$Au^{+,3+}$ and $Pt^{2+,4+}$ ions in CeO_2 rf-sputtered thin films: HAX/SX PES study

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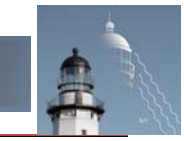


The interaction of gold and platinum with CeO_2 layers was investigated using XPS and synchrotron radiation soft X-ray and hard X-ray photoelectron spectroscopy.

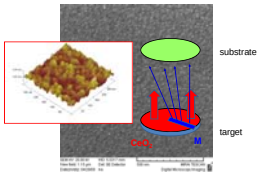
65 nm thick Au doped CeO_2 layers were deposited by rf-magnetron sputtering on a Si(001) substrate by using a composite CeO_2 – Au target. PES showed the formation of stoichiometric Ce^{4+} (CeO_2) and the appearance of new $Au^{+,3+}$ states with ionized Au species in excess of 50% of total Au amount. Depth resolved measurements, by varying the emission angle or photon energy, indicated formation of an Au^0 overlayer and deeper $Au^{+,3+}$ species. Formation of $Au^{+,3+}$ ions was found to be strongly dependent on cerium oxide stoichiometry.

30 nm thick Pt and Sn doped CeO_2 layers were deposited simultaneously by rf-magnetron sputtering on a Si(001) substrate and a carbon diffusion layer of a polymer membrane fuel cell by using a composite CeO_2-Pt-Sn target. The laboratory XPS and synchrotron radiation soft X-ray and hard X-ray photoemission spectra showed the formation of cerium oxide with completely ionized $Pt^{2+,4+}$ species, and with Pt^{4+} embedded in the film bulk. Hydrogen/air fuel cell activity measurements normalized to the amount of Pt used revealed high specific power of up to 5.4 x 10^4 mW/mg(Pt). The activity of these materials is explained by the strong activity of embedded Pt^{n+} cations.

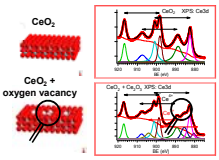
M-CeO_2 film thickness and surface morphology were determined by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). Typical SEM and AFM images of the Pt doped cerium oxide reference film show typical morphology of the layer surface.

PES was performed with X-rays of three different energies in order to vary the probing depth. Soft X-ray PES measurements were performed at MSB at the Elettra synchrotron light source in Trieste (hν = 180 eV, ΔE = 200 meV). HAXPES was performed at BL15XU beamline of the SPring8 synchrotron facility (hν = 5946.8 eV, ΔE = 280 meV). XPS was measured by using an Al X-ray source (hν = 1486.6 eV, ΔE = 1 eV).

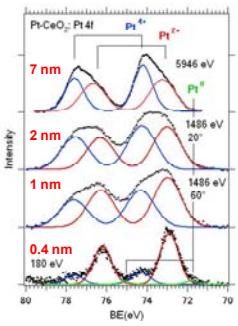
Preparation of M-CeO_2 catalyst by rf co-sputtering

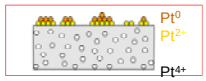


PES Study of Ceria Catalysts – XPS Ce 3d

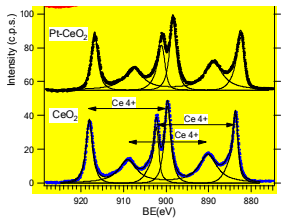


PES study - rf sputtered thin films Pt-CeO_2





HX PES, Ce 3d

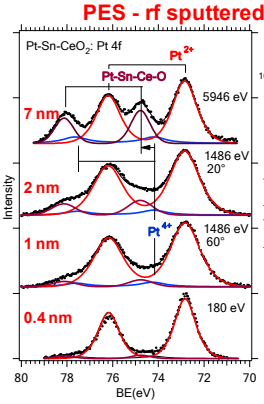


The Pt 4f PES spectra obtained for the Pt doped ceria films reveal 2 - 3 doublets for different information depths.

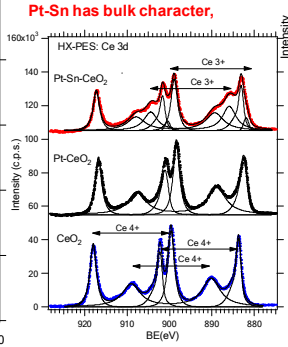
SX PES : Pt $4f_{7/2}$ at 72.9 eV (Pt^{2+}), 74.3 eV (Pt^{4+}) and 71.8 eV (Pt^0), Pt^0/Pt = 0.035.
HX-PES: Pt^{4+}/Pt^{2+} = 1.45.
XPS 60° Pt^{4+}/Pt^{2+} = 0.77, 20° Pt^{4+}/Pt^{2+} = 1.06.

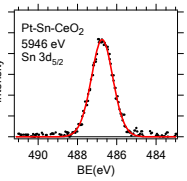
A simple estimation based on the enhancement of the Pt^{4+} signal as a function of λ leads to a structural model with very low concentration of metallic platinum on the surface, Pt^{2+} rich Pt-ceria interface and surface region, and Pt^{4+} dispersed in the ceria film bulk.

PES - rf sputtered thin films Pt-(Sn)-CeO_2



Pt-Sn has bulk character,





Ceria doped with Pt and Sn during the film growth shows the formation of a new chemical states of Pt-Sn-Ce mixed oxide. Ce 3d HAXPES indicates a partial reduction of ceria which can be seen as appearance of the Ce^{3+} states in the film bulk (Ce^{3+}/Ce^{4+} = 0.28).

SPUTTERED FILMS DEPOSITED ON SUITABLE SUBSTRATES REPRESENT NEW AND EFFICIENT CATALYSTS.

Pt-CeO_2 polycrystalline films deposited on CNT exhibit excellent properties as anode material for hydrogen polymer FC. Pt atoms embedded in the film bulk are completely ionized by forming $Pt^{2+,4+}$ oxidic species.

High activity of Pt doped ceria films is given by Pt – ceria interaction. High specific power (W/mg(Pt))of FC with Pt doped CeO_2 anode results from an enhancement of protonic hydrogen formation by Pt ions. We expect that there are two steps of the hydrogen interaction with the catalysts.

1. Dissociation of H_2 molecules on platinum ions Pt^{n+} (n=2,4) to protonic hydrogen:

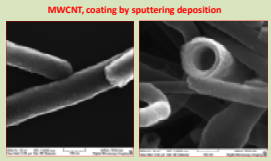
$$Pt^{n+} + H_2 \rightarrow Pt^{(n-2)+} + 2H^+,$$

2. Moving of protons H_M^+ across the membrane and electron current through external circuits:

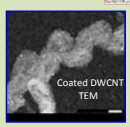
$$Pt^{(n-2)+} + 2H^+ \rightarrow Pt^{n+} + 2H_M^+ + 2e^-.$$

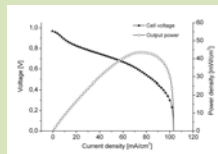
Pt-Sn phase and Ce^{3+} formation leads to additional increase of FC performance.

MWCNT, coating by sputtering deposition



Pt-CeO_2 sputtered on CNTs



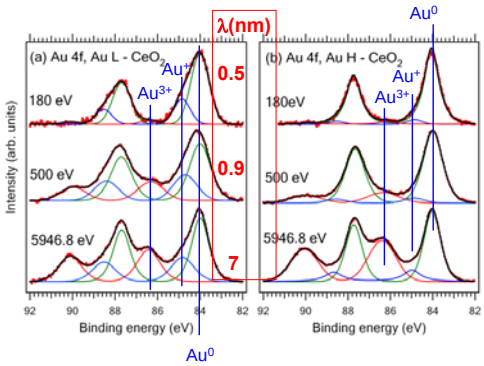


GDL/CNT/Pt-CeO_2
SP = 54 W/mg(Pt)
PD = 43 mW/cm_2

Au^+ and Au^{3+} ions in CeO_2 rf-sputtered thin films

Gold nanoclusters supported on various oxides have been reported to be significantly active catalysts. The high activity observed for different catalytic reactions was predicated on the presence of cationic gold, e.g CO oxidation [1,2], 2-propanol oxidation [3], water gas shift reaction (WGS) [4,5].

[1] Hutchings G J, Hall M S, Carley A F, Landon P, Solsona B E, Kiely C J, Herzing A, Makkee M, Moulijn J A, Overweg A, Fierro-Gonzalez J C, Guzman J, B. C. Gates 2006 *J. Catal.* 242 71
[2] Guzman J, Carrettin S, Corma A 2005 *J. Am. Chem. Soc.* 127 3286
[3] Liu S Y, Yang S M *2008 Applied Catalysis A: General* 334 92
[4] Fu Q, Saltsburg H, Flytzani-Stephanopoulos M 2003 *Science* 301, 935
[5] Fu Q, Kudriavtseva S, Saltsburg H, Flytzani-Stephanopoulos M 2003 *Chem. Eng. J.* 93, 41

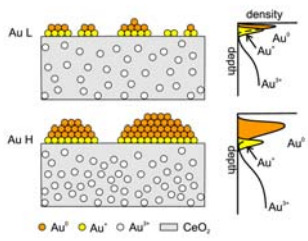


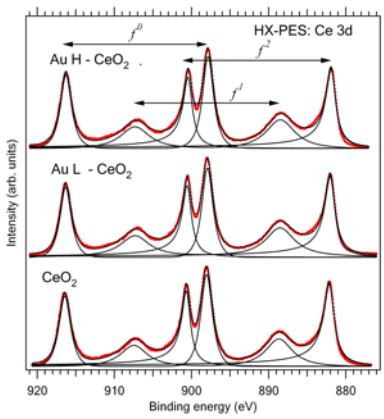
hν / sample	Au^+/Au^0		Au^{3+}/Au^0	
	Au L	Au H	Au L	Au H
180 eV	0.31	0.05	0.05	0.04
500 eV	0.31	0.07	0.29	0.22
5947 eV	0.48	0.23	0.63	0.91

XPS analysis by using the XPS atomic sensitivity factors (emission angle 20°):
Au L = 6.5 at % Au in ceria, Au H = 16.9 at % Au in ceria

For HAXPES the kinetic energy of the Au 4f electrons is about 5860 eV corresponding to an inelastic mean free path in CeO_2 of λ = 7 nm.
SX PES detects low Au^{3+} and Au^+ signals. The HAXPES Au 4f spectrum shows a considerable increase of the Au^{3+} intensity. This can be explained by a bulk-like character of the Au^{3+} species.
Au^{3+}/Au^0 and Au^+/Au^0 ratios obtained for both the Au L and the Au H samples are presented in Table.
Ce 3d spectra show that there is no measurable influence of added gold on the cerium oxide stoichiometry.

We can see that for both Au L and Au H samples the Au^{3+}/Au^0 ratio increases considerably with information depth, which clearly indicates that Au^{3+} has bulk character whilst Au^0 is located at the surface. In the case of the Au^+/Au^0 ratio this tendency is less evident showing that Au^+ and Au^0 are situated at the surface.





The most probable picture of the Au-CeO_2 rf sputtered films structure is that of the Au^{3+} cations embedded in the growing film and of a partial segregation of metallic gold at the surface. The amount of surface gold increases with increasing concentration of the Au dopant. Surface gold forms particles separated from the ceria film by the Au^+ rich interface, i.e. a Ce-O-Au structure is formed. The formation of Au^{3+} ions can be explained by the location of gold atoms in Ce substitutional sites as proposed in [6]. Embedded isolated Au atoms strongly interact with cerium oxide oxygen which can be easily released due to the oxygen storage capacity of cerium oxide. Thus gold oxide is formed, however the overall cerium oxide reduction is slight because of low gold concentration. Oxidation of gold, which is atomically dispersed in oxygen rich CeO_2, leads to the formation of new material, which can be characterized as Au-Ce mixed oxide.

[6] Chen Y, Hu P, Lee M-H, Wang H 2008 *Surface Sci.* 602, 1736