CHEMISTRY OF MATERIALS
Article

Chem. Mater. **2010,** *22,* 1119–1125 1119
DOI:10.1021/cm9022908

Preparation of Nanoparticle Core−Shell Electrolyte Materials for Proton Ceramic Fuel Cells[†]

Zohreh Khani,[‡] Mélanie Taillades-Jacquin,[‡] Gilles Taillades,[‡] Deborah J. Jones,[*,‡]
Mathieu Marrony,[§] and Jacques Rozière[‡]

[‡] *Laboratoire des Agrégats, Interfaces et Matériaux pour l'Energie, Institut Charles Gerhardt UMR 5253, Université Montpellier II, 34095 Montpellier, France and* [§] *European Institute for Energy Research, Karlsruhe, Germany*

Received July 26, 2009. Revised Manuscript Received November 27, 2009

The sinterability of yttrium-doped barium zirconate (BZY) has been improved through an original synthesis approach giving a core−shell type arrangement in which nanoparticulate BZY is enrobed by a thin coating of yttrium-doped barium cerate (BCY). A flash combustion route was first used to prepare BZY10 (10% yttrium-doped) in a nanopowder form with average particle diameter of 12−17 nm. The nanoparticles were then dispersed in a hydrogel generated from 3,3′,3″-nitrilotripropionic acid complexed metal (yttrium, barium, cerium) acrylates. After thermal elimination of the organic moieties, a material of novel macroscopic architecture is obtained, which can be densified (apparent density ≥ 97%) by sintering compacted pellets at 1300 °C for 10 h, i.e. some 200 °C lower than is generally used to densify BZY. X-ray diffraction indicates that two phases corresponding to BCY10 and BZY10 are present and that no discernible migration of atoms occurs between the zirconate core and the cerate shell. Proton conductivities of densified pellets were determined in a moist nitrogen atmosphere in the range 300−600 °C using impedance spectroscopy. The total conductivity is in the range 4.1×10^{-4} S/cm (300 °C)−9.5×10^{-3} S/cm (600 °C), which is an order of magnitude higher than that of BZY10, prepared under equivalent conditions and the core−shell material displayed improved stability against carbonate formation in a CO_2 atmosphere. The densification, proton conductivity, and CO_2 uptake properties of the novel core−shell structured proton ceramic all differ from those of yttrium-doped barium zirconate cerate solid solution containing a similar ratio of yttrium, zirconium, and cerium, and of a physical mixture of BCY10 and BZY10, and show an improved set of properties compared with those of BCY10 or BZY10 alone.

Introduction

Proton conducting perovskite-type oxides were first described by Iwahara[1] in 1981, and their potential use as electrolytes in range of applications ranging from hydrogen pumping to fuel cells was predicted.[2] Since then, a broad range of aliovalent metal ion-doped M(II) cerates, zirconates, and titanates have been reported, and their structural and electrical properties have been investigated.[3,4] The intermediate temperature range of fuel cell operation is attracting considerable attention, in particular with a view to stationary applications, since on the one hand the high temperature aging mechanisms associated with solid oxide fuel cells can be alleviated, while on the other the temperature limitations of polymer membrane technologies are overcome and high quality heat for cogeneration is obtained. However, although the perovskite proton ceramics have been known for some 25 years, there are still very few literature reports on elaboration and characterization of a complete proton ceramic-based single cell. Our work is developed in this direction, with the optimization of cermet electrodes[5] and perovskite-type cathodes[6] alongside the development of novel methods for preparation and proton ceramics in a form suitable for thin film deposition.[7−9] Of the proton conducting oxides, rare-earth metal-doped barium cerate and barium zirconate perovskites have been the most widely studied. Yttrium-doped barium cerate exhibits higher proton conductivity than doped barium zirconate in the same conditions, but it is less chemically inert in air, since carbonate formation tends to occur by reaction with carbon dioxide.[10] This sensitivity reduces its potential for

---

[†] Accepted as part of the 2010 "Materials Chemistry of Energy Conversion Special Issue".

*Corresponding author. Tel.: +33 467 143330. Fax: +33 467 143304. E-mail: Deborah.Jones@univ-montp2.fr.

(1) Iwahara, H.; Esaka, T.; Uchida, H.; Maeda, N. *Solid State Ionics* **1981**, *3−4*, 359.
(2) Iwahara, H. *Solid State Ionics* **1988**, *28−30*, 573.
(3) Kreuer, K. D. *Annu. Rev. Mater. Res.* **2003**, *33*, 333.
(4) Norby, T. *Solid State Ionics* **1999**, *125*, 1.
(5) Essoumhi, A.; Taillades, G.; Taillades-Jacquin, M.; Jones, D. J.; Rozière, J. *Solid State Ionics* **2008**, *179*, 2155.
(6) Ruiz de Larramendi, I.; Lopez Anton, R.; Ruiz de Larramendi, J. I.; Baliteau, S.; Fauvy, F.; Grenier, J. C.; Rojo, T. *J. Power Sources* **2007**, *169*, 35.
(7) Khani, Z.; Taillades, G.; Taillades-Jacquin, M.; Marrony, M.; Jones, D. J.; Rozière, J. *J. Solid State Chem.* **2009**, *182*, 790.
(8) Jacquin, M.; Ying, Y.; Essoumhi, A.; Taillades, G.; Jones, D. J.; Rozière, J. *J. New Mater. Electrochem. Systems* **2007**, *10*, 243.
(9) Taillades, G.; Jacquin, M.; Khani, Z.; Jones, D. J.; Marrony, M.; Rozière, J. *ECS Trans.* **2007**, *7*(Solid Oxide Fuel Cells 10), 2291.
(10) Ryu, K. H.; Haile, S. M. *Solid State Ionics* **1999**, *125*, 355.

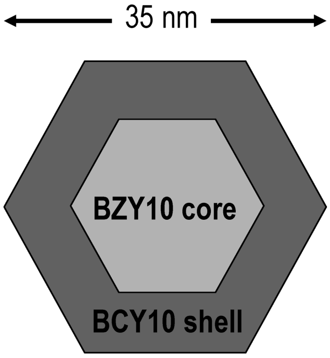

Figure 1. Scheme of core−shell arrangement of nanoparticle yttrium-doped zirconium (core) and yttrium-doped zirconium (shell).

fuel cell application since performance can decrease with time. On the other hand, barium zirconate shows excellent chemical and mechanical stability, but exhibits high grain boundary resistance and is highly refractory, requiring the use of very high temperatures (ca. 1500 °C) to obtain fully densified ceramics. The influence of grain size on the conductivity of barium zirconate has recently been demonstrated by Haile,[11] and the addition of some transition metal oxides such as ZnO,[12] but not others such as titania and alumina,[13] improve sinterability. Other recent results correlate the synthesis route and sintering temperature of yttrium-doped barium zirconate to the existence of structural polymorphs having different bulk conductivity.[14,15] Solid solutions have been investigated as one possible means of associating the properties of conductivity of barium cerate and the chemical stability of barium zirconate when doped with yttrium,[16] gadolinium,[10] or neodymium.[17] In the case of yttrium-doped barium zirconate cerate, substitution of 40% of the cerium by zirconium is needed to eliminate sensitivity to CO_2, and at this level of substitution, the conductivity at 600 °C is a factor of 2 lower than that of yttrium-doped barium cerate.

We have recently shown that nanoparticulate (<35 nm) yttrium-doped barium cerate and zirconate can be prepared at low temperature (900 °C) from reaction media in which either the metal ions are sequestered in a hydrogel of 3,3′,3″-nitrilotripropionic acid or when precipitated from a microemulsion and that such nanopowders lead to well-sintered ceramics at lower sintering temperature.[7] Here, we have built on this methodology to prepare core−shell nanoparticles, Figure 1, in which yttrium-doped (10%) barium zirconate (BZY10) is enrobed by yttrium-doped (10%) barium cerate (BCY10) so as to benefit from the high chemical stability of the former as well as the good sinterability properties of the latter. The possible advantages of a core−shell arrangement of perovskite proton ceramics were first explored by Irvine et al.[18] In that study, the temperature of 1450 °C required for densification promoted interdiffusion of cerium into BZY10 and zirconium into BCY10, and two solid solutions $BaZr_{0.85}Ce_{0.05}Y_{0.1}O_{2.95}$ and $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95}$ were obtained as particles of size ca. 0.5 μm. The total conductivity of this system was 2.5×10^{-4} S/cm at 500 °C. Other proton conducting core−shell compositions $M(IV)O_2-M(III)_2O_3-P_2O_5$ have been proposed by Shirai et al.[19]

We describe here an optimized route for the preparation of a nanoparticle core−shell structure which makes use of a metal ion containing hydrogel to disperse the BCY10 phase around a BZY10 core prepared by flash combustion in a previous step.[8] The proton conductivity and chemical stability in a CO_2 atmosphere of this new core−shell structure proton ceramic are compared with those of BCY10, BZY10, the corresponding solid solution (BCZY10), and also a physical mixture of BZY10 and BCY10 (BZY10 + BCY10).

Experimental Section

BZY10 nanopowders were prepared by flash combustion.[8,20] Stoichiometric amounts of barium, zirconium, and yttrium nitrates (99%) purchased from Sigma-Aldrich were dissolved in water and glycine fuel was added, using a glycine to nitrate mole ratio of 1:2.5. The aqueous solution was concentrated by heating at 200 °C, and the viscous liquid that was generated was fired at 600 °C for 10 h. Polyacrylate salts and especially sodium polyacrylate are effective dispersants for oxide ceramics and basic salts.[21,22] The BZY10 nanopowder was dispersed in a solution of sodium polyacrylate (1 wt %). In a separate reaction vessel, a BCY10 precursor hydrogel was prepared from acrylic acid, metal (yttrium barium, cerium) acrylates, and ammonium hydroxide.[7] The BZY10-polyacrylate dispersion was then added to the BCY10 precursor hydrogel in proportions varying from 10, 20, and 30% wt of BZY10 (90, 80, and 70% wt BCY10 gel, respectively). After thorough mixing using ultrasound, the resulting gels were heated at 400 °C for 3 h and at 900 °C for 4 h to give core−shell materials (BZY10-*csh*-BCY10).

A solid solution BCZY10 of composition $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{2.95}$ was also prepared by hydrogelation of acrylates. Appropriate amounts of barium, cerium, zirconyl, and yttrium acrylates prepared from their acetate salts[7] were mixed separately with an aqueous solution of NH_4OH and acrylic acid. Each mixture was then refluxed overnight and concentrated separately by rotary evaporation. The resulting solutions were mixed and refluxed again. The mixture obtained was rotary evaporated to remove solvents and to obtain a gel. The viscous gel was heated for 3 h at 400 °C and annealed at 900 °C for 4 h, to give the solid solution BCZY10.

---

(11) Yamazaki, Y.; Hernandez-Sanchez, R.; Haile, S. M. *Chem. Mater.* **2009**, *21*, 2755.

(12) Babilo, P.; Haile, S. M. *J. Am. Ceram. Soc.* **2005**, *88*, 2362.

(13) Duval, S. B. C.; Holtappels, P.; Stimming, U.; Graule, T. *Solid State Ionics* **2008**, *179*, 1112.

(14) Azad, A.; Savaniu, C.; Tao, S.; Duval, S.; Holtappels, P.; Ibberson, R. M.; Irvine, J. T. S. *J. Mater. Chem.* **2008**, *18*, 3414.

(15) Duval, S. B. C.; Holtappels, P.; Vogt, U. F.; Stimming, U.; Graule, T. *Fuel Cells* **2009**, *9*, 613–621.

(16) Katahira, K.; Kohchi, Y.; Shimura, T.; Iwahara, H. *Solid State Ionics* **2000**, *138*, 91.

(17) Wienstroer, S.; Wiemhofer, H.-D. *Solid State Ionics* **1997**, *101−103*, 1113.

(18) Savaniu, C. D.; Canales-Vazquez, J.; Irvine, J. T. S. *J. Mater. Chem.* **2005**, *15*, 598.

(19) Shirai, T.; Satou, S.; Saito, Y.; Kuwano, J. *Phos. Res. Bull.* **2007**, *21*, 31.

(20) Chick, L. A.; Pederson, L. R.; Maupin, G. D.; Bates, J. L.; Thomas, L. E.; Exarhos, G. J. *Mater. Lett.* **1990**, *10*, 6.

(21) Cesarano, J.; Aksay, I. A.; Bleier, A. *J. Am. Ceram. Soc.* **1988**, *71*, 250.

(22) Lamarche, J. M.; Persello, J.; Foissy, A. *J. Am. Chem. Soc.* **1983**, *22*, 123.

BZY10 (10 wt %) prepared by flash combustion was mixed and ground with BCY10 (90 wt %) prepared by hydrogelation of acrylates to obtain a macroscopic, physical mixture (BZY10 + BCY10).

The morphology and the grain size of the powders were examined using transmission electron microscopy (TEM, JEOL 1200 EX). The samples were hand ground, suspended in ethanol and sonicated to separate any agglomerated particles before depositing drops of the suspension. For densification powder samples were first ground and compacted into pellets (diameter 13 mm and thickness 0.8−1 mm) by cold pressing (room temperature) at 370 MPa under 20 Torr reduced pressure. The pellets were placed between two alumina plates (thickness 2 mm) and were sintered in ambient laboratory air at 1350 °C for 10 h with a ramp rate of 1 °C/min. After sintering, the surface layer in contact with the alumina was removed by light abrasion. The apparent density of the pellets was determined from the geometric dimension and pellet weight. Compared with the calculated value, the relative density of all pellets was ≥97%. Densified pellets were observed by scanning electron microscopy (SEM, HITACHI 52600 N).

The above materials were characterized by X-ray diffraction (XRD) at room temperature with a Philips X'Pert diffractometer using Cu Kα radiation. XRD patterns were recorded in the 2θ range between 20 and 80° with a step size of 0.02° and a counting time of 5 s at each step.

The proton conductivity of sintered pellets was determined from impedance spectra recorded between 300 and 600 °C in the 10 Hz−10 MHz frequency range using an HP4192A impedance analyzer. Platinum electrodes were sputtered on the surfaces of surface abraded samples. After placing the sample in a closed measurement cell, moist nitrogen (3% H_2O, 97% N_2) was passed over the sample by flowing N_2 (50 cm^3/min) through a water bubbler at room temperature. Impedance spectra were recorded after equilibration at each temperature.

The chemical stability to CO_2 of all powders was determined using a gravimetric method. The sample was placed in the crucible of a Netzsch TG 439 thermobalance, and CO_2 was then flowed (50 cm^3/min) over the sample while the temperature was increased (8 °C/min) to 1300 °C. After a dwell time of 1 h at this temperature, the sample was cooled down (cooling rate 8 °C/min), and the procedure repeated to assess reproducibility of the CO_2 uptake. Weight changes were measured and recorded by the thermobalance.

Results and Discussion

Influence of Core−Shell Composition on Properties. The objective of this study was to prepare an electrolyte material both with proton conductivity properties comparable with those of BCY10 and also improved chemical stability, and to achieve these aims, materials of several core−shell BCY10−BZY10 compositions have been prepared and their properties compared. First, different quantities of the BZY10 nanopowder (between 10 and 30% wt) were dispersed into the BCY10 gel precursor to obtain core−shell materials. The powders were densified following the same protocol, and their proton conductivity in the range 400−600 °C, and their stability against carbonate formation, was determined.

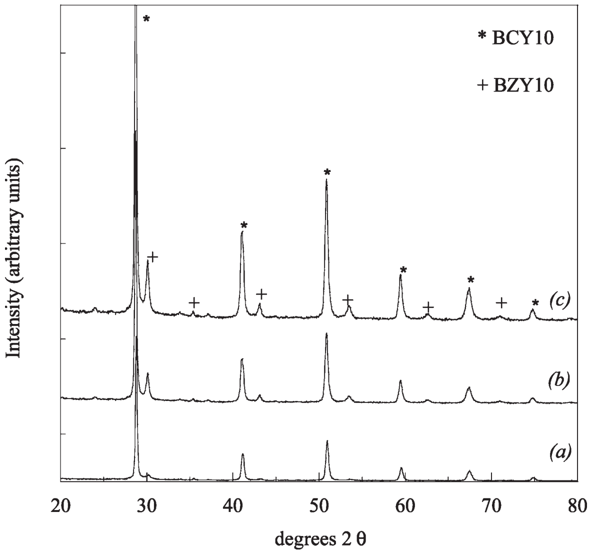

Figure 2. X-ray diffraction patterns of (a) 10BZY10-*csh*-90BCY10, (b) 20BZY10-*csh*-80BCY10, and (c) 30BZY10-*csh*-70BCY10 after calcination at 900 °C.

Table 1. Unit Cell Parameters and Relative BCY10 and BZY10 Contributions of Core−Shell Material Containing 10 wt % BZY10

BCY10[a]					BZY10[a]		
a/nm	*b*/nm	*c*/nm	R_{obs}	RC[b]	*a*/nm	R_{obs}	RC[b]
0.8770(5)	0.6242(4)	0.6206(4)	2.87	0.909(6)	0.4202(4)	3.12	0.091(6)

[a] Space group *Pmcn* for BCY10 and $Pm3\overline{m}$ for BZY10. [b] Relative content in the core−shell material, calculated from XRD.

XRD patterns of the core−shell 10BZY10-*csh*-90BCY10, 20BZY10-*csh*-80BCY10, and 30BZY10-*csh*-70BCY10 samples after calcination at 900 °C are shown in Figure 2. The core−shell powders in each case comprise two distinct phases corresponding to BZY10 and BCY10. The refined lattice parameters and relative contributions to the X-ray diffraction intensities for 10BZY10-*csh*-90BCY10, taken as an example, are given in Table 1. The relative contributions of 0.914(7) for BCY10 and 0.086(7) for BCZY10 correspond to 91 and 9 mol %, respectively, and are in good agreement with the proportions used experimentally. The lattice parameter of BZY10 is in the high value range of reported lattice parameters for materials sintered at 1500 °C, i.e., in the range associated with the β-type BZY10 phase.[14] This result is not unexpected for a BZY10 material prepared by flash combustion and sintered at 1400 °C, given that the α-type phase is the thermodynamically stable form, which dominates in materials sintered at significantly higher temperature (1720 °C). The proportion of BZY10 in the present core−shell particles is, however, too low to distinguish between relative amounts of α- and β-type components.

From the above lattice parameters, identical to those reported,[23−25] it may be concluded that no migration of cerium into the zirconate, nor zirconium into the cerate phase, occurs, at least at the level of XRD detection. This result differs from the core−shell barium cerate zirconate

---

(23) Takeuchi, K.; Loong, C. K.; Richardson, J. W., Jr.; Guan, J.; Dorris, S. E.; Balachandran, U. *Solid State Ionics* **2000**, *138*, 63.
(24) Knight, K. S. *Solid State Ionics* **2000**, *127*, 43.
(25) Schober, T.; Bohn, H. G. *Solid State Ionics* **2000**, *127*, 351.

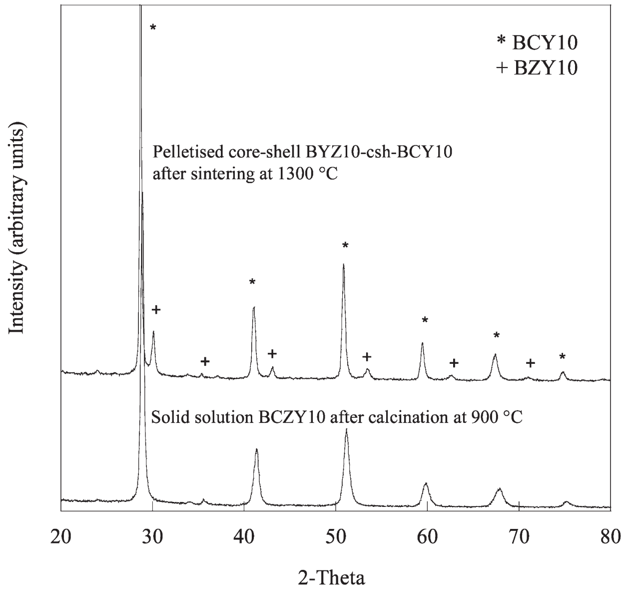

Figure 3. X-ray diffraction patterns of solid solution BCZY10 powder after calcination at 900 °C and core–shell BZY10-*csh*-BCY10 pellet sintered at 1300 °C. Lines marked * and + are given by BCY10 and BZY10, respectively.

Table 2. Relative Density after Sintering at 1300 °C of BCY10, BZY10, and Core–Shell Materials Containing 10 to 30 wt % of BZY10, Their Total Conductivity at 600 °C, and Weight Increase in Carbon Dioxide Atmosphere

material	relative density (%)	total conductivity at 600 °C (S/cm)	CO_2 uptake (%)
BCY10	98	0.0182	13
10BZY10-*csh*-90BCY10	97	0.0095	7
20BZY10-*csh*-80BCY10	95	0.0064	5
30BZY10-*csh*-70BCY10	92	0.0032	5, 9
BZY10	95 (at 1500 °C)	0.0020	0

described by Irvine, where two solid solutions rich respectively in cerium and in zirconium were identified by XRD. The BCZY10 reference solid solution prepared in this work is a single phase material after calcination at 900 °C (Figure 3); it corresponds to JCPDS file no. 81-1386. The space group of BCZY10 is *Imma* with the lattice parameters a = 0.8777 nm, b = 0.6227 nm, and c = 0.6225 nm.

One of the aims of this work was to develop a method allowing incorporation of chemically stable BZY10 into a material that could be sintered at lower temperature than is usually necessary for zirconate ceramics. A sintering temperature of 1300 °C (temperature generally required to densify barium cerate materials) was sufficient to obtain samples having a relative density of ≥92% (Table 2), which is indirect evidence for core–shell architecture materials. At this sintering temperature, the relative density increases as the quantity of BZY10 decreases. The most fully densified material (97%) was 10BZY10-*csh*-90BCY10, obtained after sintering at 1300 °C.

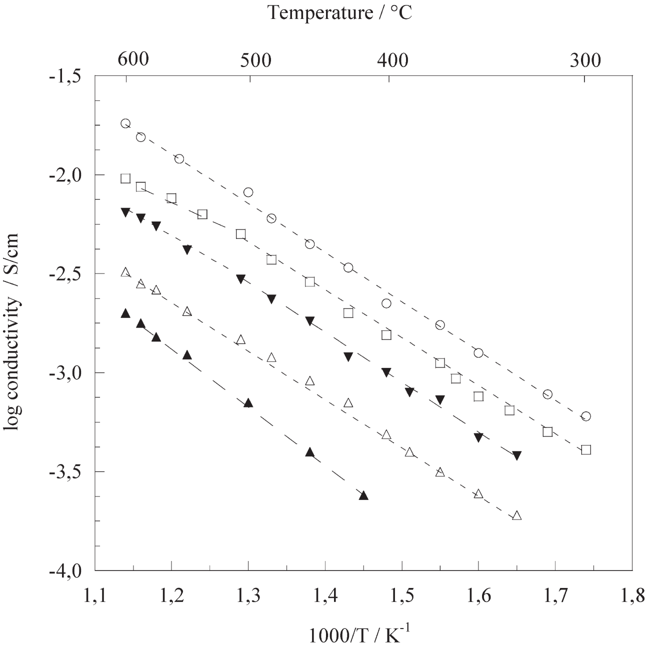

Figure 4. Temperature dependence of total conductivities of (○) BCY10, (□) 10BZY10-*csh*-90BCY10 (Csh10), (▼) 20BZY10-*csh*-80BCY10 (Csh20), (△) 30BZY10-*csh*-70BCY10 (Csh30), and (▲) BZY10.

The proton conductivity of BCY10, BZY10, and the core–shell structured samples was determined between 300 and 600 °C in an atmosphere of humidified nitrogen. The results (the average of three measurements) are plotted in Figure 4. The conductivity obtained for BCY10 and BZY10 prepared by hydrogelation of acrylates and reverse micelles respectively is similar to, or higher than, that reported for materials of the same composition prepared by the other, direct ceramic solid state synthesis routes.[3,26] For example, at 600 °C, the total conductivity is 2×10^{-2} S/cm for BCY10 and 2×10^{-3} S/cm for BZY10. A higher conductivity phase BZY20 sintered at 1600 °C in the presence of excess barium has been reported to give conductivity of 7.9×10^{-3} S/cm.[27] In the core–shell material series, the highest conductivity was observed for the sample containing 10% BCY10, the conductivity decreasing as the quantity of BZY10 in the samples increases. At 600 °C, the total conductivities are 9.5×10^{-3}, 6.4×10^{-3}, and 3.2×10^{-3} S/cm for samples containing 10, 20, and 30 wt % BZY10, respectively. The conductivities determined here for the core–shell samples are in all cases higher than that of BZY10. The trend in conductivity is a result not only of the intrinsic conductivity of the components but also of the relative density of each of the samples, which tends to lower values as the proportion of BZY10 increases.

Sintered powders of core–shell materials containing 10, 20, and 30 wt % of BZY10 were exposed to a CO_2 atmosphere between room temperature and 1300 °C in order to compare their chemical stability. The samples respond rapidly to the CO_2 atmosphere and increase in weight until about 800 °C, when the maximum CO_2 uptake was observed for all samples. Above ca. 1100 °C, carbon dioxide is eliminated. The carbonation process is reversible, and below 1050 °C, the samples take up CO_2 and increase in weight. Among all samples, the highest CO_2 uptake (13 wt %) was observed for the non

---

(26) Slade, R. C. T.; Flint, S. D.; Singh, N. *Solid State Ionics* **1995**, *82*, 135.

(27) Babilo, P.; Uda, T.; Haile, S. M. *J. Mater. Res.* **2007**, *22*, 1322.

core–shell end-member BCY10, which is in agreement with previous descriptions.[7,28] In contrast, BZY10 is more stable against carbonation under these conditions, since no weight change was observed. In the case of the core–shell samples, the CO_2 uptake reached intermediate values of 7 and 5 wt % for 10BZY10-*csh*-90BCY10 and 20BZY10-*csh*-80BCY10 samples, respectively, which indicates them to be markedly more stable to carbonation than BCY10. It is interesting to note that the stability of core–shell powder to carbonation does not appear to be a regular function of the relative quantities of BZY10 and BCY10 in the material. Rather, the results indicate that BCY10-enrobed 10 and 20 wt % BZY10 have a significantly increased chemical stability compared with BCY10 alone. For samples containing 30 wt % BZY10, the results were less reproducible and weight increase was in the range 5–9%. This is interpreted as indicating that for this material richest in BZY10, the core–shell arrangement is less well respected than in the other samples and, in consequence, the quantity of BZY10 exposed at the surface of the sample varies between experiments. This is also in agreement with SEM and conductivity results obtained for this material. In fact, considering the relative density, proton conductivity, and CO_2 uptake values of core–shell material containing 30 wt % BZY10, it is concluded that the quantity of BCY10 gel precursor was not sufficient to enrobe the BZY10 nanopowder, and as a result, the grain boundary resistance of BZY10 is less modified by the presence of BCY10 than in samples with 10 and 20 wt % of BZY10.

Comparison of the Properties of Core–Shell 10BZY10-*csh*-90BCY10, Yttrium-Doped Barium Zirconate Cerate Solid Solution $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{2.95}$ and a Physical Mixture of BCY10 and BZY10. It was observed that when the quantity of BZY10 in the samples is increased beyond 10%, densification becomes more difficult and the conductivity obtained sharply decreases, while the chemical stability of the samples to CO_2 improves slightly. From these preliminary studies, summarized in Table 2, a composition of 10% wt BZY10 (core) and 90 wt % BCY10 (shell) was chosen for comparison of the properties of core–shell materials with those of other macro- or nanoscopic organisations (physical mixture and solid solution).

Transmission electron micrographs of the core–shell material after thermal treatment at 900 °C are shown in Figure 5. The crystallites are nanometric in dimension, and homogeneous in size and shape, the average particle size being ≤35 nm. These images are interpreted as showing the (lighter) barium yttrium zirconate core surrounded by the (heavier) barium yttrium cerate shell. The dark areas observed in TEM are a projection of cerate and zirconate regions in superimposed particles, and although their relative dimension cannot rigorously be used to determine composition, an approximation may be made. If the core–shell particles are considered as having an approximate spherical morphology, then the total core–shell particle volume may be calculated as 2.2×10^4 nm^3 (particles of dimension 35 nm), and using an inner (BZY10) dimension of 15 nm and an outer (BCY10) dimension of 10 nm provides a volume for the BZY10 core of 1.8×10^3 nm^3. This calculation leads to a composition of 92% BCY10 and 8% BZY10, in good agreement with the ratios used in the synthesis. Scanning electron micrographs show the pellets to be highly compact and well-densified, Figure 6. At this scale, it was not possible to distinguish the core–shell form of the grains. However larger grains surrounded by small ones were observed in core–shell surface fracture images. The properties of the core–shell material described below, which differ from those of a solid solution or physical mixture of nominally the same composition, are believed to arise from the particular structural arrangement.

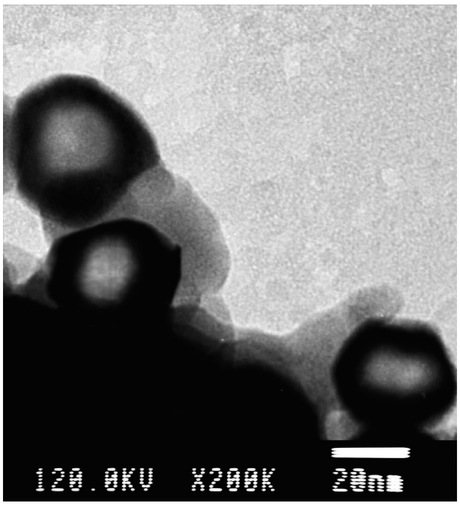

Figure 5. TEM micrograph of core–shell BZY10-*csh*-BCY10 after calcination at 900 °C.

The proton conductivity of the calcined (1350 °C) and densified pellets was measured between 300 and 600 °C under nitrogen that was humidified by bubbling through water at room temperature. The conductivity of all samples was measured under strictly identical conditions to enable comparison between the various materials. Impedance spectra at 405 and 450 °C are provided in Figure 7. The spectra were fitted with two R(CPE) components, allowing determination of the contribution of the grain boundary resistance to the total resistance as being 68% for the physical mixture of yttrium-doped barium cerate and zirconate, 47% in the solid solution, and only 30% in the core–shell sample at 405 °C. The results of this analysis confirm the validity of our approach.

The dependence of conductivity on temperature is shown in Figure 8. The total conductivity of the core–shell sample is 4.1×10^{-3} S/cm at 300 °C, increasing to 9.5×10^{-3} S/cm at 600 °C. These values are higher than those of BZY10 alone, slightly lower than those of BCY10 alone,[3,26,29,30] and thus could, in a first analysis,

---

[28] Zakowsky, N.; Williamson, S.; Irvine, J. T. S. *Solid State Ionics* **2005**, *176*, 3019.

[29] Bonanos, N.; Ellis, B.; Knight, K. S.; Mahmood, M. N. *Solid State Ionics* **1989**, *35*, 179.

[30] Snijkers, F. M. M.; Buekenhoudt, A.; Cooymans, J.; Luyten, J. J. *Scr. Mater.* **2004**, *50*, 655.

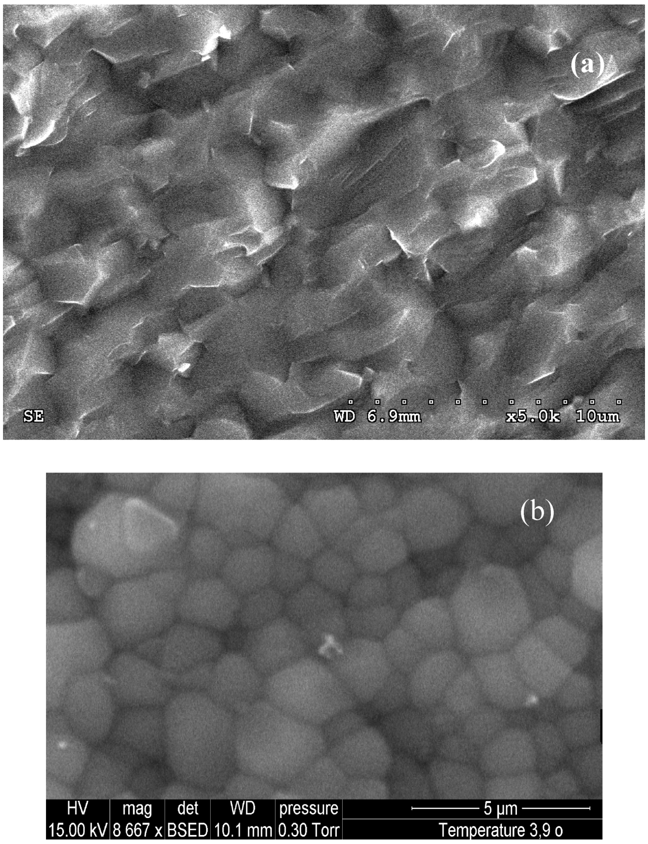

Figure 6. SEM micrographs of core−shell after sintering for 10 h at 1300 °C. (a) Edge. (b) Surface.

be considered to simply correspond to a weighted average of the conduction properties of the individual components. However, comparison with the properties of the solid solution BCZY10 and the physical mixture (BCY10 + BZY10) provides support that the core−shell material does indeed have a different macroscopic architecture from either of these, since its conductivity is higher than that of both of the BCZY10 solid solution of the same composition (2.8×10^{-4} S/cm at 300 °C and 7.6×10^{-3} S/cm at 600 °C, in agreement with previous results[16]) and the physical mixture (3.8×10^{-4} S/cm at 350 °C and 5.9×10^{-3} S/cm at 600 °C), in which statistical distributions of cerium and zirconium at the atomic and nanometer grain-size levels, respectively, are expected. The conductivity of the present core−shell material is higher than that reported by Irvine for a solid solution type core−shell material (2.5×10^{-4} S/cm at 500 °C), in which a submicronic zirconium-rich shell is surrounded by a 20 nm cerium-rich shell[18] and where, as could be expected from the relative amounts of cerium and zirconium, the conductivity is close to that generally observed for rare-earth element-doped barium zirconate.[3] Finally, a slight change in slope in the dependence of conductivity on reciprocal temperature at around 500 °C is probably due to a decrease in proton concentration in the sample bulk.[31]

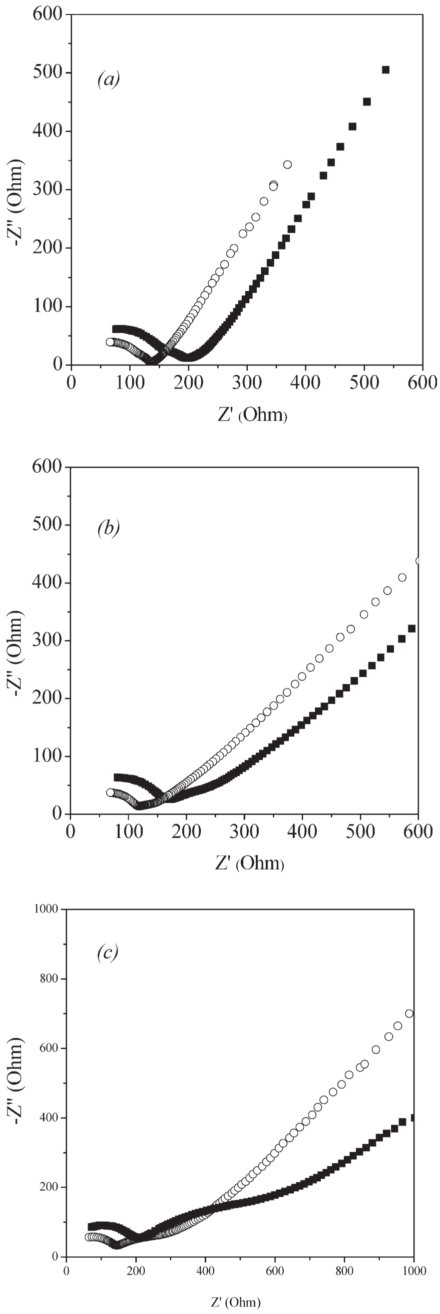

Figure 7. Impedance spectra of (a) core−shell BZY10-*csh*-BCY10, (b) solid solution BCZY10, and (c) BZY10 + BCY10 at 450 (○) and 405 °C (■) in nitrogen humidified at room temperature.

In terms of the activation energies, the obtained value from the total conductivity of BZY10 is 0.69 ± 0.01 eV, close to that (0.72 eV) reported in previous work.[7,18] On the other hand, the activation energy for all cerate containing samples is lower, ca. 0.48 ± 0.01 eV.

The chemical stability in a carbon dioxide atmosphere of the core−shell material 10BZY10-*csh*-90BCY10 was examined and compared with that of BCY10, BZY10, the solid solution sample, and a physical mixture of BCY10 and BZY10. This is an accelerated test (undiluted CO_2 gas) for the tendency of each material to form a surface layer of carbonate. The results are shown in Figure 9. BZY10 is the most stable material, since no weight change through CO_2 uptake was observed

---

[31] Schober, T.; Friedrich, J. *J. Am. Ceram. Soc.* **1999**, *82*, 3125.

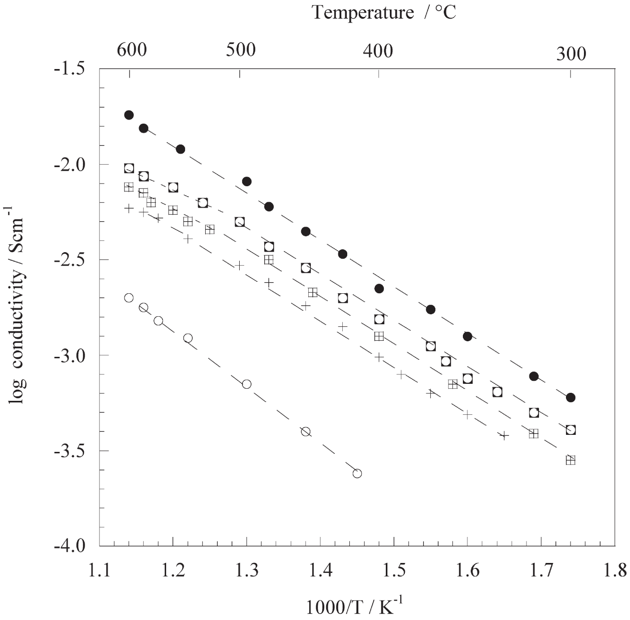

Figure 8. Temperature dependence of total conductivities of (●) BCY10, (◘) BZY10-*csh*-BCY10, (⊞) solid solution BCZY10, (+) the physical mixture of BZY10 and BCY10 in proportions of 10/90 wt %, and (○) BZY10. Conductivity was measured in a humidified nitrogen atmosphere.

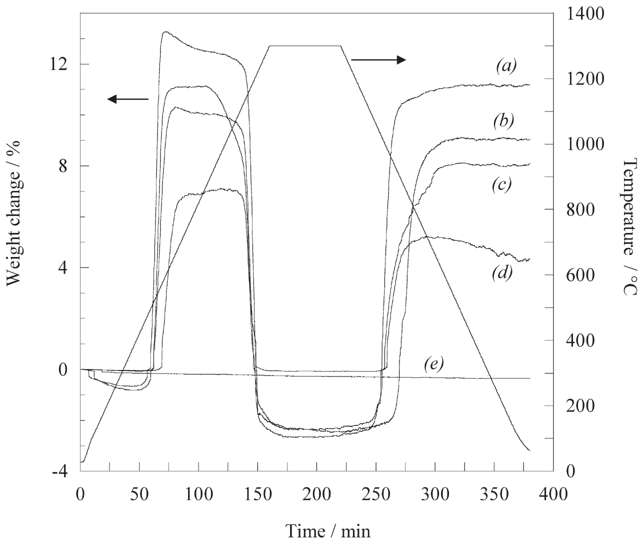

Figure 9. Weight change of (a) BCY10, (b) BZY10 + BCY10, (c) BCZY10, (d) core−shell BZY10-*csh*-BCY10, and (e) BZY10 powders in a CO_2 atmosphere.

through the heating/cooling cycle between 20 and 1300 °C (Figure 9e). A weight increase was observed for all the other samples at temperatures >475−500 °C (Figure 9a−c) except for the core−shell powder, which resists carbonation until 580 °C, Figure 9d. At 700 °C, the maximum weight increase is reached by all samples, and there are no further weight changes until about 1000 °C, when CO_2 loss begins and is complete at 1200 °C. In the cooling cycle, the masses stay constant until 1050 °C, when the samples start to increase in weight again by uptake of CO_2.

The highest CO_2 uptake (13%) was observed for BCY10 powder[28] (Figure 9a), followed by the solid solution BCZY10 (10%, Figure 9c). This result is in agreement with a previous report that partial substitution of Ce by Zr in BCY10 increases chemical stability.[10] Weight increases between 8 and 11% were observed for the physical mixture of BZY10 + BCY10 (Figure 9b). It is possible that in this sample the two components are not fully homogeneous at the nanograin level, leading to some variation in the CO_2 uptake depending on the relative amount of exposed BCY10 or BZY10 surface. For the core−shell material, a significantly lower CO_2 uptake was observed, being 7% in the first cycle and 5% in the second cycle. Although there is no direct evidence, this result implies that the surface of the core−shell particles is perhaps not comprised uniquely of BCY10 but also includes BZY10 domains that reduce the overall CO_2 uptake. Although such an arrangement could explain why the increase in weight of the core−shell powder is lower than would be expected from the respective proportions of BZY10 and BCY10 alone, any such surface BZY10 domains are sufficiently small and distributed that the sinterability of the core−shell material compared with BCY10 is unaffected. The durability of these properties and the positive impact on fuel cell performance awaits use of the core−shell material as electrolyte in a proton ceramic fuel cell (PCFC), when further optimization of the composition may be required.

Conclusion

Modification of the grain boundary impedance of nanoparticulate yttrium-doped barium zirconate prepared by flash combustion synthesis by enrobing with a 5−10 nm layer of yttrium-doped barium zirconate deposited from a complexed mixture of the component metal acrylates is an effective means of reducing the temperature required for sintering of barium zirconate, increasing the relative density that can be obtained at such temperatures, and improving its electrical properties. The core shell BZY10-*csh*-BCY10 prepared here shows a delay in the onset temperature for carbonate formation, and lower CO_2 uptake than nonmodified BCY10, as well as of reference solid solutions and physical mixtures of BCY10 and BZY10. Investigations by TEM, SEM, TGA, and XRD provide information consistent with the observed electrical properties and a coherent description of the macroscopic structural arrangement of the nanoparticle core−shell system. The methodologies developed are currently being applied to other perovskite type proton conductors, and membranes of the materials obtained being used as electrolyte supports in membrane electrode assemblies for a PCFC.

Acknowledgment. Funding by the Plan d'Action National pour l'Hydrogène et les Piles à Combustible (PAN-H) de l'Agence Nationale de la Recherche under the Tectonic project (ANR-05-PANH-015-03) is acknowledged. A bursary from the Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME) is acknowledged with thanks.