TEM-based Pair Distribution Function study of interatomic distances in C-supported Pt

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Abstract. The interatomic distances have been characterised for a Pt on Carbon based fuel cell catalyst studied by analysing the atomic pair distribution functions (PDF) obtained from electron diffraction (ED) data taken in a transmission electron microscope (TEM). The experimental PDFs have been compared with atomistic models to examine C-C and Pt-Pt interatomic distances. Further, the models have been refined by reverse Monte-Carlo simulations (RMC) based on the experimental PDF, enabling the investigation of Pt-C interatomic distances. This has demonstrated the existence of an interatomic contact between the Pt and C.

1. Introduction

Most TEM-based studies of Pt on Carbon type fuel cell catalysts only focus on the particles while considering the supporting media as background. However, the Pt-C interaction has an important role on the stability of the system under catalytic conditions, as it affects diffusivity of the Pt on carbon. This in turn causes changes in size, shape, dispersion, and crystallographic ordering of nanoparticles. This interaction needs to be understood at the atomic level. However, it is very challenging to atomically observe Pt particle-carbon interaction by the popular high-resolution (HR)TEM and aberration-corrected scanning (S) TEM due to difficulties of getting a particle edge on in an amorphous structure.

For amorphous/disordered structures, electron diffraction (ED) yields diffuse scattering rather than sharp Bragg peaks, similar to X-ray/neutron diffractions. Subsequent Fourier analysis of the diffraction data gives a new representation of data in real space, called atomic pair distribution function (PDF), which is actually the function of interatomic distances, resulting in the probability densities of finding atomic pairs [1]. Beside X-ray/neutron diffractions, ED data can also be used to achieve PDFs [2]. More quantitative ED-based PDFs can be obtained by appropriate background corrections and scaling using the scattering factors for electrons [3].

Here we have used the same ED based methodology to study Pt nanoparticles on amorphous carbon support. The experimental PDF has been compared with the theoretical PDFs calculated from atomistic models of Pt supported on disordered carbon. These models have been then refined in RMC simulations in order to extract the Pt-C interatomic pair distributions.

2. Methods

2.1. Experimental methods of TEM-based PDFs

The imaging and ED experiments of Pt nanoparticles supported on carbon was performed using the JEOL ARM200CF TEM operating at 200 kV acceleration voltage. The sample was imaged in STEM mode, including bright field (BF) and high angle annular dark field (HAADF) signals. Using the Orius SC200D CCD camera, selected-area ED data was acquired (without any beam stoppers) for the
momentum transfer \((Q)\) range from \(Q_{\min} \sim 2 \text{ Å}^{-1}\) to \(Q_{\max} \sim 14 \text{ Å}^{-1}\). The routines to obtain the PDF from the ED data were carried out using the software SUePDF [3].

### 2.2. Observations and modeling methods

In order to build appropriate models which are as close to reality as possible, HRSTEM images of the C-supported Pt, shown in Figure 1, were examined. The particle predominant sizes are between \(~2 – 5\) nm. The C support, as seen in Figure 1(a, b), exhibits some disordered graphitic structures. The metallic Pt, in contrast, exists in two forms: fcc-crystalline nanoparticles and individual atoms (Figure 1(b, c)). It is noted that, the Pt atomic dispersion may suggest a significant interaction between the metal and the C-support. The particles are generally based on truncated octahedral (TO) symmetry in shape. Their landing direction onto the C support appears to be random. The direction can be the basal planes, the edge planes, or planes in between these, due to the disordered nature of the C-support.

Following the observation of the particles and the C-support, two different atomistic models of C-supported Pt were built. The first model consists of a 481-atom TO-based Pt particle (~2.5 nm) landing toward the basal planes of a 528-atom graphite structure. The second model is larger, having a 1127-atom TO-based Pt particle (~3.5 nm) supported vertically to the edge planes of a 2546-atom disordered graphitic structure. To build the initial Pt-C contact in both models, Pt and C atoms were randomly moved into a range of 2.0-2.4 Å.

These models were used as the initial inputs for RMC simulations [5, 6] where the atomistic structures are refined to fit better with the experimental data. In our RMC simulations, the atoms of both Pt and C were allowed to move and the calculation of theoretical PDFs included the convolution with the termination function [4] caused by the limited experimental \(Q\) range. To maintain the physical meaning of interatomic distances, minimum distance constraints were set for Pt-Pt, Pt-C and C-C pairs as 2.55 Å, 2.00 Å and 1.15 Å, respectively.

### 3. Results and discussion

The ED intensity profile of the C-supported Pt is shown in Figure 2a, which has been background-subtracted and scaled using the electron scattering factors for Pt and C. The inset of Figure 2(a) shows the reconstructed ED ring pattern, cropped to a dimension of 20 Å\(^{-1}\). The corresponding PDF is shown in Figure 2(b) with 6 first peaks labelled as P1-P6. The peak P1 (1.41 Å) is clearly attributed to the 1\(^{st}\)-shell C-C distances. The peaks P3 (2.77 Å), P5 (3.87 Å) and P6 (4.86 Å) can be identified for the 1\(^{st}\)-shell, the 2\(^{nd}\)-shell (lattice constant) and the 3\(^{rd}\)-shell Pt-Pt distances, respectively, of the fcc structure. The minor peaks P2 (2.28 Å) and P4 (3.37 Å) are less clear to identify because they are more sensitive to the termination ripples [4]. However, the range \(~2 – 2.4\) Å where P2 is located may contain the signal of interatomic spacing between Pt and C atoms. Models of C-supported Pt, allowing extraction of Pt-Pt,
C-C and Pt-C partial PDFs (free from termination ripples) will then be necessary to interpret all of the PDF peaks.

**Figure 2.** (a) Background-subtracted and normalized ED intensity profile and the corresponding reconstructed ring pattern (inset); (b) The corresponding PDF with peak identification (inset) for P1-P6.

Figure 3 shows the theoretical PDFs of basal-plane supported (Figure 3(a)) and edge-plane supported (Figure 3(b)) models compared with the experimental PDF, before and after the RMC simulations. It can be seen that most of the experimental PDF peaks are correlated with the theoretical ones, confirming the reliability of both the experimental data and the models. However, the initial basal-plane graphite supported model has lower fitness compared with the edge-plane supported one which is based on a disordered carbon structure, due to the disordered nature of the actual C-support (see Figure 1). The fitness of both models has been improved after the RMC refinements, as shown in the bottom panels of Figure 3a & b, together with the corresponding RMC-refined atomistic visualizations (insets).

**Figure 3.** Experimental PDF (orange-solid) compared with theoretical PDFs of initial models (purple-dot) and RMC-refined models (blue-dot), including model visualizations (inset) of Pt (blue) and C (brown) atoms: (a) Basal-plane supported model; (b) Edge-plane supported model.

The Pt-Pt, C-C and Pt-C partial PDFs are shown in Figure 4, exhibiting how the different interatomic distance distributions have been refined after the RMC simulations. The fcc pattern was maintained in the refined Pt-Pt PDFs, consistent with the HRSTEM observation. The C-C PDF of the basal-supported
model has a major change from graphite to a disordered graphitic structure. The peaks emerging at ~2.25 Å in the refined Pt-C PDFs of both models clearly indicate a Pt-C interatomic contact between the metal and the support. It is noted that, the Pt-C interatomic peak is more pronounced in the basal-plane supported model compared with the edge-plane supported one, consistent with the fact that the basal planes have more C atoms per unit area than the edge planes do. The strongest peaks in the refined Pt-C PDFs, located at the same position with the first Pt-Pt peak (~2.77 Å), are explained as the indistinguishability between Pt and C atoms during the RMC simulations in the region around 2.77 Å. These peaks correlate with the intensity decrease in the refined first Pt-Pt peaks and the shifts of the refined C-C second peaks, observed in both models.

4. Results and discussion
TEM-based PDF analysis has been carried out on Pt nanoparticles supported on disordered graphitic carbon. Two models of Pt nanoparticles supported on graphite basal planes and edge planes of disordered graphic carbon have been built and refined in RMC simulations to interpret the experimental PDF. A Pt-C interatomic contact, peaking at ~2.25 Å, has been revealed from both RMC-refined models. The work has also presented the interatomic-distance measurements of the Pt nanoparticles and the disordered graphitic C-support.

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