

Stabilized Zirconia –Based Materials for Solid Oxide Fuel Cells (SOFC) obtained by MOCVD and Aerosol-CVD
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Zirconium dioxide is one of the most studied ceramic materials under various forms (film, powder, bulk, etc.). Pure ZrO₂ is monoclinic at room temperature and it undergoes phase transitions to the tetragonal and cubic structures above 1170 and 2370 °C, respectively. The introduction of MgO, CaO, Sc₂O₃, Y₂O₃ and other aliovalent oxides¹ in the ZrO₂ structure allows the ZrO₂ stabilization in the cubic fluorite structure from room temperature to its melting point (2680 °C), thus enabling the production of materials for high temperature applications.^{2,3} At the same time, the doping of ZrO₂ increases oxygen ion vacancies with a significant rise of the ZrO₂ ionic conductivity. In fact, stabilized ZrO₂ is used in oxygen sensors and in Solid Oxide Fuel Cells (SOFC) as electrolyte and anode support.¹ Nowadays almost all SOFC use an yttria-stabilized zirconia (YSZ) electrolyte, strontium lanthanum manganite cathode, a mixed nickel/YSZ cermet anode and a doped lanthanum chromite as the interconnect.¹

The Metal Organic Chemical Vapor Deposition (MOCVD) process, thanks to its high number of tuning chemical and physical parameters, represents a suitable and versatile tool to realize thin films of all the materials for SOFC. In fact, thin films of nanostructured and dense electrolyte can be conveniently obtained by MOCVD, while the porous cermet anode could be deposited by liquid injection or aerosol-CVD systems, by using the same reaction chamber employed for the deposition of the electrolyte mixed oxide materials.

Herein we report the results of two processes to obtain thin film of nanostructured stabilized ZrO₂: the former corresponds to a MOCVD deposition of ZrO₂ stabilized with aliovalent metal oxides such as CaO, MgO, Y₂O₃, Sc₂O₃, and to be used as SOFC electrolyte; the latter consists of an Aerosol-CVD process to produce porous films of stabilized ZrO₂ and Ni/c-ZrO₂ for SOFC anode applications.

MOCVD depositions of stabilized ZrO₂ were carried out in a cold wall reactor at 670 °C and 10 mbar by using Si(100) as substrates and Zr(tmhd)₄, Ca(tmhd)₂, Mg(tmhd)₂·H₂O, Y(tmhd)₃ and Sc(tmhd)₃ as metal precursors. The used carrier gas was N₂, while the co-reagent gas was a mixture of O₂/H₂O. Aerosol-CVD depositions were performed by using an air blast spray system for the precursor feeding and a substrate heating element working at 350-500 °C for the precursor thermal decomposition. An aqueous solution of metal nitrates was sprayed at atmospheric pressure on the hot substrate surface. Here, the nitrates pyrolysed to oxides releasing gaseous nitrogen oxides and forming porous films suitable as catalyst with high specific surface area. All samples have been characterized by XRD, FEG-ESEM

and EDS analyses. XRD measurements showed that films deposited on Si(100) by MOCVD were polycrystalline. Moreover, the Lotgering factor, higher than 0.7 for all differently doped samples, ultimately indicated a cubic-fluorite ZrO₂ phase with a significant (200) preferred orientation. In this regard, it is noteworthy that a not complete ZrO₂ stabilization was limited to the Sc₂O₃-ZrO₂ system, as demonstrated by the co-existence of both the distorted fluorite tetragonal and cubic phases. Deposits obtained by Aerosol-CVD were amorphous, and they became polycrystalline, with ZrO₂ stabilized in the cubic phase without preferential orientation, after an annealing treatment in air at 800 °C.

The Ni/c-ZrO₂ system was obtained by firstly exposing all the as grown deposits to a thermal treatment in air at 800 °C (to get the NiO/c-ZrO₂ mixed oxide) and, afterwards, by annealing NiO/c-ZrO₂ in H₂ atmosphere to reduce all the NiO to Ni to obtain the cermet. This behaviour was confirmed by X-ray diffraction. EDS data were consistent with a good compositional control of the stabilizing oxides, as required for SOFC applications, even if a slight CaO excess was always revealed. All samples were uniform, crack-free and well adherent to the substrate. The comparison between the FEG-ESEM micrographs of the films deposited with the two methods highlighted a different surface morphology (Figure 1). ZrO₂ obtained by MOCVD was colorless, dense, as desired for SOFC electrolyte, with a lenticular texture, while the one deposited by Aerosol-CVD was highly porous with a sponge-like morphology, suitable for SOFC anode or catalyst support.

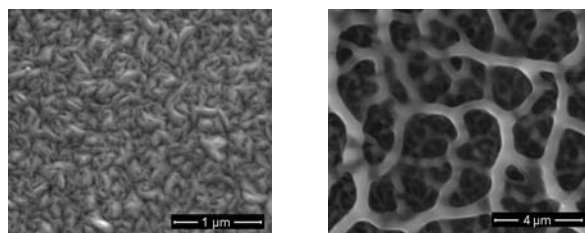


Figure 1. Comparison between c-ZrO₂ obtained by MOCVD (left) and by Aerosol-CVD (right).

In conclusion, these results show that the MOCVD and Aerosol-CVD are well suited processes to obtain nanostructured material with a good compositional control, and with peculiar morphological and structural features for different applications. Moreover, we demonstrate the possibility to integrate the two deposition method to obtain mixed oxide materials.

Acknowledgments

This work is supported by funds of ‘Progetto FISIR’ of Ministero dell’Istruzione dell’Università della Ricerca Scientifica. Thanks to Fila Industria Chimica SPA for the use of the FEI Quanta 200 FEG-ESEM Instrument.

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