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Sol-gel synthesis of polymer-YSZ hybrid materials for SOFC technology

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Abstract

Pure nanocrystalline cubic yttria-stabilized zirconia (YSZ) samples have been produced at temperatures as low as 800 °C by annealing in air hybrid free-standing sol-gel-derived films. The addition of polyvinylpyrrolidone (PVP) to the sol allows the preparation of crack free gel films. By casting the sol onto a mercury surface, films with thickneses in the range 80–100 μm were obtained. The thermal evolution of hybrid PVP–YSZ xerogels has been followed using FTIR spectroscopy, thermogravimetric analysis, X-ray diffraction and scanning electron microscopy. The influence of the polymer addition on final ceramic structure and microstructure has been studied by changing the polymer content. The ''matrix effect'' of PVP in controlling crystallite sizes has been found and related to the thermal degradation of the polymer.

Keywords: Composition-structure relationships; Fuel cells; Nanocomposites; Sol-gel process; YSZ

1. Introduction

The sol-gel technique as a soft chemical process offers a versatile access to advanced materials. The use of alkoxide precursors in the sol-gel chemistry allows the molecular design of ceramic precursors with a significant improvement of the final ceramic microstructure and properties. However, the sol-gel technique presents several drawbacks, such as the undesirable phenomenon of crack formation during the drying and sintering processes, particularly for transition metal oxides. A solution to this problem comes from the introduction of an organic moiety in the inorganic network, which could act as ''space-filler'' [1,2] and promote the stress relaxation during the densification process. This goal can be achieved by the synthesis of hybrid organic–inorganic (O/I) materials[3,4] where the organic phase is introduced as a polymer dissolved into the starting alkoxide mixture. These systems belong to class I hybrid O/I materials,[5] characterized by weak chemical interactions like hydrogen-bonding or van der Waals forces between organic and inorganic counterparts. Although the role of polymers in the preparation of dense and crack-free ceramic films has been known for a decade,[6] only recently has this synthetic approach been successfully used for the preparation of crack-free ceramic films.[2]

In the present study, polyvinylpyrrolidone–yttria–stabilized zirconia (PVP–YSZ) hybrid gels have been prepared as monolithic disks, which have been converted by thermal treatment into YSZ ceramics. PVP–YSZ gels have been prepared from zirconium-*n*-propoxide and yttrium acetate solutions containing PVP. The reproducible reaction and the preparation of free-standing films are described. YSZ finds application as solid electrolyte in solid oxide fuel cells (SOFC). For this application, the ceramic performances are conditioned by structural and microstructural properties, which can be modulated changing the pre-ceramic composition. Therefore, this study is addressed to the study of the influence of PVP content on the final ceramic features, using different analytical techniques.

2. Experimental

2.1. Synthesis of PVP–YSZ gels

A 0.14 M solution of the yttrium precursor was prepared by adding yttrium acetate tetrahydrate in

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2-methoxyethanol and refluxing for 4 h under nitrogen. PVP–K15 (MW = 10,000) in molar ratio $R = 1.0$, 0.5, 0.3 or 0.1 (related to zirconium-*n*-propoxide) was dissolved at room temperature in *n*-propanol (molar ratio *n*-PrOH/Zr = 10.0). Zirconium *n*-propoxide was dropped into the solution. After 15 min stirring, the appropriate volume of yttrium solution was added in order to obtain gels with composition 10 mol% Y_2O_3/90 mol% ZrO_2. The reaction mixture was refluxed for 2.5 h before addition of acetic acid (HOAc/Zr = 1.0) and further refluxed for 1.5 h. The clear solution was heated to 85 °C and water (H_2O/Zr = 10.0) was added drop by drop. After 15 min the homogeneous sols were cast in polypropylene vessels (~ 2 cm) and on mercury surfaces. Yellowish gel disks were obtained within several days and dried at room temperature for 2 weeks. To obtain crack-free unsupported films as thin as possible, holders made of several materials have been tested. Only by sol casting on mercury, was it possible to produce free-standing films with thicknesses lower than 100 μm as demonstrated in Fig. 1, which shows a representative micrograph (irrespectively from the polymer content) of hybrid PVP–YSZ films having a thickness of 80 μm.

2.2. Thermal treatment and characterization techniques

Xerogel samples were thermally treated at different temperatures in air with 5 °C/min heating rate. In some cases samples have been pyrolyzed under flowing Ar up to 600 °C and then heated in air up to 1200 °C. FT-IR spectra were recorded in transmission mode on KBr-pellets in the 4000–400 cm^{-1} interval on a Nicolet 5 DXC spectrophotometer (64 scans, 2 cm^{-1} resolution). 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 K_α radiation and a monochromator on the diffracted beam, operating at 40 kV and 30 mA. A modified Rietveld method analysis[7] was employed for the phase evaluation and the mean crystallite sizes calculation. Density-measurements were performed in helium using a Micromeritics multivolume 1305 pycnometer. 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.

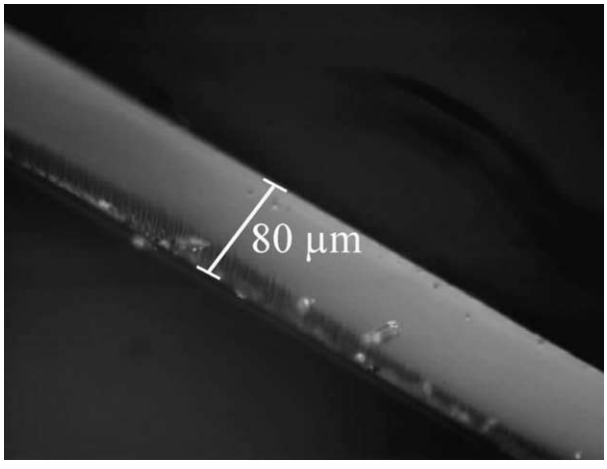

Fig. 1. Optical micrograph of hybrid film prepared from PVP–K15, $R = 1.0$.

3. Results and discussion

The synthesis procedure here reported for the preparation of PVP–YSZ hybrid gels allows obtaining homogeneous sols that can be used for the preparation of free-standing xerogel films. Our experimental results clearly demonstrated that the incorporation of PVP inhibits crack formation during gel drying. However, the preparation of monolithic free-standing films depends on the substrate choice. We found that only on mercury we were able to avoid any interaction between PVP–YSZ gelling solution and substrate and therefore obtaining free-standing, crack-free films.

The chemistry in solution and the chemical interaction in gels have been already discussed in an earlier published work.[8] The PVP role as a "space-filler" and the presence of hydrogen bonding between polymer and metal oxo-clusters in solution as well as at the xerogel state have been clearly demonstrated using FTIR spectroscopy. A relation between the intensity of hydrogen-bonding interaction and polymer to zirconium ratio has been detected using a PVP with average molecular weight $M_r = 10\,000$ (PVP–K15). This paper is focused on the characterization of the thermal conversion of hybrid gels, prepared with different amounts of PVP–K15, into YSZ ceramics. PVP–YSZ xerogels were heat-treated in air at different temperatures ranging from 200 to 1200 °C, with 1 h isotherm at the end-temperature. After heating, ceramic white disks were obtained.

The thermal evolution has been followed by TG analyses and the weight losses, calculated from the TG curves, are reported in Fig. 2 as a function of PVP–K15 amount. Two different steps are present in the TG curves (not reported) and their intensities depend on the chemical composition. The first mass loss (1) is found below 240 °C and decreases with increasing amount of polymer. The second mass loss (2), corresponding to the range 240–1000 °C, increases with increasing polymeric content. For the total mass loss (3), the same trend of curve 2 is found. From these data, we can conclude that the main contribution to the total mass loss is given by the burning out of polymer. Acetate groups are mainly responsible for the first mass loss, whereas the second mass-loss step is ascribable to the polymer decomposition.

The evolution of the FT–IR spectrum as a function of temperature for the highest amount of PVP–K15 (R 1.0) is shown in Fig. 3 in the range 2000–400 cm^{-1}. The stretching vibrations of –OH at 3500 cm^{-1} (alcohol and water) decrease with increasing temperature and almost vanish at 400 °C. Aliphatic contributions are found around 2950–2800 cm^{-1} (ν CH_2 and ν CH) and can be detected up to 300 °C. The two main peaks of PVP (ν C=O and ν C–N, indicated with * in Fig. 3), which are located at 1660 and 1290 cm^{-1} are detected up to 200 °C and at 300 °C they are no longer visible. Peaks at 1570 and 1450 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of the acetate groups bonded to metals (marked with ■ in Fig. 3). Even in this case, these bands completely disappear at 300 °C. Newly derived compounds are visible starting at 300 °C. At this temperature the FT-IR spectrum shows two main broad bands which suggest the presence of aromatic compounds. Indeed, the band at 1385 cm^{-1} can be assigned to the deformation vibration of $–CH_3$ bonded to aromatic rings. Traces of vibrations in the range 1650–1550 cm^{-1} are the first evidences of aromatic compounds (ν C=C). These FTIR results seem to show that starting at 300 °C, the characteristic peaks of either the acetate and the PVP vanish indicating that, for both compounds, the decomposition starts at a temperature lower than 300 °C. At 1000 °C no vibration of functional groups are detectable via FT-IR, in agreement with the end of thermal evolution found in TG curves.

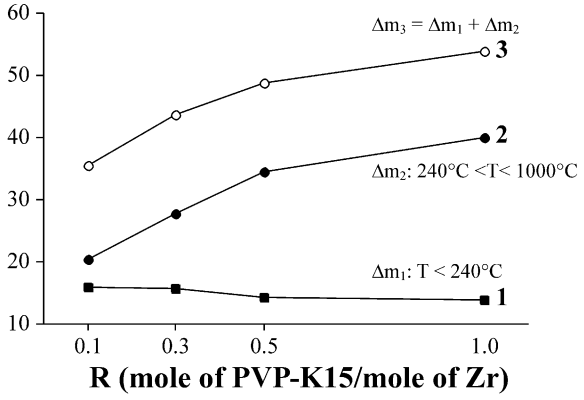

Fig. 2. Mass losses measured in the temperature range indicated, for gels produced from PVP–K15 as a function of *R*.

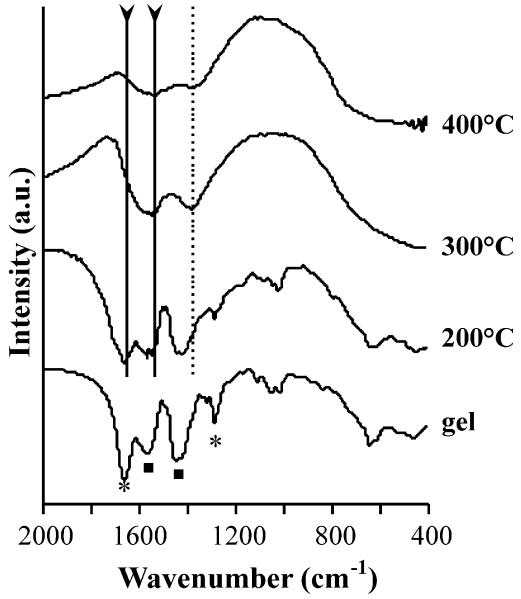

Fig. 3. FT-IR adsorption frequencies for sample *R* 1.0 (solid lines show borders for aromatic range, dashed line indicates 1385 cm^{-1}).

The phase evolution with temperature has been studied by XRD. The crystallization process begins below 800 °C. At this temperature, the XRD patterns show the presence of a pure cubic phase of yttria-stabilized zirconia (Fig. 4). The segregation of other phases is not observed during the pyrolysis process and the further heat treatment up to 1200 °C produces the completion of YSZ crystallization and the increase of the mean crystallite size (Table 1). YSZ crystallites of few nanometers in size are present at 800 °C. The average crystallite size increases with increasing temperature and shows a net dependence on the polymer content in the starting xerogel, with a decrease in crystallite size as the PVP ratio increases. These results indicate that the PVP, through its thermal degradation process, produces a "matrix effect", which can control the crystallite growth leading to nanocrystalline YSZ ceramics. Moreover, the crystallization is affected by the thermal treatment. The same samples pyrolyzed in Ar up to 600 °C and after being heated in air at 1200 °C show an increase in crystallite dimensions: for example for R 0.1 (PVP–K15) at 1200 °C, crystallite sizes are 63.8 nm for the air-treated sample and 90.8 nm for the sample with Ar treatment. This fact further supports the idea of the influence of the polymer degradation pathway on the ceramic features. Indeed, by annealing in Ar, the decomposition of the polymer in a carbon-based phase is first obtained and the burn out starts only at higher temperatures. On the

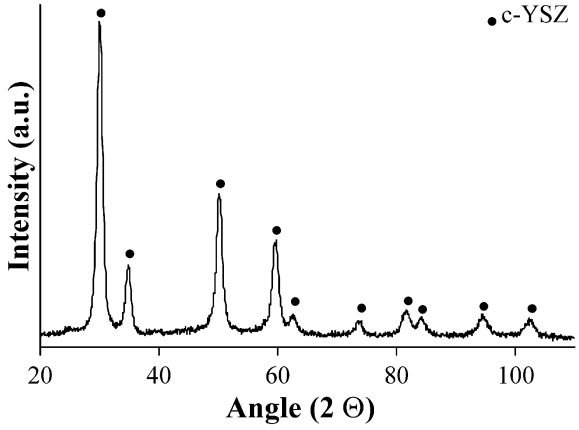

Fig. 4. XRD pattern of YSZ (PVP–K15, $R = 1.0$) heat treated at 800 °C in air for 1 h.

Table 1
c-YSZ crystallite dimensions (nm) measured for the ceramic samples as function of PVP content (R), and annealing temperature

Sample	Temperature (°C)		
	800	1000	1200
R 0.1	4.50±0.04	19.7±0.2	63.8±2.4
R 0.3		18.6±0.2	
R 0.5		17.3±0.1	
R 1.0	3.40±0.02	16.3±0.1	55.2±0.9

Table 2
Densities for samples treated at 1200 °C

Sample	Density (g/cm^3)	d/d_{th} (%)
R 1.0	4.94±0.05	82.8
R 0.5	5.31±0.04	88.9
R 0.3	5.79±0.05	97.2
R 0.1	5.94±0.03	99.7

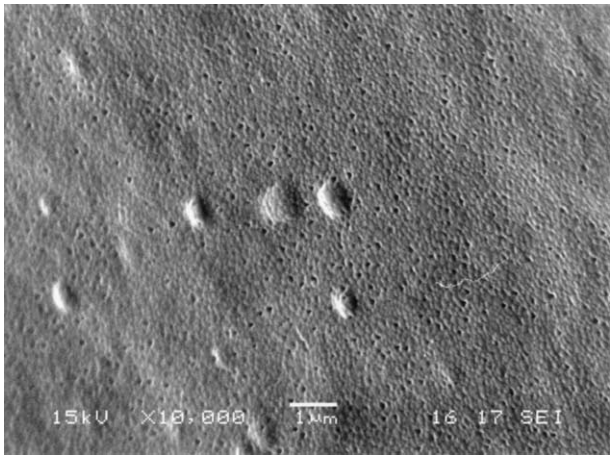

Fig. 5. SEM micrograph of R 1.0, sample heated at 1200 °C.

other hand, during the air treatment the combustion and the organics removal start at lower temperatures (240 °C) as shown by the TG results.

The results of density measurements on samples with a different content of PVP–K15 heated at 1200 °C are reported in Table 2 and compared to the theoretical density of cubic YSZ phase ($d_{th}=5.959$ g/cm^3). The increase in PVP amount decreases the density of the final material: at 1200 °C the values range from 82.8 to 99.7% of the theoretical density for $R=1.0$ and 0.1, respectively.

SEM investigation of the fracture surfaces of the samples annealed at 800 and 1000 °C in air results in featureless microstructures, typical of glassy materials. Only at 1200 °C, the presence of homogeneously distributed grains with a size well below 1 μm can be clearly observed for the samples prepared with PVP contents from $R=0.1$ to 1.0. Fig. 5 presents the SEM micrograph of $R=1.0$ sample annealed at 1200 °C in air, which is representative for all the samples at this temperature. EDS-analysis demonstrated that in all samples yttrium is homogeneously distributed into the crystalline phase without any indication of phase separation.

4. Conclusions

Crack free polyvinylpyrrolidone–YSZ hybrid films with thickness as lower than 100 μm can be prepared by the sol-gel method. By annealing in air, the hybrid gels have been converted to pure, cubic nanocrystalline YSZ. The polymer amount in the starting gels has been found to affect the crystallite sizes and the ceramization pathway.

Acknowledgements

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References

1. Saegusa, T. and Chujo, Y., An organic/inorganic hybrid polymer. *J. Macromol. Sci.*, 1990, **27**, 1603–1612.
2. Kozuka, H., Kajimura, M., Hirano, T. and Katayama, K., Crack-free, thick ceramic coating films via non-repetitive dip-coating using polyvinylpyrrolidone as stress relaxing agent. *J. Sol-Gel Sci. Techn.*, 2000, **19**, 205–209.
3. Schmidt, H. and Seiferling, B., Chemistry and application of inorganic-organic polymers (organically modified silicates). *Mater. Res. Soc. Proc.*, 1986, **73**, 739–750.
4. Wen, J. and Wilkes, G. L., Organic-inorganic hybrid network materials by the sol-gel approach. *Chem. Mater.*, 1996, **8**, 1667–1681.
5. Judeinstein, P. and Sanchez, C., Hybrid organic–inorganic materials: a land for multidisciplinarity. *J. Mater. Chem.*, 1996, **6**, 511–525.
6. Yoshida, M. and Prasad, P. N., Sol-gel-derived poly (vinylpyrrolidone)/silicon oxide composite materials and novel fabrication technique for channel waveguide. *Mater. Res. Soc. Symp. Proc.*, 1995, **392**, 103–108.
7. Lutterotti, L., Ceccato, R., Dal Maschio, R. and Pagani, E., Quantitative analysis of silicate glass in ceramic materials by the Rietveld method. *Mater. Sci. Forum*, 1998, **278–281**, 87–92.
8. Egger, P., Sorarù, G. D. & Dirè S., PVP–YSZ interaction in hybrid sols and gels for the preparation of SOFC free-standing electrolytes. *Proceedings of III Workshop Italiano Sol-Gel,* Trento, Italy, June 13–14, 2002, (ISBN 88-8443-027-5) pp. 158–65.