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TEM Characterization on Oxygen-Deficient Titania Supported Pt Electrocatalysts for Energy Conversion

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Platinum-based catalysts supported on carbonaceous materials (Pt/C) have become the standard catalyst-support choice in Proton exchange membrane fuel cells (PEMFC) [1]. Corrosion of the carbon support is one degradation mechanism leading to poor durability and unacceptable lifetimes hindering further market penetration [2-4]. Discovery of a support that offers comparable electrical conductivity, surface area, structure, and Pt activity enhancement that can be manufactured at a competitive price to carbon and possesses a greatly increased corrosion resistance would represent a breakthrough in attempts to commercialize PEMFCs. Several reviews of potential support materials have recently been published [5,6] on alternative materials to carbon. Of particular interest are the sub-stoichiometric titanium oxides of the general formula Ti_nO_{2n-1} (Magnéli phases), where n is a number between 4 and 10 [7]. These Magnéli phases are characterized by extended planar defects and crystallographic shear planes [8] which vary according to the oxygen deficiency.

The aim of this project is basis research on Pt nano-particles on ball-milled Ti_4O_7 particles. High-quality characterization of these particles is required to investigate their composition and their structure. In order to evaluate the chemical composition, scanning transmission electron microscopy (STEM) and high-angle annular dark field were performed on the specimens to get information on microstructure, atomic structure and atomic number. X-ray Energy dispersive spectroscopy (XEDS) permits sub-nanometer elemental identification and compositional analysis. The addition of electron energy loss spectroscopy (EELS) and energy-filtered imaging allows for the detection of elements at higher spatial resolution, phase identification and bonding information. For structure analysis, the Z-contrast image was particularly suited to imaging catalyst particles with high Z that are often used to grow nanotubes. In the Z-contrast image, the support was seen more clearly in the phase contrast image. Due to the large size of the Ti_nO_{2n-1} particles, even after ball-milling, imaging in electron transmission modes is challenging. Fig. 1a is illustrative of the as-received Ti_nO_{2n-1} particles (i.e., prior to Pt deposition); Fig. 1b shows the resulting size after 100 hours of ball-milling at 400 rpm. It is also worth noting that the z-contrast between Pt (z = 78) and Ti (z = 22) is slightly smaller than Pt and C (z = 6). Fig. 2 shows a bright field view of the top surface of a Ti_nO_{2n-1} particle that may have been cleaved from a larger particle. Fig. 2a shows that the support is again evenly covered in Pt particles with an average size of ~2.3 nm. Deposition appears to be concentrated along the left side edge of the Ti_nO_{2n-1} particle which measures 150 nm in width and over 165 nm in height. Fig. 2b shows another Ti_nO_{2n-1} particle that is approximately 30 nm in diameter and tilted to display the Pt attached to the surface. The attached Pt particles range from 2-3.8 nm in size and appear to be coated in a film that is approximately 5Å in thickness [8]. Such a coating would have potential implications for the reactivity of these particles [9].

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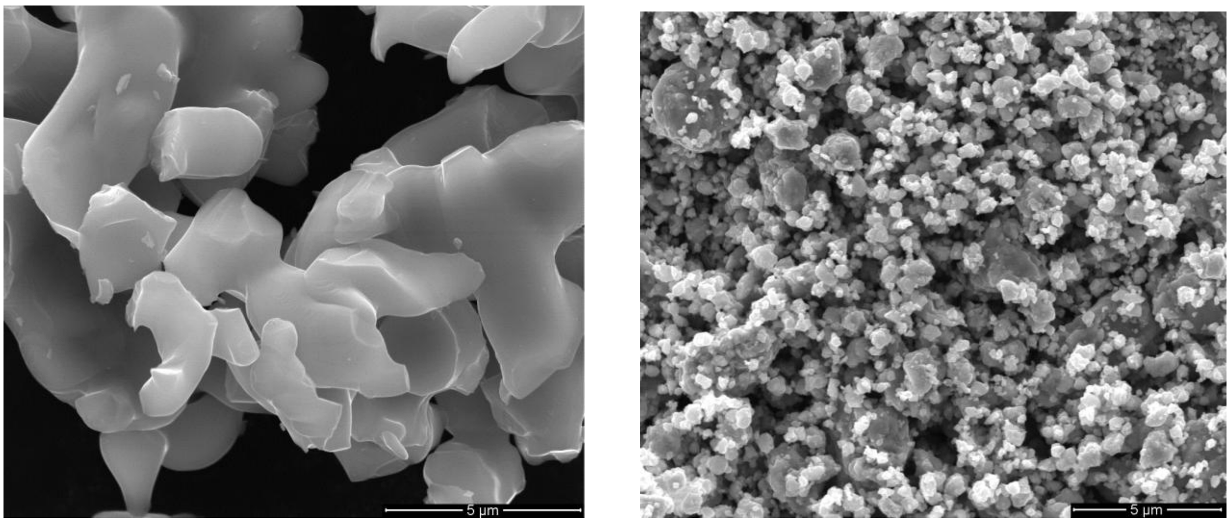

Figure 1. SEM images of a) pre and b) post ball milled Ti_nO_{2n-1}.

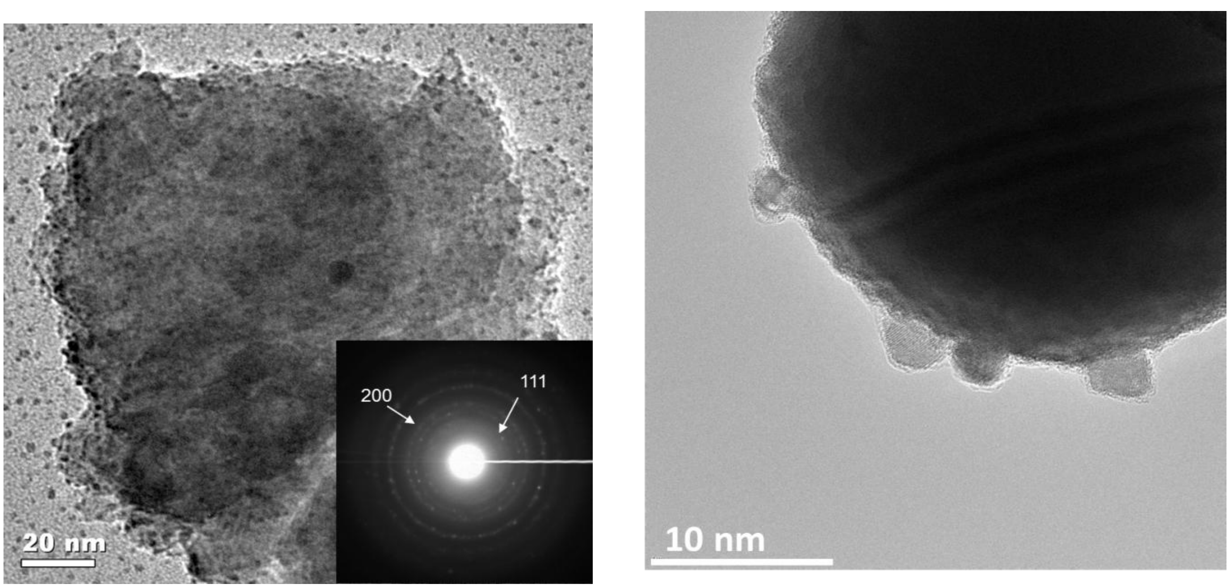

Figure 2. TEM images of Pt deposited Ti_nO_{2n-1} a) cleaved Ti_nO_{2n-1} particle and b) an area of another support particle revealing the attached Pt.

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