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Oxygen Reduction Reaction

The Effect of Size on the Oxygen Electroreduction Activity of Mass-Selected Platinum Nanoparticles**

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The use of proton exchange membrane fuel cells (PEMFCs) could become widespread by improving the kinetics of the oxygen reduction reaction (ORR), where Pt is the typical electrocatalyst. Improvements to the reaction kinetics, however, require understanding of the fundamental factors that control the ORR activity of Pt, in particular the dependence of the ORR rate as a function of the particle size. This has been the topic of numerous studies in the last few decades.[1] Most articles report an increase in the specific activity with increasing particle size. Nørskov, Rossmeisl, and co-workers rationalized this phenomenon using density functional calculations.[2] They proposed that the active sites for the ORR are located on the terrace sites of Pt. Undercoordinated sites at terrace edges or steps should provide a negligible contribution to the activity, because they bind strongly to the O-containing intermediates of the ORR.[2b,d] The increased population of undercoordinated sites on small nanoparticles (especially below 5 nm) explains their lower activity. Moreover, they predicted that the activity of nanoparticles with diameters greater than around 10 nm should be equal to that of extended surfaces.[2d]

Recently, Arenz and co-workers raised doubts regarding the reliability of earlier measurements of the ORR activity on Pt nanoparticles on high surface area supports because of the influence of uncompensated resistance and support capacitance.[1e] By correcting for these effects, they observed results that could not be explained by the theoretical model described above, namely that 1) there was no size effect on the ORR activity for Pt nanoparticles with a diameter below 5 nm, 2) Pt-black particles with a diameter of around 30 nm exhibited a two-fold improved ORR activity relative to particles with a diameter of 5 nm, and 3) the extended Pt surfaces showed a two-fold improved ORR activity relative to Pt-black particles. Also, some stepped Pt single-crystal surfaces, for example, Pt(331), actually exhibit an improved oxygen reduction activity relative to Pt(111),[3] even though the stepped crystals have a high density of undercoordinated sites. The higher activity of the stepped single crystals, could, at first glance, seem to be in contradiction with the theoretical models described above.[2b,d] However, it turns out there are sites on these single crystals, presumably on the terrace sites, that bind more weakly to O-containing species than Pt(111), which explains their higher activity[4] as discussed in greater detail elsewhere.[4b] Nonetheless, it is unknown whether this phenomenon, observed upon extended surfaces of Pt, should occur on nanoparticulate catalysts. In summary, the controversies regarding the ORR activity of Pt nanoparticles strongly motivate the use of model systems, with control over variables such as the particle size, dispersion, and the influence of the support material.

Herein, we investigate the effect of size upon the ORR activity of Pt particles with diameters ranging from 2 to around 11 nm. The particles prepared through the gas aggregation technique, mass-selected, and deposited directly onto planar glassy carbon supports under ultrahigh vacuum (see details in the Supporting Information). By supporting the catalysts on planar surfaces, we avoid the need to correct for capacitive currents. By using mass-selected particles, we avoid effects from surfactant molecules that would be present on particles produced by chemical synthesis methods. Earlier studies taking similar approaches to ours have restricted the nanoparticle size to below 3.5 nm, albeit without mass selection.[1i] By encompassing a larger size range in the current study, we make a link between extended surfaces and nanoparticulate catalysts.

To determine whether the active sites for the ORR are located on terrace sites, as predicted by theory, we have quantified the proportion of the terraced surface area of the Pt nanoparticles by performing in vacuum CO temperature programmed desorption (TPD) experiments. Figure 1 shows the CO desorption spectra obtained from four different samples, in comparison to the particle size histograms and representative transmission electron microscopy (TEM) micrographs.

The features of the CO TPD spectra on Figure 1 are redolent of those obtained on Pt single crystals,[5] despite variations in the nanoparticle morphologies and their unknown facet terminations. On the basis of the single-crystal studies, we have fitted the TPD spectra to three Gaussian

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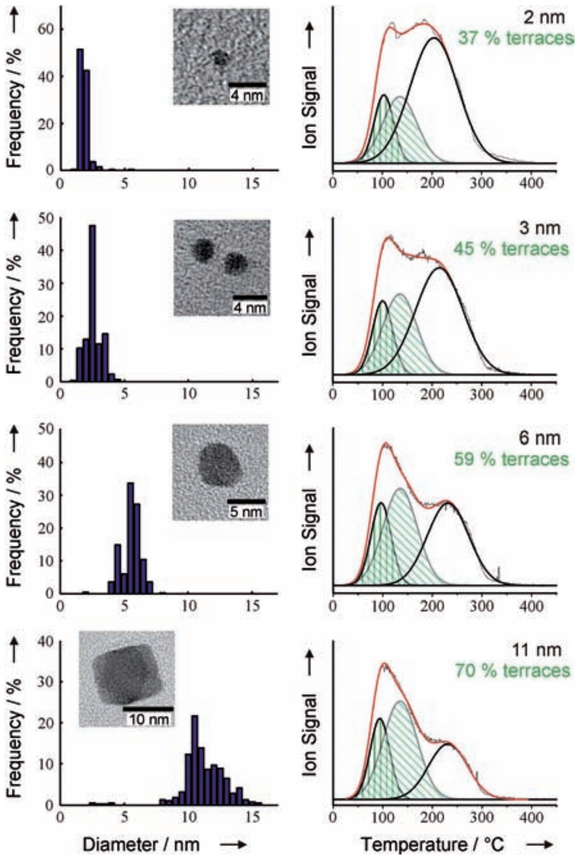

Figure 1. Nanoparticle size distributions and the associated CO desorption profiles of Pt/SiO_2 samples for particle sizes of 2, 3, 6, and 11 nm. Included with each TPD profile are the integrated proportions of the terraced particle surface area.

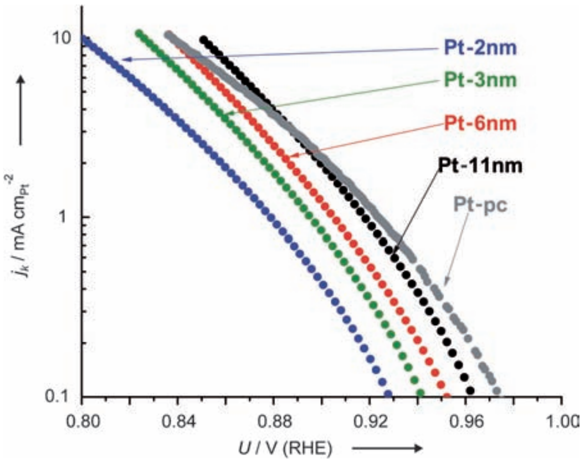

Figure 2. ORR Tafel plots of Pt-pc (grey), Pt-2 nm (blue), Pt-3 nm (green), Pt-6 nm (red) and Pt-11 nm (black) extracted from polarization curves recorded in oxygen-saturated electrolyte solutions (0.1 M $HClO_4$) at 50 mV s^{-1} and 1600 rpm.

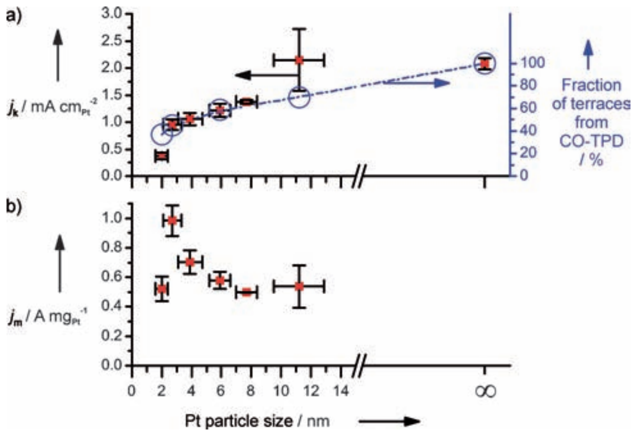

Figure 3. a) ORR kinetic current densities and b) mass activities at 0.9 V (reversible hydrogen electrode, RHE) of different particle sizes, from cyclic voltammograms in a O_2-saturated 0.1 M $HClO_4$ solution at a sweep rate of 50 mV s^{-1} and 1600 rpm at 23 °C. The blue circles in plot (a) represent proportions of the terraced particle surface area calculated from CO TPD profiles.

functions: a low-temperature peak, corresponding to CO bound weakly at high coverages on the terrace sites, an intermediate-temperature peak at around 400 K corresponding to more strongly bound CO at low coverages on the terrace sites, and a high-temperature peak extending to 600 K, corresponding to CO bound strongly to undercoordinated sites. A similar deconvolution of oxygen TPD curves into Gaussian functions has been used to interpret the coordination-dependent binding interactions of oxygen on stepped Pt surfaces.[6] We used the fit functions to determine the proportions of the terraced surface area (see the Supporting Information). Evidently, the fraction of terrace sites increases with increasing particle size, which is in line with our expectations.

The ORR activity of the glassy carbon-supported Pt nanoparticles and a polycrystalline Pt sample (Pt-pc), have all been measured by voltammetry in a 0.1 M $HClO_4$ electrolyte solution using a rotating ring disc electrode (RRDE) assembly (see the Supporting Information). Tafel plots of ORR specific activity are shown in Figure 2. Clearly the ORR specific activity increases with the particle size. The ORR specific activity and mass activity for the different catalysts studied is plotted in Figure 3. Our results agree well with earlier theoretical predictions (see the Supporting Information). In particular 1) extended Pt surfaces exhibit the same activity as nanoparticles with a diameter of 11 nm, and 2) there is a four-fold increase in the ORR activity going from 2 nm Pt particles to extended surfaces.[2b,d] Moreover, we confirm that the Pt mass activity for the ORR shows a maximum for a particle size of 3 nm.[1a,2d]

The electrochemical experiments are also supported by the CO-TPD results: the ORR activity approximately scales with the proportion of terraces, as shown in Figure 3. The main outlier to this trend, given the experimental error, is the smallest nanoparticle with a diameter of 2 nm. This modest discrepancy could be explained by the differences in the surface structure induced by the electrochemical environment.[2d] Small particles are more susceptible to corrosion than the larger nanoparticles.[7] Corrosion would reduce the lateral size of each exposed facet and increase the number of undercoordinated sites.[2d]

Our study complements earlier investigations of industrial catalysts, which generally reported lower ORR activities[1a,d,e] than those reported here. We consider that our experimental conditions provide a more accurate measure of the intrinsic activity of Pt nanoparticles. We hypothesize that the high activity of our samples compared with commercial catalysts is due to the more idealized environment: high diffusion of oxygen and the absence of surfactant molecules.

In summary, we have shown that the specific activity of the oxygen reduction reaction on Pt nanoparticles decreases with decreasing particle size, with a maximum in mass activity for particles with a diameter of 3 nm. The ORR activity roughly correlates with the proportion of the terrace sites. We conclude that the active sites for the ORR are only located on the terrace sites of the nanoparticles, in agreement with earlier theoretical predictions.[2b,d] The close agreement between experiment and theory confirms that we are starting to build a more coherent picture of the factors that control the activity of nanoparticles for the ORR and other (electro)-catalytic reactions.

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