DEPOSITION OF MIXED CONDUCTING OXIDES THIN FILMS ON POROUS CERAMIC SUBSTRATES

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Oxide materials with mixed oxygen ionic and electronic conductivity are interesting for potential applications in ceramic membranes for solid oxide fuel cells (SOFC), oxygen separation, and catalytic oxidization of CH_4 and C_2H_6 gases. In the case of oxygen permeation, mixed-conducting oxides are generally used in a form of thick layers of sintered crystalline grains (i.e. between about 0.5 and 3 mm). Ultra-thin layers supported on porous substrates would be therefore interesting for improving the efficiency of the oxygen permeation. However, excepted for oxygen, a gas-tightness property is required for such layers. For oxygen permeation, O^{2-} conducting multi-metal oxides exhibit appropriate properties. These oxides are mainly perovskites doped compounds $(La_{1-x}A_x)(B_{1-y}B'_y)O_3$ (A=Ba, Sr, Ca – B=Fe, Co, Mn and B'=Ni, Cu) (1-5) or K_2NiF_4 type structures as La_2NiO_4 (6-7). But for most of these oxides generally used for deposition on porous substrates, thermomechanical deficiencies such as cracks occur due to mismatches in thermal expansion coefficients between layer and support or electrolyte material used in devices.

In the present study, gas-tight ultra-thin La_2NiO_4 or $LaNiO_3$ layers were obtained from a spray pyrolysis process on composite ceramic substrates covered with zirconia. Reasons for this choice were a good oxygen ionic conductivity of the La_2NiO_4 compound and a weak difference of thermal expansion coefficients between La_2NiO_4 or $LaNiO_3$ and ZrO_2, about 10^{-5} and 1.1 10^{-5} K^{-1} respectively. From the results of this study, one has however to point out that porous ceramic substrates must be very clean and without defects in order to fabricate gas-tight layers of 1 µm thickness.

The layers were deposited by an aerosol-CVD process for which a solution of precursors is pulverized by an ultrasonic system in the form of droplets which coming in contact with a heated substrate and decomposed by pyrolysis. $La(thd)_3$ and $Ni(thd)_2$ precursors were dissolved in 1,2 dimethoxyethan (monoglyme) with a total concentration of 0.02 mol.l^{-1}. The ultrasonic system was working at 800KHz and at a power of 60W. The spray, constituted of droplets of less than 4µm diameter, was carried away using a N_2 laminar gas flow, up to the surface of a heated flat porous ceramic substrate. Pyrolysis performed at 580°C or at 700°C led to a growth of amorphous layers at a rate of 1µm/h. Samples were afterwards crystallized under air at 700°C for 15 h and with 2°C.min^{-1} heating and cooling rates.

Leak measurements were performed by applying an overpressure of 50 kPa with respect to atmospheric pressure on samples before and after depositing. For initial porous ceramic substrate of good quality, the leak was found to be about 300 ml.min^{-1}. Deposited layers were characterized by X-ray diffraction in a θ/2θ scan mode and by scanning and transmission electron microscopy (SEM and TEM). Samples for TEM investigations were prepared by mechanical and ionic thinning on side of the ceramic substrate only.

In the case of ceramic substrates without defects, gas tight layers were obtained using a multilayer deposition procedure. A first layer of 0.5µm was deposited at 580°C in an amorphous state for which the leak reduced to 0.02 ml.min^{-1}, and then crystallized at 700°C, the leak increasing up to 0.13 - 0.2 ml.min^{-1}. Then a second layer of 0.5µm was deposited and crystallized in the same conditions as previously. Leak measurements show that a gas tightness property was then obtained. From SEM observations after the first annealing procedure, the first layer exhibits through crystallization a surface smoothing but also presents small cracks resulting probably of the small mismatch of thermal expansion coefficients between the deposited layer and the porous substrate. The role of the second layer deposition was then to obstruct cracks formed by crystallization in the first layer.

Layers were studied by θ/2θ X-ray diffraction and T.E.M.. For instance, TEM and X-ray diffraction results exhibits a foam-like microstructure of the as-deposited layer. It is not completely amorphous as it contains a few crystals between 50 to 300 nm in diameter. Annealing treatment at 700°C of the layers deposited at 580°C led to the formation of a crystalline $LaNiO_3$ phase of perovskite structure, and to a crystalline La_2NiO_4 of Ruddlesden-Popper phase in the case of layers deposited at 700°C. However, the crystallization is not complete in the case of deposition at 580°C as crystals are observed to be embedded in remaining amorphous matrix, which gives rise to a large diffuse scattering ring centered at about 2 Å^{-1}. As, in all cases, from electrical measurements the films were found to be conductive after annealing and insulator before it means that a percolation between crystallized particles occurs, and that a permeation of oxygen can be expected to occur. But further studies on tests for the oxygen conduction have to be carry out in order to check whether such a layer microstructure is convenient or not.

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