Quantitative analysis of core-shell catalyst nanoparticles for industrial applications

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Abstract. Pd@Pt core-shell designed nanoparticle catalysts have been shown to dramatically increase the activity and selectivity of the oxygen reduction reaction in fuel cells. Aberration corrected electron microscopy offers the spatial resolution and chemical sensitivity to unlock these structures at the atomic scale. Understanding the particle size, shape and the exact nature of the shell coverage (whether it is full, partial or whether the particle is alloyed) is vital to understanding their behaviour. This paves the way for even more effective catalyst designs. We present a semi-statistical investigation into the size, morphology and bimetallic content of various core-shell particle designs, pre- and post- fuel cell cycling, using high resolution HAADF STEM and EDX. In addition, careful quantitative analysis of our datasets will allow us to extract information, not only of the morphology, but also the thickness and coverage of the particle shells. We compare this with chemical findings about activity and selectivity to understand how shell coverage and content affect catalytic activity.

1. Introduction

Though proton exchange membrane fuel cells are one of the promising candidates for meeting the demand of our increasing energy consumption, their effectiveness is limited by the oxygen reduction reaction at the cathode. Pd@Pt core-shell designed nanoparticles electrocatalysts are designed such that the precious Pt metal only comprises a thin outer shell and the core is filled with a different element. The combination alters the electronic structure of the Pt and the catalyst shows an increase in activity and selectivity [1].

Understanding the structural details of these industrial catalysts is vital to understanding their function and aiding in improved designs. However, such small and complicated structured materials are difficult to visualise directly at high resolution, while statistically averaged methods like extended X-ray absorption fine structure (EXAFS) assume homogeneity across a large number of samples and thus lacks detailed information about individual particles. With the common-place usage of aberration correction, it is now readily possible to directly image the atomic configuration of small nanoparticles.

While energy dispersive X-ray (EDX) spectroscopy can offer an unambiguous identification of composition, the lack of spatial resolution and poor signal to noise, especially for small beam sensitive samples, makes it insufficient as a technique for detailed analysis of the catalytic surface of the nanoparticles.
High angle annular dark field scanning transmission electron microscopy (HAADF STEM) has often been chosen for such heavy elements on light supports for its strong correlation between atomic number and imaged intensity, known as Z contrast and also the incoherent nature of its detection which greatly simplifies image interpretation [2]. However, though it offers many advantages, meaningful quantitative compositional information is challenging to extract because intensities are dependent on both composition and thickness. Recently, much progress has been made towards quantification of HAADF STEM by calibrating the detector such that the images are scaled to the incident beam [3], enabling full comparisons with simulations. Analysis by cross section can then be applied to identify the composition of individual atomic columns [4]. In this paper we will investigate how quantitative analysis of HAADF STEM images can lead to better understanding of both the size distribution and also structure of various catalysts.

2. Method
Core-shell catalysts were prepared by pre-forming Pd cores of size 5nm on a support of carbon black, followed by Pt deposition from a Pt(acac)₂ pre-cursor by proprietary methods [5]. Several thicknesses of Pt shell were considered: ½ monolayer (ML), 2ML and 4ML, where a monolayer is considered to be a complete coverage of the Pd core by one atom thick of Pt. Catalysts were investigated pre-cycling (as made) and post- fuel cell cycling of 1000 hours in H₂SO₄ as described elsewhere [6]. Calibrated HAADF STEM images and EDX data were collected using a JEOL-2200MCO [7] and a JEOL ARM-200F at 200kV and 80kV. Simulations were carried out using an absorptive potential multislice code.

3. Size Distribution
Particle size distribution was estimated from medium magnification HAADF STEM images, each of various catalyst designs pre- and post- cycling (Table 1). Imaging was carried out on a JEOL2200-MCO at 200kV. Both major and minor axes of particles were measured to account for the non-circular shapes. In each sample 200+ particles though those that were out of focus and obfuscated by other overlapping particles were discarded. In total 40+ measurements were made for each sample. The catalysts with thicker shell designs had a larger average diameter but also a larger range of sizes. From the micrographs it is clear that there are clusters of very small (< 2nm diameter) particles in the 2ML and 4ML designed samples. EDX analysis identifies them as pure Pt. Post cycling, the particle size distribution of the 2ML does not change and the small clusters are still present, suggesting that the particles are reasonably stable, as confirmed by stability cycling tests.

Unfortunately, it is difficult to extract compositional information at this low resolution by comparisons of HAADF intensities alone as those particles that oriented on zone axis channel the beam down the columns and thus appear brighter, thus making intensity not only dependent on thickness and composition but also on orientation.

| Design / state   | Average particle diameter /nm | standard deviation /nm | error /nm |
|------------------|-----------------------------|------------------------|-----------|
| ½ ML / pre-cycled| 4.9                         | 1.2                    | 0.2       |
| 2ML / pre-cycled | 5.8                         | 2.3                    | 0.3       |
| 4ML / pre-cycled | 6.1                         | 1.9                    | 0.3       |
| 2 ML / post-cycled| 5.5                         | 2.1                    | 0.3       |

4. Shell Coverage
Catalytic processes are primarily concerned with the surface atoms of nanoparticle catalysts; therefore it is important to understand the precise nature of the shell coverage and thickness.
4.1. HAADF and EDX

EDX of small nanoparticles suffers from low signal to noise and damage due to the long collection times necessary. We carried out EDX maps at 200kV on a JEOL ARM-200F with a 48pA probe and with a fast cumulative scan to minimise damage. Combined with the spatial resolution of HAADF, it is possible to ascertain the distribution of Pt and Pd in the nanoparticle.

A cumulative EDX spectrum (Figure 1b) of the ½ ML catalyst nanoparticle (shown in Figure 1a) showed that both Pt and Pd were present. The higher signal to noise ratio afforded by combining the spectra from each pixel of the whole map allows for a meaningful quantification to be done in order to determine the composition ratios of Pt and Pd in the nanoparticle. A simple Cliff-Lorrimer k-factor quantification suggests an 80/20 atomic% ratio of Pd/Pt, which corresponds to the catalyst design for ½ML coverage. However, there is no information about the uniformity of the coverage because the spectrum was integrated over the whole particle.

The normalised intensity of the HAADF image (Figure 1a) suggests that there is very little Pt in the particle as the intensity is mostly around 5% of the incident beam. There is sufficient intensity at the edges to indicate thin Pt coverage. It is unlikely to be purely Pd as the discontinuous change in intensity seen would mean a large thickness variation over a small lateral distance.

**Figure 1a)** Calibrated HAADF STEM image of a ½ML designed particle, where the scattering intensity is mapped as a function of incident probe current. The strong scattering of the Pt decoration can be clearly seen on the edges of the particle, the intensity is too strong to be Pd. Step-like edges between the (100) and (111) faces are clearly visible (red box) which suggest non-perfect faceting, commonly seen in nanoparticles. **b)** EDX collected from the whole particle shows the presence of both Pt and Pd. A simple Cliff-Lorrimer k-factor quantification suggests 80/20 atomic% ratio of Pd/Pt which corresponds with the catalyst design for ½ML coverage.

4.2. HAADF and Image Simulations

As all images are 2D projections of 3D objects, even the seemingly clearly core-shell nanoparticle may in fact not be. The 2ML designed particle in Figure 2a shows a large uniform intensity region when viewed along the [110] direction perhaps suggesting large (110) facets. Facets of (110) are thermodynamically less favourable in fcc structures than (111) and (100). However, it is possible that a large (110) facet is terminated by stepped edges onto (100) and (111) faces. Evidence of this is seen in projection (Figure 1a and 2a, red squares)

By imaging as a fraction of the incident beam using a calibrated detector and known probe currents [7], it is possible to compare experiment to simulation absolutely. Since nanoparticles are highly beam-sensitive, calibrating experimental parameters while imaging can lead to damage and makes
accurate quantification of the original sample impossible as the sample is changed by the beam. Thus analysis of the individual columns by the absolute cross section of scattering [4] yields a powerful parameter robust method of comparing individual columns to simulations.

![Figure 2](image)

**Figure 2a)** Calibrated HAADF image of a core-shell nanoparticle with 2ML design pre-cycling showing clear core-shell structure. The two neighbouring columns highlighted by the red arrows suggest a composition change as the difference in intensities (shown in the line profile) rule out a cliff edge due to thickness. Analysis by cross section suggests edge decoration on steps by Pt. Facets terminated by step-like structure can be seen in the red box. **b**) Atom model (scaled down) showing sites of preferential Pt deposition at step-like edges.

Comparison by cross section to absorptive potential multislice simulations [4] reveals possibilities for compositions in neighbouring columns (marked 1 and 2). Column 1 could either be 70 Pd or (40 Pd + 4Pt). Column 2 could be 45Pd or (20Pd + 2Pt). Since it is thermodynamically unlikely that neighbouring columns would differ in height by 25 atoms, it is more reasonable to conclude that the compositions are 45 Pd for column 2 and (40 Pd + 4Pt) for column 1. The intensity comprising the “shell” is likely due to preferential deposition of Pt at step-like edges of the nanoparticle (shown schematically in Figure 2b).

**5. Conclusions**

Understanding the precise size, morphology and structure of these core-shell nanoparticles can be achieved through a combination of calibrated HAADF imaging, comparison with simulation and low voltage EDX analysis. Medium magnification HAADF STEM yielded particle size distributions for various catalyst designs, with the ½ ML designs being the most uniform in size distribution and the 2ML design the least uniform. The 2ML design did not show significant change in size or distribution post cycling, confirming the design’s electrochemical stability. However, we show that though the 2ML Pt shell on Pd core design shows the best electrochemical stability and catalytic activity and selectivity, its functionality is not due to a purely core-shell type structure but a combination of step type edge decoration of Pt and small sub 2nm Pt clusters.

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