

## Particle Size and Support Effects in Electrocatalysis

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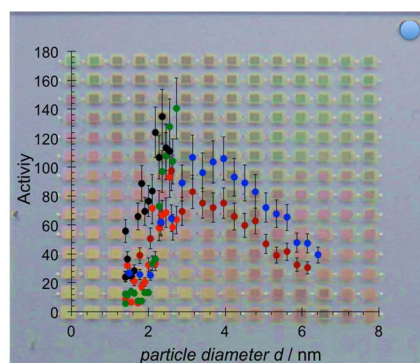
### CONSPECTUS

Researchers increasingly recognize that, as with standard supported heterogeneous catalysts, the activity and selectivity of supported metal electrocatalysts are influenced by particle size, particle structure, and catalyst support. Studies using model supported heterogeneous catalysts have provided information about these effects. Similarly, model electrochemical studies on supported metal electrocatalysts can provide insight into the factors determining catalytic activity.

High-throughput methods for catalyst synthesis and screening can determine systematic trends in activity as a function of support and particle size with excellent statistical certainty. In this Account, we describe several such studies investigating methods for dispersing precious metals on both carbon and oxide supports, with particular emphasis on the prospects for the development of low-temperature fuel-cell electrocatalysts.

One key finding is a decrease in catalytic activity with decreasing particle size independent of the support for both oxygen reduction and CO oxidation on supported gold and platinum. For these reactions, there appears to be an intrinsic particle size effect that results in a loss of activity at particle sizes below 2–3 nm. A titania support, however, also increases activity of gold particles in the electrooxidation of CO and in the reduction of oxygen, with an optimum at 3 nm particle size. This optimum may represent the superposition of competing effects: a titania-induced enhanced activity versus deactivation at small particle sizes. The titania support shows catalytic activity at potentials where carbon-supported and bulk-gold surfaces are normally oxidized and CO electrooxidation is poisoned. On the other hand, platinum on amorphous titania shows a different effect: the oxidation reduction reaction is strongly poisoned in the same particle size range. We correlated the influence of the titania support with titania-induced changes in the surface redox behavior of the platinum particles. For both supported gold and platinum particles in electrocatalysis, we observe parallels to the effects of particle size and support in the equivalent heterogeneous catalysts.

Studies of model supported-metal electrocatalysts, performed efficiently using high throughput synthetic and screening methodologies, will lead to a better understanding of the mechanisms responsible for support and particle size effects in electrocatalysis, and will drive the development of more effective and robust catalysts in the future.



### 1. Introduction

In order to ensure the optimum utilization of catalyst material such as precious metals, high dispersion of the active materials on a support should yield optimal mass activity. This does not take into account the apparent structural sensitivity of many catalytic reactions, and a decrease in specific activity or selectivity with increased dispersion may counteract the positive effect of dispersion on mass activity. It is also recognized that the selection of a support may induce activity in metal supported particles, with low temperature oxidation on titania supported gold<sup>1</sup> and ceria supported transition metals<sup>2</sup> perhaps the most

notable examples. Surface studies at model supported metal catalysts have provided a significant insight regarding the origin of the particle size, structure and support effects.<sup>3</sup> An important example of a structurally sensitive electrocatalytic reaction, particularly in fuel cell applications, is the apparent deactivation of the oxygen reduction reaction with decreasing platinum particle size. The increase in the mass activity gained by dispersion of platinum is consequently limited, resulting in a “critical” particle size.

At present, carbon-supported platinum-based catalysts are universally applied in polymer electrolyte membrane

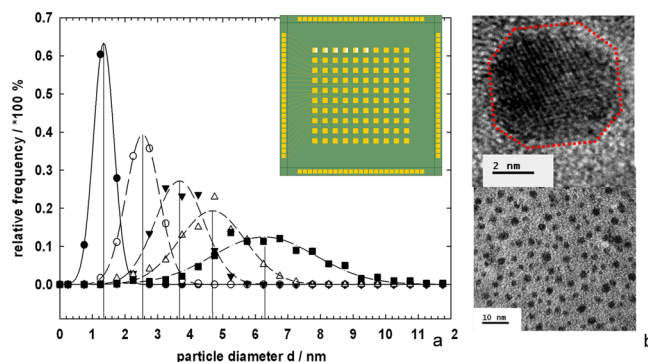
fuel cell (PEMFC) anodes and cathodes. In the oxidizing environment of the cathode, the degradation of the catalyst with time is ascribed to the loss of platinum largely due to the oxidation of the support. Alternative supports for platinum have been sought in order to improve the durability of the catalyst, improve the catalyst activity and provide a more hydrophilic environment at the three-phase boundary. Titania has been proposed as a candidate for such a support. It is therefore of interest to develop model systems for the study of particle size and support effects in electrocatalysis in order to investigate the possibility of providing improved electrocatalysts, and also to make comparisons with the effects that have been observed in heterogeneous catalysis.

High-throughput thin film synthetic methods employing the use of MBE (molecular beam epitaxy) sources in the UHV environment<sup>4,5</sup> have provided a powerful tool for the synthesis of model supported metal particle electrocatalysts. When combined with high-throughput electrochemical screening methods,<sup>6,7</sup> the effects of support, and the trends in surface electrochemical behavior and reactivity as a function of particle size, are quickly accessible with excellent statistical certainty.

## 2. High Throughput Synthesis and Screening of Model Catalysts

A physical vapor deposition method using MBE elemental sources has been adapted to produce controllable compositional gradients of a wide range of materials over a substrate format compatible with prefabricated MEMS screening array chips<sup>4</sup> and characterization methods. The MBE based method has the additional advantage that the deposition rates are sufficiently controllable to allow the nucleation and growth of nanoparticles on substrates, a method extensively used to produce model supported metal heterogeneous catalysts.<sup>3</sup> This advantage can be extended to synthesize in high-throughput on a single substrate ranges of nucleated nanoparticles in the range of 1–10 nm.<sup>4,5,8</sup> Figure 1a shows the particle size distributions obtained during the nucleation and growth of Au on amorphous titania.<sup>9</sup> The differing particle sizes are shown for five of the rows on the screening chip (inset) and have been determined by TEM. Figure 1b shows a typical particle distribution, and a typical particle which equilibrate during deposition at a substrate temperature of 200 °C to produce truncated cuboctahedral particles.

Screening catalysts on an array of electrodes that are independently addressable allows a highly sensitive and effectively parallel measurement of activity and surface redox behavior. The sensitivity achieved with this approach

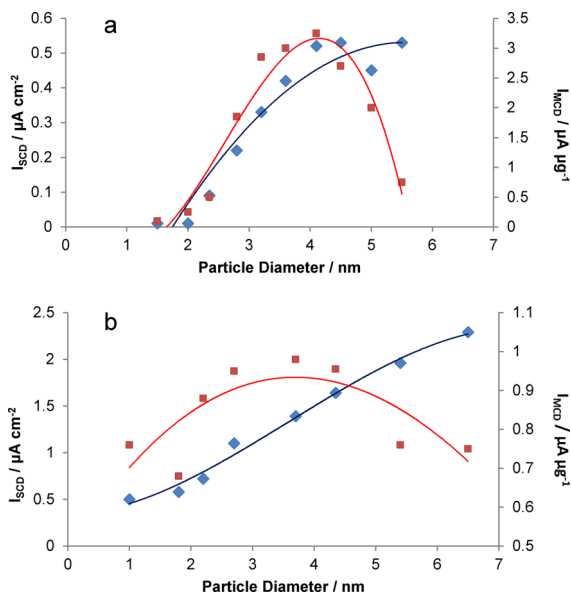


**FIGURE 1.** (a) Particle size distributions of gold nucleated on titania on a microfabricated screening array (inset). Reprinted in part with permission from ref 5. Copyright 2006 American Chemical Society. (b) Distributions of particles at an equivalent thickness of 0.78 nm.

is sufficient to allow the measurement of reactions (using cyclic voltammetry or chronoamperometric (steady-state) measurement) on continuous thin film catalysts and supported metal nanoparticles. Results show that the activity trends observed with composition and particle size are primarily determined by the surface kinetics through comparison with experiments carried out on rotating disc electrodes. The experimental approach in this laboratory has been described in detail elsewhere.<sup>7,10</sup> The microfabricated arrays are now based on a silicon nitride covered 35 mm × 35 mm silicon substrate supporting an array of 10 × 10 square gold electrodes (each 0.8 mm<sup>2</sup>) which are independently addressable through contact pads at the borders (Figure 1a): The electrode interconnect is insulated from the electrolyte by silicon nitride. Model catalysts are synthesized through contact masks that constrain the material to the electrode surfaces. The catalysts are screened ex-situ in a temperature-controlled electrochemical cell incorporating reference and counter electrodes.

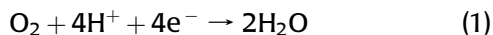
## 3. Particle Size Effects for Carbon-Supported Electrocatalysts

The oxygen reduction reaction (eq 1) is a key reaction that takes place at the cathode of low temperature fuel cells no matter what fuel is being oxidized at the anode. The optimal catalysts are platinum-based (traditionally supported on carbon), and for hydrogen fuel cells in an acid environment (PAFC or PEMFC) it is the overall rate limiting reaction. The limitation of the dispersion of platinum because of a lower specific activity (activity with respect to the platinum surface area) was first noted on practical high area carbon-supported platinum catalysts in the phosphoric acid environment<sup>11</sup> where an optimum in the mass activity was observed at a particle size of 3 nm. The larger proportion of more open packed



**FIGURE 2.** (a) Particle size dependent specific (blue diamonds) and mass (red squares) current densities for oxygen reduction in 0.5 M  $HClO_4$  at  $0.85 V_{RHE}$  on high area carbon-supported platinum<sup>6</sup> and (b) model carbon-supported platinum catalysts.<sup>8</sup>

facets (with lower activity) to close packed facets (with higher activity) on small particles as a result of strong anion adsorption was proposed as the explanation for their lower specific activity.



Similar particle size effects are also evident, however, on high area carbon-supported platinum catalysts in the weak anion electrolyte environments relevant to PEMFC<sup>6,12</sup> and within in the PEMFC.<sup>3,14</sup> Figure 2a shows the dependence of the specific current density ( $I_{SCD}$ ) for oxygen reduction at  $0.85 V_{SHE}$  (specific activity) as a function of the platinum particle size on a high area carbon-supported catalyst.<sup>6</sup> There is a clear reduction in the activity of the platinum as the mean particle diameter reduces from ca. 7 to 1 nm. Consequently there is an optimum in the mass current density ( $I_{MCD}$ ) of the catalyst (mass activity) at 4 nm. There have been suggestions that this apparent lower activity at smaller particle sizes (higher dispersions) is a result of oxygen mass transport effects in high area catalyst layers.<sup>15</sup> Figure 2b shows, however, a similar measurement made on an array of model carbon-supported Pt catalysts synthesized using the HT-PVD method and screened in perchloric acid electrolyte at  $0.85 V_{RHE}$ .<sup>8</sup> In the planar electrochemical configuration of the electrode there are no perturbations expected from mass transport effects. The results clearly show a similar decrease in the activity of the platinum as the particle size reduces, and a resulting maximum in the mass

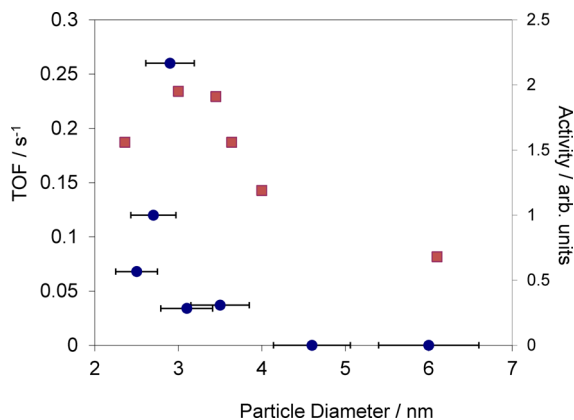
current density at 4 nm. Note that the dependence of  $I_{SCD}$  is much faster on the model system than the high area catalyst, resulting in a sharper maximum in  $I_{MCD}$ . This is likely to be a result of the narrower distributions of particle sizes synthesized on the model catalyst.

In the light of the observed structural sensitivity of the oxygen reduction reaction on single crystal platinum surfaces in such acid electrolyte,<sup>16</sup> one may expect a particle size dependence in the weakly adsorbing electrolytes (Figure 2): In this case, it is the potential dependent adsorption of the hydroxyl species that is believed to block the oxygen reduction reaction.<sup>17</sup> Smaller particles present a higher proportion of the low coordinate facets (or edge sites) which more strongly adsorb the surface hydroxide.<sup>6,12,13</sup> This model is consistent qualitatively with the optimal position of extended platinum in the theoretically predicted volcano curve for oxygen reduction.<sup>18</sup> Any increase in adsorbed oxygen or hydroxyl adsorption enthalpy would be predicted to lower the oxygen reduction activity. It is this particle size dependence of the oxygen reduction specific activity, and hence mass activity (Figure 2), that affords a limitation in the effectiveness of dispersion to achieve more cost-effective catalysts in PEMFC.

#### 4. The Influence of the Support in Electrocatalysis

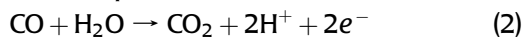
A good example of the influence of a support on metal particles on the activity of a heterogeneous catalyst can be found in the low temperature oxidation of CO and hydrocarbons afforded by titania supported gold nanoparticles. Haruta et al.<sup>19</sup> demonstrated that when gold was supported on titania, it was able to oxidize CO at low temperatures, and in addition the activity of the catalyst was strongly dependent on the particle size of the gold: Figure 3 (blue circles) shows that the turn over frequency for CO oxidation is optimal at a mean particle diameter of 3 nm.<sup>20</sup> The reactivity of titania supported gold, characterized by STM, also showed (Figure 3, red squares) that there was an optimal particle size of 3 nm for the same reaction.<sup>21</sup> There has been a considerable debate concerning the origin of the induced activity, and mechanisms involving spillover of oxygen, the modification of the electronic structure of the gold, and the enhanced activity of reaction sites at the periphery of the particle have all been suggested.<sup>1</sup>

The overall electrochemical oxidation of CO on gold in acid electrolyte (eq 2) has a standard potential  $E^0 = -0.106 V_{SHE}$ . It is likely to take place through a Langmuir–Hinshelwood reaction mechanism, and as in the case of platinum surfaces, the large



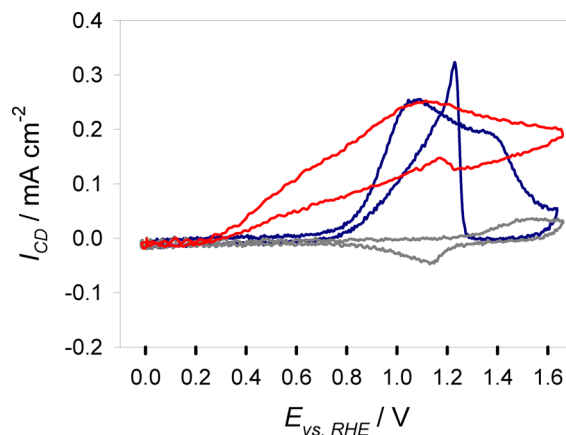
**FIGURE 3.** Particle size dependence of the low temperature oxidation of CO on high area titania supported<sup>20</sup> (blue circles) and model titania supported (red squares) gold.<sup>21</sup>

overpotential (rate-determining step) for the surface reaction is associated with the activation of water to produce the surface oxidant.<sup>22</sup> A lower overpotential is associated with the reaction in alkali media due to the favorable coadsorption of CO and the hydroxyl species at low potential.<sup>23</sup>



A structure sensitivity of the CO oxidation reaction on gold is reported on single crystal gold electrodes.<sup>24,25</sup> It would therefore not be unreasonable to expect an intrinsic particle size dependence for the reaction. In addition, there is also the possibility that the activity is influenced by the support, either by influencing the particle structure, or through some of the other mechanisms suggested (above) for titania and other reducible oxides.

Experiments have been carried out in order to compare the particle size and support effects of the CO oxidation reaction (eq 2) on supported gold particles. These have been deposited through the nucleation and growth of gold on arrays of electrodes, and a typical distribution of such particles on titania is shown in Figure 1. Figure 4 shows voltammograms for two such catalysts with 3.2 nm gold particles supported on both carbon (blue) and titania (red) carried out in CO saturated 0.5 M HClO<sub>4</sub> electrolyte.<sup>10</sup> In addition, a voltammogram is also shown for the titania supported gold nanoparticles in the absence of CO in 0.5 M HClO<sub>4</sub> to highlight the redox behavior of the gold surface. The measurements are taken on one of the array electrodes for each catalyst, and the currents are diffusion limited. For the carbon-supported particles, the onset of CO oxidation is observed in the positive-going sweep at ca. 0.8 V<sub>RHE</sub>, and this corresponds to a high overpotential for the reaction which is indistinguishable to that of a continuous polycrystalline gold

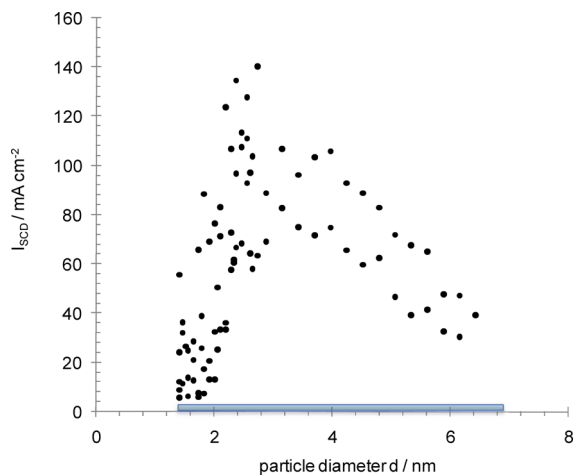


**FIGURE 4.** Cyclic voltammetry in CO-saturated 0.5 M HClO<sub>4</sub> of 3.2 nm gold supported on carbon (blue) and titania (red). The redox behavior obtained in CO-free electrolyte on carbon-supported gold is also shown (gray).<sup>10</sup>

surface. As the positive-going sweep reaches ca. 1.4 V<sub>RHE</sub> the CO oxidation current drops precipitously, and only returns on the return sweep at 1.3 V<sub>RHE</sub>. This behavior is also characteristic of polycrystalline gold, and it is a result of the oxidation of the gold surface which blocks the CO oxidation reaction: Only when oxygen is stripped from the gold surface does the CO oxidation reaction rate increase again. The corresponding potential for the onset of surface oxidation, and the surface reduction, responsible for this behavior is shown in the CO free voltammogram (gray curve). The CO oxidation behavior (Figure 4) on titania supported particles (red curve) is remarkably different than the behavior on the carbon-supported particles (blue curve). The first clear difference is that the onset of CO oxidation takes place at ca. 0.3 V<sub>RHE</sub>, at a much lower overpotential than on carbon-supported particles: CO oxidation is clearly activated by the titania support. The second striking difference is that the CO oxidation continues at potentials at which gold is normally oxidized: This implies that either the CO oxidation no longer requires an oxygen free gold site, or the redox behavior of the active gold site when on the titania support is different. There are no contributions to the currents from the titania support itself in this potential window.<sup>9,10</sup>

The promotion of the CO oxidation reaction on the titania supported gold is strongly dependent on the particle size. Figure 5 shows the effect of the mean particle size of gold on titania (Figure 1) on the specific current density for CO oxidation at 0.5 V<sub>RHE</sub> in 0.5 M HClO<sub>4</sub>.<sup>9</sup> The results shown are from measurements on a number of independent electrochemical arrays. Measurements of carbon-supported gold particles in the range 2–7 nm show that there is no CO oxidation current (activity) observed at this potential.

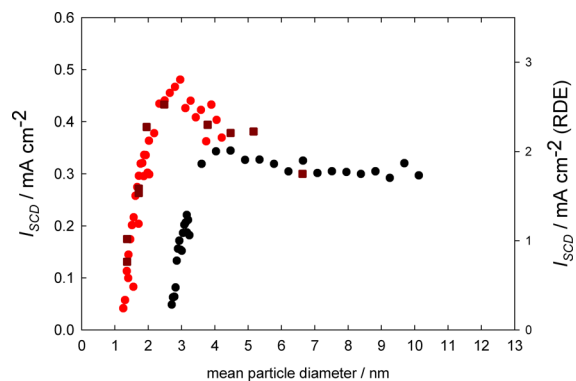




**FIGURE 5.** Particle size dependence of the specific current density for CO electrooxidation at  $0.5 V_{\text{RHE}}$  in  $0.5 \text{ M HClO}_4$  on titania supported gold particles.<sup>10</sup> The blue shaded area represents the maximum activity of carbon supported Au particles at  $0.5 V_{\text{RHE}}$ .

These results clearly indicate an optimum mean particle diameter for titania supported gold at 3 nm, and the titania support induces an activity to gold not observed on the carbon support. It is unlikely to be a coincidence that there is an enhancement in the activity induced by titania, and an optimum particle size at 3 nm for both electrocatalytic and heterogeneous CO oxidation (Figures 3 and 5). It is not unreasonable to explore a common origin for the induced activity, despite the fact that the oxidant differs in the two cases. In this regard, it is interesting to note that there is also a particle size dependence for CO electro-oxidation on the carbon-supported particles where the reaction takes place (at higher overpotential): The activity of the particles decreases with particle size,<sup>10</sup> and decreases most strongly at mean particle diameters below 3 nm. This has led to the suggestion<sup>10</sup> that there are two contributions to the overall behavior observed in the case of the titania supported gold (Figure 5). There is a support induced activity imparted by the titania which results in an increase in activity with particle size. Superimposed is a substrate independent decreasing activity associated with the intrinsic behavior of the small particles.

In order to support the proposition that there is a superposition of an intrinsic particle size effect on the substrate induced promotion of activity, Figure 6 shows the specific current density of gold particles supported on titania and carbon in carrying out oxygen reduction in  $0.5 \text{ M HClO}_4$ .<sup>26</sup> The oxidation currents are measured at  $0.3 V_{\text{RHE}}$ . For the carbon-supported gold, the activity is that observed on a continuous thin film of gold, and remains constant as the particle size reduces to ca. 4 nm, below which the activity



**FIGURE 6.** Particle size dependence of the specific current density for oxygen reduction in  $0.5 \text{ M HClO}_4$  at  $0.3 V_{\text{RHE}}$  on carbon (black circles) and titania (red circles) supported gold particles. Results from RDE experiments for titania supported gold are also shown (red squares).<sup>26</sup>

drops precipitously. In the case of the titania support, before dropping precipitously at particle sizes below ca. 2 nm, an increase in activity is observed over the carbon-supported gold particle activity, ascribed to the effect of the titania support. Note that measurements of the kinetics on RDE samples (red squares) on the titania support show that the trend in the kinetically limited currents are consistent with those measured on the array (red circles). The reduction in activity on both can be explained by an intrinsic particle size effect.

The deactivation of the CO electrooxidation<sup>9,10</sup> and oxygen reduction reaction<sup>26</sup> on both carbon and titania supported Au for mean particle diameters below ca. 3 nm (Figures 5 and 6) has led to the suggestion<sup>10</sup> of a common origin to the effect, and since it appears insensitive to the support. In this respect it is similar to the intrinsic particle size effect observed for the reduction of oxygen on carbon-supported platinum, which was ascribed to deactivation at small particle sizes (Figure 2) resulting from an increasing adsorption energy of the blocking hydroxyl group on small particles.

In the case of Au, however, it is the weak binding of O or OH which is correlated with the low activity for oxygen reduction<sup>18</sup> and one may expect qualitatively that an increasing binding energy on small particles may result in increasing oxygen reduction activity: Increasing the adsorption energy expected on smaller particles of gold<sup>27</sup> should lead to a higher activity. One may expect a similar argument for CO oxidation in that a stronger interaction of the oxidant may promote oxidation. Alternatively, if the adsorption energy of oxidizing surface intermediates was increased sufficiently strongly on Au that small particles were irreversibly oxidized, this could account for the observed deactivation in both oxygen reduction activity<sup>26</sup> and CO oxidation activity<sup>10</sup>

for small gold particles on carbon. There is, however, no evidence that such irreversible oxidation takes place:<sup>10</sup> Surface oxidation still takes place on carbon-supported gold at higher potentials and blocks oxidation (Figure 4). Perhaps the answer is associated with the activation barrier associated with water or oxygen activation on gold, and this barrier increases with decreasing particle size.

It has been suggested that it is the superposition of this "intrinsic" particle size effect (above) with a particle size dependence of support induced activation which is responsible for the maxima observed in CO oxidation<sup>9,10</sup> and oxygen reduction<sup>26</sup> on titania supported gold (Figures 5 and 6). It should be emphasized that the enhanced activity is unique to the titania support. In view of the extensive literature on the support induced activity for titania supported gold in heterogeneous catalyzed CO oxidation, and the common particle size dependence of activity with a maximum observed at ~3 nm (Figure 3) it was reasonable to seek a common explanation for the effects.<sup>9,10</sup> Promotion of the heterogeneous catalysis of CO oxidation of gold by reducible oxides, most notably titania frequently exhibit the maximum activity at 3 nm particle size.<sup>21,28–30</sup> In the comparison with the similar particle size dependence in electrocatalytic CO oxidation (Figure 5) it is important to keep in mind that the oxidant is provided through the activation of water rather than oxygen. The models proposed to account for activation in heterogeneous oxidation, which can be considered to explain the electrocatalytic promotion, can be divided into three main promotional mechanisms.<sup>10</sup>

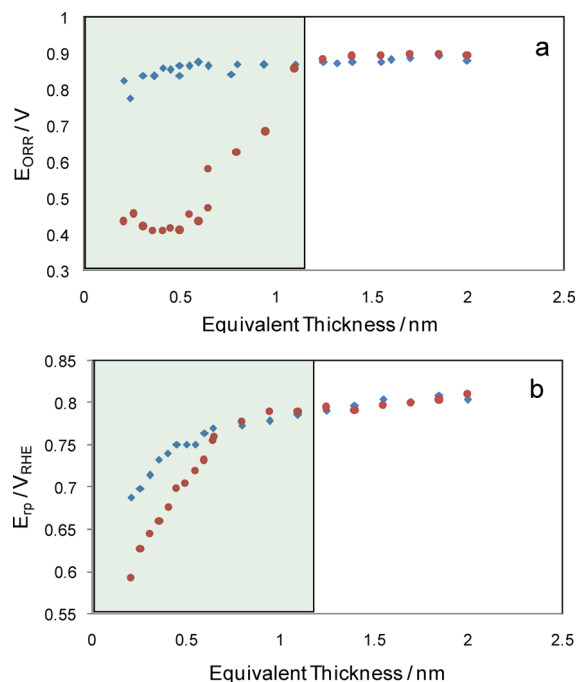
The morphology of the gold particles induced by titania may lead to changes in concentration of surface reactant species, or the lowering of activation barriers. This could lead in the case of electrooxidation to a higher concentration of adsorbed CO, or sites that promote the activation of water to produce a surface hydroxyl species. There is indeed strong evidence of a surface structural dependence in CO electrocatalytic oxidation on Au.<sup>24</sup> There was no evidence, however, for different morphologies of Au particles on carbon and titania supports (Figure 1).<sup>5</sup>

The electronic structure of gold is modified by titania resulting in changes in concentration of surface reactant species, or the lowering of activation barriers. This can be a result of either substrate-induced strain in the Au particle or charge transfer. Indeed, the maximum activity of model supported gold particles<sup>21</sup> at 3 nm in diameter (Figure 3) as correlated with a band gap of 0.2–0.6 eV was measured by STS. It is not possible to exclude the operation of an electronic effect in the case of electrocatalysis. However, the

activity is certainly not correlated with the existence of atomically dispersed gold (activity would be observed at the lowest Au effective thicknesses),<sup>31</sup> or with monolayer or bilayer structures (which are not formed here).<sup>21,32</sup> The possible involvement of partially oxidized clusters,<sup>33,34</sup> however, may be an explanation for the continued activity of the gold particles supported on titania even above potentials where surface oxidation normally blocks the reaction (Figure 4).

Spillover of oxygen from the support at the particle support interface, or active sites at the particle perimeter itself may be responsible for the enhancement of CO oxidation. Titania in an aqueous environment will be hydroxylated, depending on the pH. While there is no evidence that additional water can be activated to produce surface hydroxyls at low potential, it is not impossible that hydroxyl groups on the titania are available through spill over at the gold surface, circumnavigating the high overpotential necessary to activate the water on the gold. In this respect, it is interesting to note that the overpotential for CO oxidation in alkali electrolyte,<sup>23</sup> where there is a higher concentration of the adsorbed OH specifically adsorbed at the surface, is at potentials similar to those observed for the titania activated gold particles. The possibility of a high activity induced by the activation of water at perimeter sites of gold particles cannot be ruled out<sup>9,10</sup> at least insofar as the maximum in activity as predicted by such a model was at a particle diameter of ~2.5 nm.

Titania as a support also has a considerable effect on the ability of platinum to oxidize CO or reduce oxygen.<sup>35,36</sup> Figure 7a shows the onset potential  $E_{\text{ORR}}/V_{\text{RHE}}$  for oxygen reduction on carbon and amorphous titania supported platinum.<sup>35</sup> The particle size was not measured at the time in these experiments, and so the activity is plotted as a function of the equivalent thickness of Pt on the support. However, below an equivalent thickness of ca. 1.1 nm (shaded region), the platinum forms discrete particles (observed in TEM) in the range 1.5–7 nm (smallest at the lowest equivalent thickness), and above the equivalent thickness of about 1.1 nm the particles have nucleated to produce a continuous thin film. As a measure of catalyst activity, the onset potential  $E_{\text{ORR}}$  is plotted (rather than a specific current density at a particular potential). As the equivalent thickness is reduced to produce particles on carbon, a small reduction in  $E_{\text{ORR}}$  is observed (a small increase in the overpotential) consistent with the lowering of the specific activity (at constant potential) shown for the same system in Figure 2b. In the case of the amorphous titania support, as soon as particles are formed, a very large reduction of  $E_{\text{ORR}}$  is observed (a large increase in the overpotential): This corresponds to a significant poisoning of



**FIGURE 7.** (a)  $E_{\text{ORR}}$ , the potential at which  $0.01 \text{ mA cm}^{-2}$  is reached during oxygen reduction, for carbon (blue) and titania (red) supported platinum. (b) The oxide reduction peak potential ( $E_{\text{tp}}$ ) (open circles) for carbon (blue) and titania (red) supported platinum. The dependence is shown as a function of the effective thickness of platinum, and particles are produced at low thicknesses (shades region).<sup>35</sup> Reproduced by permission of the PCCP Owner Societies.

the activity of the platinum by titania. In the case of both carbon and titania supports, a concomitant reduction in the platinum surface reduction potential  $E_{\text{tp}}/V_{\text{RHE}}$  is observed, with a slightly larger reduction in the case of the titania support: This is normally interpreted (section 3) as a more stable surface oxygen species at the surface, and more stable hydroxyl groups will block (deactivate) oxygen reduction. It is therefore tempting to use this explanation to account for the larger oxygen reduction deactivation on the titania support, where the lower potential for surface reduction is found (Figure 7b). It has been pointed out,<sup>35</sup> however, that such an explanation is not sufficient to explain the differences between the supports, since for a large particle size region where the oxygen reduction is strongly deactivated on the titania (between an equivalent thickness of 0.6 and 1.1 nm),  $E_{\text{tp}}$  is very similar on the two supports.

CO oxidation in stripping voltammetry is also shown to be significantly hindered on small platinum particles supported on titania,<sup>36</sup> over and above the effect of the intrinsic effect of small particle sizes observed on the carbon support.<sup>6,36,37</sup> With respect to the titania induced changes in oxygen reduction on platinum particles, this change in the CO oxidation behavior and the poisoning of the oxygen reduction (Figure 7) have

been associated with an increased irreversibility of the surface redox process induced by the substrate.<sup>36</sup> This is a kinetic effect that results from the hindering of both surface oxidation (from water or oxygen) and surface reduction reactions. This may be a result of either differences of particle morphology, or electronic perturbation of the platinum, by the titania. There is no simple relationship<sup>35</sup> between the surface reduction potential and the activity of the supported particles (Figure 7). The alternative possibility of spill over of hydroxyl groups from titania poisoning the platinum surface for oxygen reduction, however, is not consistent with the observation<sup>36</sup> that CO oxidation is poisoned in stripping voltammetry. CO oxidation is hindered (moves to higher overpotentials) on titania supported platinum particles, that is, where such spill over would negate the need for water activation on the platinum itself, which dominates the high overpotential on the extended platinum surfaces.

## 5. Prospects for the Development of Supported Metal Electrocatalysts

The ultimate goal of understanding the particle size and support effects is to develop more cost-effective and robust electrocatalysts. The oxygen reduction catalysts in PEMFC fuel cells are a good example; the efficiency of the fuel cell is limited by the activity of platinum-based electrocatalysts for oxygen reduction. In addition, the particle size dependence described above limits the cost effectiveness of the platinum through dispersion. Additionally, the carbon support is prone to oxidation at the cathode resulting in long-term instability, and alternative supports are being sought. One of the alternatives being considered is titania, since it would be stable under the oxidizing environment of the cathode. The results on the model catalysts have shown, however, that titania can not only produce an enhancement of activity, but can also result in a considerable reduction in activity.

In the light of this result, one may at first be pessimistic concerning the use of titania as a support for platinum as an oxygen reduction catalyst. It appears, however, that the bulk morphology, oxide stoichiometry, and the doping of the bulk materials to impart conductivity in a practical electrocatalyst all influence the activity of the catalyst.<sup>38</sup> Keeping the particle size constant at 2 nm, it was shown that the overpotential for oxygen reduction on both crystalline titania, and rutile was significantly reduced over that found for the amorphous support. Niobium is also considered as a good candidate for imparting electrical conductivity to titania in a practical catalyst. It was also shown that there is an optimum in the catalytic activity as a function of the Nb

doping of the oxide. It is clear that the optimization of the particle size and support in platinum-based catalysts for oxygen reduction, even in the absence of considerations of robustness to sintering over longer periods, is not straightforward. It is also interesting to note in the search for alternative supported metals, in the case of Pd on carbon, both the specific and the mass activity of the dispersed metal continually decreases with particle size.<sup>8</sup>

A better understanding of the origin of the support induced modification of the metal nanoparticle electrochemistry is essential for any a priori development of effective dispersed electrocatalysts. While there are parallels to be drawn between electrocatalysis and heterogeneous catalysis which may help our understanding, because the mechanisms are responsible for substrate effects in heterogeneous catalysts are uncertain, it is not easy to draw clear conclusions through such comparison. In the case of electrocatalysis, a better understanding of the mechanisms responsible for particle size and support effects will only come from detailed studies on model nanoparticle catalysts in a variety of electrolytes, combined with both ex-situ and in situ characterization of the structures.

#### BIOGRAPHICAL INFORMATION

**Brian Hayden** obtained his Ph.D. in Bristol in 1979 in Surface Science. He was a postdoctoral fellow at the Fritz Haber Institute of the Max Planck Society (1979–1984), developing surface sensitive optical spectroscopies, and a lecturer at the University of Bath (1984–1988), using supersonic molecular beam to study surface reaction dynamics. He became lecturer at the University of Southampton in 1988 where he has held a Personal Chair since 1995. Present research interests include surface science and surface electrochemical studies in modelling surface reactions and processes relevant to heterogeneous catalysis and electrocatalysis, and high throughput methods for materials development. He is a founder (2004) and Chief Scientific Officer of Ilika plc involved in materials discovery for the electronics and energy sectors using high throughput methodologies. He is author of over 125 refereed papers and over 12 active patents for low temperature fuel cells and solid state Li-ion batteries. He is a Fellow of the Royal Society of Chemistry and the Institute of Physics.

#### FOOTNOTES

The author declares no competing financial interest.

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