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YSZ freestanding films from hybrid polymer–oxide composites by the sol–gel process: Influence of polymer features on ceramic microstructure

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Abstract

Hybrid polymer–yttria–zirconia xerogels have been used to prepare freestanding and crack free cubic yttria-stabilized zirconia (YSZ) films. Depending on the final ceramic properties, these materials could find application as components in solid oxide fuel cells. Different types of organic and bioorganic molecules such as albumin, starch, sucrose, dextran, carboxymethylcellulose, and polyvinyl alcohol, have been studied in order to prepare polymer–oxide nanocomposites. The reason for adding a polymer to a sol–gel-derived inorganic network stays in avoiding cracks formation during the pyrolysis process, which converts the preceramic into the ceramic material. Polymers behave as stress relaxing agents and allow obtaining dense and crack free final ceramics.

The differences in polymer chemical structure and solubility impose variable synthesis procedures, and limit the availability of suitable yttria precursors. We present here a study concerning the influence of different polymers on the microstructural properties of yttria–zirconia films. Thermogravimetric analyses (TGA), SEM, XRD, N_2 sorption and density measurements have been used to characterize the polymer-to-ceramic transformation and the final ceramic materials.

Keywords: Sol–gel processes; Bioorganic molecules; Y_2O_3; ZrO_2; Microstructure-final

1. Introduction

Yttria-stabilized zirconia (YSZ) is recognized as one of the most suitable electrolyte material in solid oxide fuel cell technology (SOFC).[1] Yttria addition assures zirconia stabilization in the cubic structure at high temperature and also provides oxygen vacancies. The highest conductivity is ensured at a molar ratio of 10 mol% yttria/90 mol% zirconia.

We recently published our results on the use of polyvinyl pyrrolidone as stress relaxing agent in the synthesis of YSZ films by the sol–gel process.[2] PVP addition allowed to prepare crack-free freestanding YSZ discs by pyrolysis of class I hybrid organic–inorganic composites.[3] As a matter of fact, the ability of the polymer to act as a stress relaxing agent during pyrolysis allows to contrast the tendency to crack formation, which is typical of sol–gel-derived products particularly in the case of transition metal oxides.[4]

We are now interested in modifying the nature of polymers, with the aim to study their influence on the final ceramic features. Different organic and bioorganic molecules such as albumin, starch, sucrose, dextran, polyvinyl alcohol (PVA), and carboxymethylcellulose (CMC) have been introduced into the sol–gel-derived inorganic network. We selected organic compounds with different structural elements, i.e. various degree of polymer branching and chain length with the goal of modifying the microstructural features of the prepared materials. For instance, albumin is a globular protein, characterized by regular structural elements of amino acid sequences[5,6] and is expected to promote the formation of pores with regular shape.

One common feature of these organic compounds is their solubility in water, due to water ability to form hydrogen bonds with hydroxyl groups or polar substituents of the polymers chain. Unfortunately, the solvent is also a limiting factor for the availability of suitable yttria precursors.

We report here the synthesis of hybrid yttria–zirconia xerogels, which have been converted into freestanding, dense and crack free cubic YSZ films by controlled heat treatment. The

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study concerning the influence of different organics on the microstructural properties of the ceramic films is presented.

2. Experimental

2.1. Synthesis of polymer–YSZ xerogels

In the first step, ZrO_2 sol was prepared by hydrolysis of zirconium propoxide with excess water and peptization with hydrochloric acid.[7] The organic compound was added at room temperature (compound/Σ metal oxides = 20 wt.%/80 wt.%) and the mixture was stirred for 1 h. Specifications of the organic additives are the following: albumin (ovalbumin, grade II); PVA with M_r 30,000–70,000; CMC as sodium salt (substitution degree not less than 0.4; viscosity 1500 ± 400 cP for 1% aqueous solution at 20 °C), dextran with M_r 5×10^6 to 40×10^6; sucrose; starch (corn starch). Yttrium triacetate tetrahydrate was added (90 mol% ZrO_2/10 mol% Y_2O_3) and after 1 h stirring, the mixtures were cast in polypropylene vessels. White xerogel discs were obtained after drying at room temperature in air for 2 weeks. Samples were heat treated up to 500 and 1200 °C, in air with 5 °C/min heating rate.

2.2. Characterization techniques

Thermogravimetric analyses (TGA) were performed on a Netzsch STA 409 operating in the range 20–1000 °C, with a heating rate of 10 °C/min in air. XRD spectra were collected on a Rigaku Dmax diffractometer in the Bragg–Brentano configuration, using Cu Kα radiation and a monochromator on the diffracted beam, operating at 40 kV and 30 mA. A modified Rietveld method analysis was employed for phase analysis and mean crystallite size calculation.[8] N_2 sorption experiments were carried out at 77 K on a Micromeritics ASAP 2010. Surface area evaluation was obtained by the BET equation, which was linear in the interval $0.05 \leq p/p_0 \leq 0.33$ with a least squares fit of 0.998. The pore size distribution was calculated by using the Kelvin equation. The microstructure of ceramic samples was observed using SEM (Jeol JSM-5500 at 10–15 kV) on fracture surfaces after etching for 12 h in H_2SO_4 solution at pH 2. Micropore area and volume were obtained from *t*-plot. Density measurements were performed in helium using a Micromeritics multivolume 1305 pycnometer.

3. Results and discussion

The preparation of YSZ thick freestanding films by reaction of zirconium propoxide and yttrium acetate in water is made possible by the addition of water soluble organic compounds of different nature. The syntheses lead to white xerogel discs in all cases except for sucrose, which leads to powders. This result implies that macromolecules offer the possibility to stabilize the inorganic network giving monolithic samples, whereas the disaccharide structure of sucrose is not effective to this purpose. A similar behaviour was observed on the ability of increasing film thickness using PVP, while the monomeric *N*-vinyl-2-pyrrolidone appeared to be ineffective.[9]

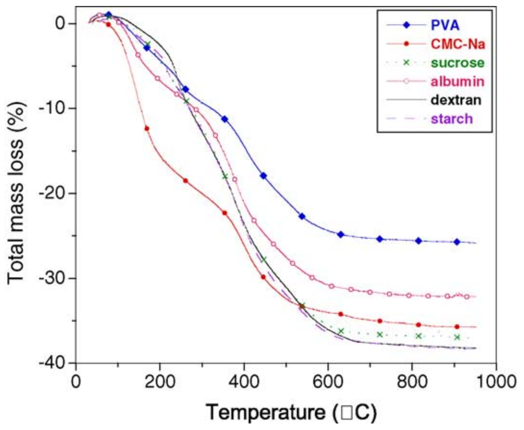

Fig. 1. Total mass loss in air as function of temperature.

The thermal evolution related to the polymer-to-ceramic transformation has been followed by TG analyses. As a general trend, the burning out of the organics finishes at 600 °C (Fig. 1). Total mass loss and shape of TG curves appear to be dominated by the nature of the organic compounds. Saccharide-derived samples present a similar total mass loss (CMC-Na, 36.0%; sucrose, 37.0%; dextran, 38.2%; starch, 38.6%). PVA and albumin-derived samples show 28.4% and 32.5% total mass loss, respectively. Despite the influence of various branching degrees or chain lengths, the shape of TG curves changes by variation of the chemical nature of organic molecules, with the only exception of CMC, which was introduced as sodium salt in the synthesis and shows different thermal behaviour in comparison to the other saccharides.

The results of density measurements of samples heated at 500 and 1200 °C are presented in Fig. 2, which reports also the theoretical density of the cubic YSZ phase

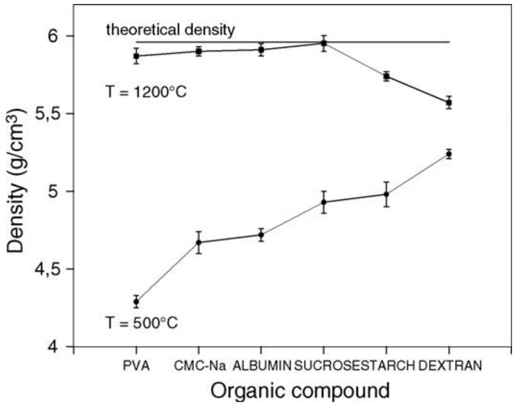

Fig. 2. Density evolution vs. temperature and composition of polymer-derived samples.

Table 1
Surface area (m^2/g), micropore volume (cm^3/g) and average pore size (Å) of polymer-derived samples at $T = 500\,°C$

Organics	Surface area	Micropore volume	Average pore size	
			BJH adsorption	BJH desorption
Albumin	35.09 ± 0.11	0.000092	161	173
CMC-Na	42.67 ± 0.17	0.000129	139	327
Dextran	17.23 ± 0.07	0.000020	185	330
PVA	35.34 ± 0.15	0.000153	152	312
Starch	27.80 ± 0.13	0.000832	151	181
Sucrose	21.07 ± 0.07	0.000039	190	244

Table 2
Surface area (m^2/g), micropore volume (cm^3/g) and average pore size (Å) of polymer-derived samples at $T = 1200\,°C$

Organics	Surface area	Micropore volume	Average pore size	
			BJH adsorption	BJH desorption
Albumin	3.66 ± 0.05	0.000325	136	140
CMC-Na	3.04 ± 0.11	0.000590	200	353
Dextran	6.55 ± 0.23	0.001176	370	221
PVA	10.08 ± 0.11	0.000730	313	329
Starch	3.68 ± 0.05	0.000575	273	224
Sucrose	4.38 ± 0.20	0.000646	207	256

(5.959 g/cm^3). At 500 °C, density values are in the order CMC < sucrose < starch < dextran. By comparing saccharides, it seems that the chemical structure plays a role during the ceramization process, and the presence of branches like in dextran seems to favour the densification at low temperature. Moreover, the comparison between different saccharide-derived samples confirms the influence of the average sizes of the organic additives on the densification process. The density is higher for dextran than for starch, and sucrose leads to the lowest value between saccharides. This result is in perfect agreement with the results of Kozuka and Kajimura about the relation between molecular weight and densification ability.[9] On the contrary, the opposite development of density has been measured at 1200 °C. These samples present density values very close to the theoretical density of cubic zirconia with the exception of starch and dextran-derived samples.

Specific surface area (SSA), micropore volume and average pore size distribution have been obtained by N_2 sorption analysis. The specific surface area values, calculated by BET equation, are summarized in Tables 1 and 2. SSA values ranging from 43 to 17 m^2/g have been found at 500 °C (Table 1). By heat treatment at 1200 °C, the surface area decreases and values between 10 and 3 m^2/g are measured (Table 2).

The average pore sizes, calculated applying the BJH model to N_2 adsorption and desorption isotherms, are also reported in Tables 1 and 2. The average pore size determined from the adsorption branch is an estimation of the cavity size distribution, whereas the desorption curve gives information on the throat size distribution. For dextran, at 500 °C large open throated pores are found, which are converted into inkbottle pores at 1200 °C. In the case of sucrose, the heat treatment from 500 to 1200 °C does not change shape and average size of pores, which can be described as open throated pores. The thermal removal of PVA leads to the formation of open throated pores at 500 °C, which are transformed into cylindrical pores at 1200 °C. These samples do not present a monomodal pore size distribution. A main peak in pore size distribution is associated to a large and broad peak at higher diameters.

The case of albumin deserves much more interest. At 500 °C, the average pore size calculated from adsorption and desorption branches is nearly identical. This means that cylindrical shaped pores are present, which derive from the tailoring effect of the globular protein. At 1200 °C, these microstructural features are retained and only a reduction of average pore size is observed. Moreover, the pore size distribution does not change by increasing the temperature. The albumin-derived sample presents very narrow and monomodal pore size distribution, both at 500 and at 1200 °C (Fig. 3). The tailoring effect of albumin on ceramic microstructure is clearly demonstrated, the ability to leave a permanent print along the whole pyrolysis process.

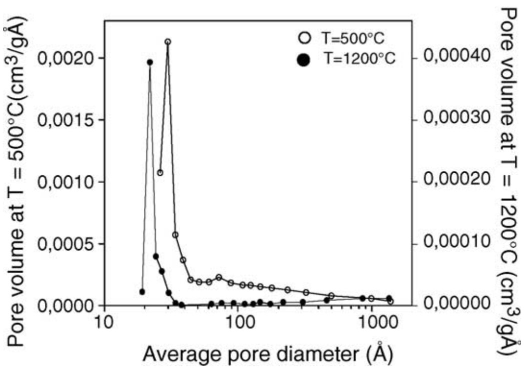

Fig. 3. Pore size distribution for albumin-derived ceramics.

Table 3
c-YSZ crystallite dimensions (Å) measured as a function of annealing temperature

Organics	*T* = 500 °C	*T* = 1200 °C
	Crystallite size	Crystallite size
Albumin	35.0 ± 0.4	782 ± 16
CMC-Na	30.7 ± 0.4	768 ± 12
Dextran	34.6 ± 0.5	519 ± 9
PVA	31.5 ± 0.4	151 ± 1
Starch	31.4 ± 0.4	617 ± 11
Sucrose	38.8 ± 0.3	341 ± 8

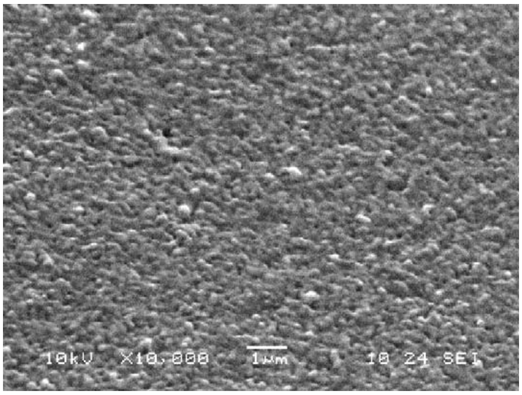

Fig. 4. SEM micrograph of PVA-derived ceramics at 1200 °C.

The crystallization process has been studied by XRD, and phase analysis and calculation of mean crystallite size have been obtained by a profile fitting procedure based on a modified Rietveld model.[8] The crystallization process begins at 500 °C. At this temperature, all XRD patterns show the presence of the pure cubic phase of yttria-stabilized zirconia, with crystallite sizes in the range 3–4 nm (Table 3). No segregation of other phases is observed. Further heat treatment up to 1200 °C completes the YSZ crystallization and leads to the increase in mean crystallite size (Table 3). At the final temperature, the crystallite size strongly depends on the starting gel composition, with sizes ranging from 15 nm for PVA to 78 nm for albumin. The ceramic samples at 1200 °C appear dense and homogeneous to SEM analysis. The SEM micrograph of PVA-derived sample at 1200 °C (Fig. 4) shows homogeneously distributed grains with size well below 1 μm.

4. Conclusions

Dense, crack free pure cubic YSZ thick films have been synthesized by adding polysaccharides, proteins or polyalcohol to yttria–zirconia sols. Only the addition of sucrose does not allow to obtain a monolithic sample. The choice of the organic molecules makes it possible to modify the microstructural features of the final YSZ ceramics. In the case of albumin, the burning out of the globular protein led to the formation of cylindrical pores, and a narrow monomodal pore size distribution was determined. YSZ ceramics were nanocrystalline, with crystallite size depending on the added polymer.

Acknowledgement

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