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Physical Characterization of Electrocatalysts

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10.1 Introduction

In recent years, fuel cells have attracted considerable attention due to their high energy efficiency with zero emissions [1]. Electrocatalysts are some of the key materials used in low-temperature fuel cells such as the polymer electrolyte membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC). Creating high-performance catalysts is widely recognized as a key step for the further development and commercialization of low-temperature fuel cells.

The physical characterization of electrocatalysts is very important for several areas of research: (1) preparing new types of electrocatalysts with high activity and high selectivity, (2) recognizing electrocatalyst structures, and (3) investigating the mechanisms of catalysts and certain additives.

Electrocatalysts for application in low-temperature fuel cells (including PEMFCs and DMFCs) constitute a special type of heterogeneous catalyst. The most important difference between an electrocatalyst and a normal heterogeneous catalyst is that the former should have good conductivity, whereas most typical heterogeneous catalysts are insulators; therefore, most characterization techniques for electrocatalysts are the same as for regular heterogeneous catalysts, but some special techniques are required for electrocatalysts because of their conductivity.

For most PEM fuel cell catalysts, carbon black and other order carbon materials (such as carbon nanotubes) are usually used as support materials. These supports can give catalysts good electron conductivity, a very important feature in a fuel cell catalyst. Platinum and its alloys are popular active components, generally highly dispersed on the surface of support materials as micro- and nano-particles. Catalyst performance is related not only to the conductivity and supporting amounts of noble metals, but also, and more importantly, to the dispersion and composition of the active components. Because the hydrogen molecule is small and easily diffused in catalysts, in general the catalyst pore structure is not more important than the surface area.

Physical characterization of PEMFC catalysts includes measurement of the surface area, the electrochemical active surface area, the phase and composition of
active components, the particle size and size distribution of active components, the morphology and crystal planes, and other features.

10.2 Analysis of Composition and Phase of Catalyst

10.2.1 X-ray Diffraction (XRD) and Electron Diffraction (ED)

Principles
X-ray diffraction (XRD) is the most widely used technique to characterize materials. It is a non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

X-rays were discovered by Wilhelm Conrad Röntgen in 1895. X-rays interact with electrons in matter and are scattered in various directions by these atomic electrons. If the scattering centers are separated by distances comparable to the wavelength of the X-rays, then interference between the X-rays scattered from particular electron centers can occur. For an ordered array of scattering centers this activity can give rise to interference maxima and minima.

Each crystalline substance has a characteristic arrangement of atoms which diffracts X-rays in a unique pattern. X-ray reflection takes place from lattice planes according to Bragg’s Law:

\[ n\lambda = 2d \sin \alpha \quad (n = 1, 2, 3, \ldots) \]

where \( \lambda \) is the wavelength of the X-rays, \( d \) is the lattice spacing, \( \alpha \) is the half-value of the diffraction angle, \( n \) is the order of the reflection and can be any whole number, and \( \lambda \) is determined by the type of X-ray tube; typical wavelengths used for X-ray experiments lie between 0.6 and 1.9 Å. Scanning a range of angles of reflection with a detector therefore gives a pattern of peaks with certain spacings and intensities. Planes going through areas with high electron density will reflect strongly whereas planes with low electron density will yield weak intensities.

Crystallography
About 95% of all solid materials can be described as crystalline. In crystallography, it is convenient to characterize a given crystal in terms of a set of planes. A real 3-dimensional crystal contains many sets of planes. The orientation and interplanar spacings of these planes are conventionally defined by the three integers \( h, k, \) and \( l \), called Miller indices. These are determined by the points at which a given crystal plane intersects the three axes. Each plane can satisfy Bragg’s Law and give a bright spot due to constructive interference. To account for all possible planes, Bragg’s Law is usually rewritten (for a cubic system) as:

\[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \]