Characterization Of Nanocrystalline Fuel Cell Catalysts By X-ray Profile Fitting Methods

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Nanophase catalysts are essential elements of high performance low temperature fuel cells. Fuel cells require large electrode triple phase reaction areas to maximize electrode kinetics and thin electrode layers to maximize mass and electron transport rates. These requirements can only be met with extremely small particle size materials.

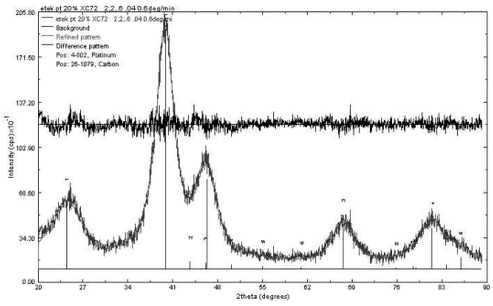
Typical polymer fuel cell electrode materials include platinum and/or platinum alloy catalysts (Pt-Cr,Pt-Co,Pt-Ru). These materials are typically prepared as nanocrystalline carbon supported and unsupported anode and cathode materials. The choice of catalyst type depends on whether the application is for hydrogen, hydrogen reformate or direct methanol fuel cells (DMFCs). 2nm crystallite size Pt supported on carbon is the anode and cathode catalyst most commonly used for hydrogen fuel cells while Pt-Ru alloys of 3-5nm are currently being used for anode catalysts in some hydrogen reformate and DMFC systems.

Characterization of the average crystallite particle size, the crystallite particle size distribution, crystallinity and alloying may be measured nondistructively using X-ray scattering methods. Software and computing hardware advances allow for X-ray diffraction analysis methods to be performed quickly and routinely. Full profile methods based on the pioneering work of Reitveld, model the entire X-ray diffraction pattern rather than just peak maxima. Nanocrystalline materials almost always produce X-ray scattering patterns with very broad and poorly separated peaks. Full profile methods allow for the precise determination of lattice parameters and accurate measurement of individual diffraction line intensities even when overlapping peaks are present. Impurity phase fractions and percentages of amorphous material can also be estimated using full profile analysis techniques.

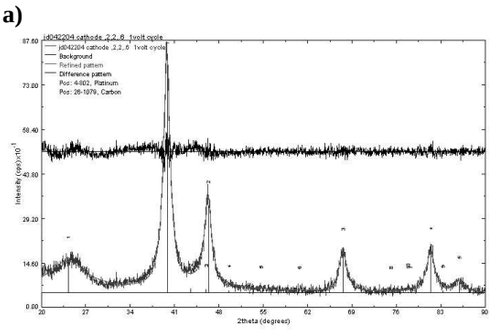
Knowledge of the catalyst crystallite size distribution curve is very valuable information for assessment of fuel cell electrode performance. Warren-Averbach Fourier transform methods allow for the determination of the particle size statistics.[1]

We have characterized many Pt and Pt alloy nanocrystalline (1.5-10nm) samples by X-ray diffraction profile fitting methods and studied aging phenomena in these materials. Many binary catalyst powders as received by the manufacturers contain significant fractions of amorphous hydrous oxides. Hydrogen reduction decreases the amorphous fractions but does not improve sample homogeneity.

Pt nanocrystals may increase in size considerably, from 2 to 7nm even during 70°C fuel operation. The growth rates of the particles are a strong function of the cycling conditions and to a lesser extent a function of temperature. The cathode catalysts show the greatest degradation in performance upon cycling between open circuit voltage and full load conditions as seen in Figure 1. Long term fuel cell performance loss can be attributed mostly to losses in cathode surface area.



a)



b)

Figure 1: X-ray profile fitting of Pt 20 weight% on carbon cathodes a) before cycling- 2nm average crystallite size and b) after cycling- 5nm average crystallite size.

Reference

1. M.S. Wilson, F.H. Garzon, K.E. Sickafus, S. Gottesfeld, J. Electrochem. Soc., Vol .140(#10) pp.2872-2877(1993).