Nanoporous platinum doped cerium oxides thin films: Ionic platinum localization and stability

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In this study, we report the characterization of nanostructured Pt-doped CeO_2 films with low platinum content and porous structure, interesting as catalysts for proton exchange membrane fuel cells. They were deposited as nanometric porous thin fils by direct liquid injection chemical vapor deposition on silicon substrate. Nanometric Pt-ceria thin films were characterized by XPS and mainly by TEM with associated analytical techniques [Advanced Materials Interfaces 4, 1600821 (2017)]. By the optimization and the suitable combination of materials and deposition (two-steps growth), we can tune the morphology of these catalysts. TEM analyses reveal that the processes involved during deposition on silicon substrate lead naturally to porous layers with columnar structure. Experiments have also been performed after deposition on a TEM membrane grid to observe directly the pristine layer (Figure 1).

Porous films are made of ca. 3-10 nm diameter particles and platinum is homogeneously dispersed through the layers. The platinum localization and concentration (1 at. %) in the nanocomposite were determined by scanning transmission electron microscopy (STEM) associated with energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) also showed that platinum is mainly in an ionic Pt^{2+} state.

After diffusion through the preformed ceria films porosity, the platinum precursor decomposes at the surface of each ceria particle forming the films, producing a homogeneous platinum-doped CeO_2 nanocomposite. This result was supported by synchrotron radiation XPS experiment where the measured relative Pt concentration demonstrated that platinum is decomposed only at the surface of ceria particles. This may be explained by the presence of nanofacets with adequate orientation at the surface of ceria grain, which can be the anchor of Pt^{2+} species. Finally, when the saturation of Pt^{2+} sites at the surface of ceria particles is reached, metallic nanoclusters are formed from platinum excess.

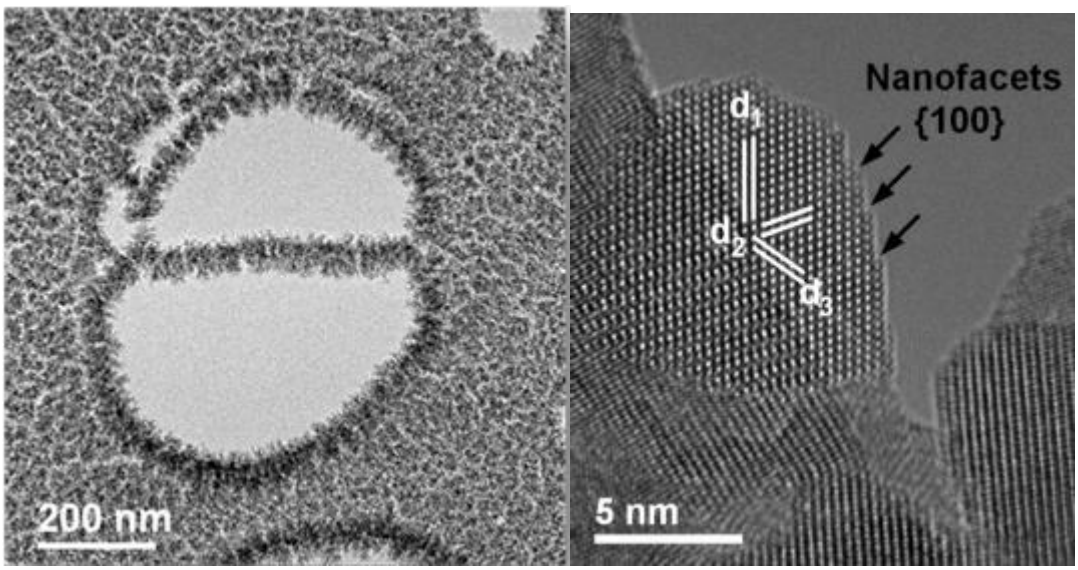

Figure 1: Platinum doped cerium oxide deposited on TEM membrane grid. HRTEM image of the surface layer: the crystallized grain is identified as CeO_2 and exhibits {100} type nanofacets.