|------------------------|---------------------------|---------------------------|-------------------------|
| 56                          | 0.0220                 | 2.78/67.0                 | 4.2                      | 2.3                     |
| 125                         | 0.0220                 | 1.73/41.7                 | 6.7                      | 2.2                     |
| 133                         | 0.0220                 | 1.78/42.9                 | 6.5                      | 2.4                     |
| 220                         | 0.0220                 | 2.81/67.7                 | 4.1                      | 2.2                     |
| 266                         | 0.0220                 | 1.80/43.4                 | 6.5                      | 2.4                     |
| 800                         | 0.0220                 | 3.45/83.1                 | 3.4                      | 2.4                     |
| 800                         | 0.0220                 | 3.8/91.6                  | 3.1                      | 3.2                     |
| 950                         | 0.0220                 | 4.66/112.3                | 2.5                      | 2.6                     |
Table IV: Calculation of Distance between Pt particles on Carbon Support

| Pt/C Sample                  | High Surface Area Carbon Support | Low Surface Area Carbon Support |
|------------------------------|----------------------------------|--------------------------------|
| Mass ratio of Pt [%]         | 50                               | 50                             |
| Carbon surface area (CSA) [m²/g] | 950                             | 125                            |
| Pt loading on Disk [mgpt/cm²] | 0.022                           | 0.022                          |
| Carbon loading [mgc/cm²]     | 0.022                            | 0.022                          |
| Pt particle size (d) [nm]    | 2.6                              | 2.2                            |
| No. of Pt particles (assuming spherical shape, no agglomeration) | $3.2 \times 10^{12}$ | $5.2 \times 10^{12}$ |
| Surface Area of carbon available for Pt particles [cm²] | 59.2                           | 7.8                            |
| Distance between Pt particles (D) [nm] | $48.5$                            | 13.8                           |

$N = \frac{\text{Pt loading} \times \text{disk Area}}{(\rho_{pt} \times \pi d^3/6)}$

$A = \text{Carbon loading} \times \text{Disk Area} \times \text{CSA}$

$D = \{\frac{A}{(\pi N/4)}\}^{1/2}$
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Fig. 1: (a) Current-potential curves for O$_2$ reduction on 40% Pt/C catalyst in a thin film; (b) peroxide re-oxidation on Pt ring electrode in 0.5 M H$_2$SO$_4$ saturated with pure O$_2$. $E_r = 1.15$ V (vs NHE). Scan rate: 10 mV/s.
Fig. 2: % mol $\text{H}_2\text{O}_2$ formed at an thin film electrode at disk rotation speed of 3000 rpm as a function of the disk potential for Pt/C catalysts with different Pt mass ratios at the same catalyst loading of 44 $\mu$g cat/cm$^2$ (all parameters are the same as in Fig. 1).

Fig. 3: Variation in Pt active area with Pt mass ratio under constant Nafion® and catalyst loading of 44 $\mu$g cat/cm$^2$ (all other conditions are the same as in Fig. 1).
Fig. 4: Peroxide generation at 0.675 V and at disk rotation speed of 3000 rpm as a function of % Pt mass ratio on same carbon support (266 m²/g) under same catalyst loading of 44 µg/cm² and same Nafion® loading in terms of (a) % mol H₂O₂ and total mol H₂O₂; (b) % mol H₂O₂ and total mol H₂O₂ normalized by active area of Pt (cm²) and (c) % mol H₂O₂ and total mol H₂O₂ normalized by Pt loading (mgPt/cm²).
Fig. 5: Variation of the % mol peroxide generation and the inverse of active area with the platinum mass ratio under constant Nation® and constant catalyst loading of 44 μgcat/cm² (all other conditions same as in Fig. 1).

Fig. 6: Variation in Pt active area as a function of the carbon support surface area for catalysts with 50% Pt mass ratio catalysts under constant Nafion® loading and catalyst loading of 44 μgcat/cm² (all other conditions are the same as in Fig. 1).
Fig. 7: Peroxide generation at 0.675 V and at disk rotation speed of 3000 rpm as a function of the active area of the carbon support (m²/g) for 50% Pt mass ratio under the same catalyst loading of 44 μg/cm² and the same Nafion® loading in terms of (a) % mol H₂O₂ and total mol H₂O₂; and (b) % mol H₂O₂ and total mol H₂O₂ normalized by the active area of Pt (cm²).
Fig. 8: Variation of the % mol peroxide generation and the inverse of active area with the carbon support surface area for 50% Pt/C catalysts under constant Nafion® loading and catalyst loading of 44 μgcat/cm² (all other conditions are the same as in Fig. 1).

Fig. 9: Variation of the % mol peroxide and total mol peroxide generation with the platinum active area for Pt/C samples with same carbon support under constant Nafion® and constant catalyst loading of 44 μgcat/cm² (all other conditions same as in Fig. 1).
Fig. 10: (a) Current-potential curves for $\text{O}_2$ reduction on 266 m$^2$/g carbon support in a thin film; (b) peroxide re-oxidation on Pt ring electrode in 0.5 M $\text{H}_2\text{SO}_4$ saturated with pure $\text{O}_2$. $E_R = 1.15$ V (vs NHE). Scan rate: 10 mV/s.
Fig. 11: % mol H₂O₂ formed on the thin film electrode at disk rotation speed of 3000 rpm as a function of the disk potential for different loadings of Carbon support (266 m²/g) (all other conditions are the same as in Fig. 1).

Fig. 12: Comparison of Peroxide current (or Ring current, Iₕ) obtained as a function of disk potential at 1000 rpm between bare carbon support and Pt/C catalysts with same carbon support.
Fig. 13: Schematic representation of a single layer (disk-like) agglomerate (of radius R) comprising of a fixed number of Pt particles (each of radius r).

Fig. 14: Schematic representation of a multilayer agglomerate comprising of a fixed number of Pt particles (each of radius r).
Fig. 15: Decrease in active area of Pt particles (plotted as the ratio of measured area to the true area) with increase in number of Pt particles in an agglomerate.

Fig. 16: Average number of Pt particles in an agglomerate (N) as the function of the carbon support surface area for experimentally analyzed Pt/C samples.
Fig. 17: Schematic representation of the edge formed by a single Pt particle attached to the carbon substrate (the contact region is approximated by an area of $1/10^6$ the radius of the Pt particle).

Fig. 18: Increase in contact (edge) area of Pt agglomerates (plotted as the ratio of agglomerate contact perimeter to the sum of contact perimeter regions for individual Pt particles) with increase in number of Pt particles in an agglomerate.