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Crystallite Size Analysis of Supported Platinum Catalysts by XRD

X-Ray diffraction (XRD) is often used in combination with transmission electron microscopy (TEM) and, for fuel cell electrocatalysts, electrochemical methods such as cyclic voltammetry, in the characterisation of supported platinum catalysts. Crystal/particle size information obtained from fresh or aged samples generally correlates with catalytic activity.

Average Pt crystallite size is frequently calculated from XRD peak broadening using the Scherrer equation (1). As a bulk technique, XRD has certain advantages over TEM digital processing of particles (2). Direct comparison of the resulting XRD volume-weighted size of the crystallite with the TEM number-weighted size of the particle (often formed from several primary crystallite grains) is however often erroneously made in the literature.

In order to obtain a realistic determination of Pt crystallite size by XRD, the effects of Pt particle shape, microstructure and very small, so-called 'XRD amorphous' Pt must be considered during X-ray analysis. The effect of interference from supports of high surface area and the presence of poorly crystalline oxidic Pt phases must also be considered. In addition, super-Lorentzian peak shapes are often encountered (Figure 1), which are a result of either a broad lognormal or multimodal Pt crystallite size distributions (3).

Issues outlined above have been successfully addressed for Pt/C catalysts by using the small angle X-ray scattering (SAXS) technique (4), as SAXS is well suited to size determination of very small particles (< 3 nm diameter). Although SAXS measurements can be made either in the laboratory or at a synchrotron facility, instrumentation is not commonplace, and data analysis of supported catalysts is often not routine.

Alternative approaches more suited to the laboratory utilise XRD whole-pattern fitting based on the Rietveld method (5), using either Fourier (6) or non-Fourier transform methodology. One non-Fourier approach that allows for the determination of metric and microstructural parameters is given in the program FormFit (7). Similar to the Rietveld method, an analytical function is used to describe the measured X-ray pattern. Each line of the pattern is described by a split pseudo-Voigt function in terms of line width, Lorentzian fraction and an asymmetry term. After accounting for the instrument apparative intensity distribution function, the microstructure of the specimen can be determined.

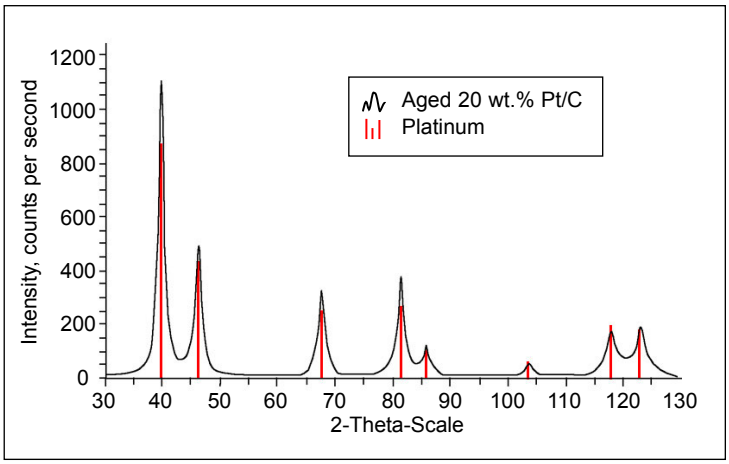

Fig. 1 X-Ray powder diffraction data for an aged 20 wt.% platinum/carbon electrocatalyst

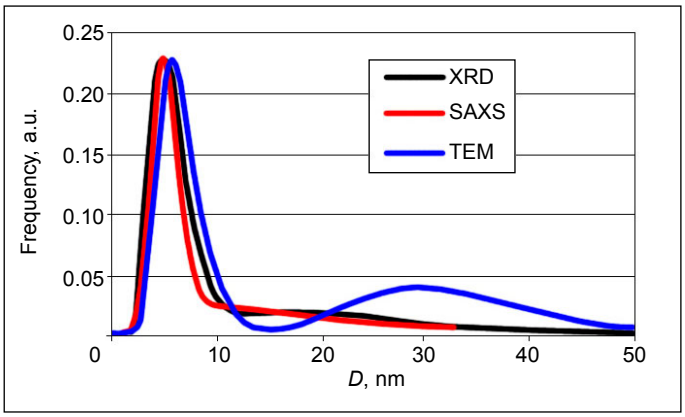

Fig. 2 Comparison of normalised, volume-weighted size distributions determined by XRD, TEM and SAXS for an aged 20 wt.% platinum/carbon electrocatalyst

It is usual to assume a lognormal distribution g_{LN} of diameters D of spherical crystallites with the median D_0 and a variance parameter σ (see Equation (i)):

$$g_{LN}(D) = [D \ln\sigma (2\pi)^{½}]^{-1} \exp[-(\ln(D/D_0))^2/2(\ln\sigma)^2] \quad \text{(i)}$$

Having an empirical relationship between this variance and the parameter η describing the Lorentzian fraction, FormFit can derive microstructural parameters for Pt such as anisotropic crystallite sizes and their distribution width, mean microstrain and stacking-fault densities calculated according to various models.

A comparison of normalised, volume-weighted FormFit XRD, TEM and SAXS approaches is summarised in Figure 2 for an aged 20 wt.% Pt/C electrocatalyst sample. All approaches give on refinement a bimodal distribution of crystallites with a close match in XRD and SAXS distributions. Differences in the magnitude of this bimodal distribution are evident on comparing to TEM. In this example many of the particles measured by TEM are likely to contain several primary crystallite grains leading to a larger TEM particle size than that measured by XRD or SAXS.

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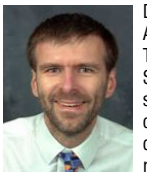

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