On the manufacture of silver-BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ composites for hydrogen separation membranes

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Abstract

Silver-BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ (Ag/BCZY) composites were investigated due to their potential application as hydrogen separation membranes, with emphasis on their fabrication and characterization. A precursor powder of BCZY was prepared via a wet chemical route and characterized by XRD, SEM and dilatometry. The precursor powder was coated with silver using Tollens reaction and then sintered under a variety of conditions. It was possible to obtain dense samples with a low level of non-percolating silver (2 vol%). Silver was present even if sintered at 1300°C as it remained trapped in the ceramic matrix. The overall conductivity of a dense sample with 2 vol% of silver increased when compared to pure BCZY, and in particular the grain boundary resistance decreased considerably. A measurement of the open circuit voltage in fuel cell mode indicates the presence of mixed electronic-protonic conductivity in the composite.

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Introduction

State of the art hydrogen-separation membranes are based on Ag–Pd alloys [1–3] but with an increasing demand for hydrogen, their manufacture will be negatively impacted by the high price of Pd. Alternatively, metal ceramic composites or ceramic–ceramic composites [4–6] or mixed protonic-electronic conductors [7] can be used to separate hydrogen, analogous to their application for oxygen separation [8]. Fig. 1 is a diagram of a pressure-driven hydrogen separation membrane using a well-mixed composite of a pure proton conductor and a metal. It is expected that such cermet membranes can operate in the temperature regime 400–800°C; this would allow integration with other devices such as fuel cells, catalytic reactors, and high temperature electrolyzers.

In a passive hydrogen separation membrane no electric current is used to drive the transport but the gas solid reactions are electrochemical. Fig. 1 shows that hydrogen is oxidized at the anode according to

\[
\frac{1}{2}H_2 \rightarrow H^+ + e^- \quad (1)
\]

Protons then migrate through the ceramic and electrons through the metal. H$_2$ then evolves at the cathode according to

\[
H^+ + e^- \rightarrow \frac{1}{2}H_2 \quad (2)
\]

While atomic hydrogen migrates through metal based membranes, protons migrate through ceramic proton...
Fig. 1 – Schematic of a passive hydrogen separation membrane. The membrane is a mixed proton-electronic conductor and the driving force is the difference in chemical potential.

collectors. The electrochemical reactions at the gas–solid interface can be manipulated to promote certain reactions by adding a suitable catalyst to the cathode surface. For example, ammonia can be formed by using palladium [9], CO2 can be reduced to CO by using iron, copper or nickel [10] or hydrogen can be produced from a variety of hydrocarbons [11,12]. This promotion of electrochemical reactions is another distinctive and desirable feature of these metal-ceramic composites compared to Pd-based metallic membranes.

In this work, BaCe0.5Zr0.3Y0.16Zn0.04O3 (BCZY) has been selected as the proton conductor due to its improved chemical stability against CO2 and its relatively low sintering temperature (T = 1300 °C) compared to many other equivalent materials (T > 1600 °C) [13]. BCZY is a perovskite with adequate proton conduction levels (2.1 mS cm-1 at 600 °C) for use in an electrochemical cell in fuel cell or electrolysis mode, and is a material that can be processed into flat sheets suitable for membrane applications by tape casting [10,14,15]. Silver was selected as the metal in this study due to the simplicity of Tollens reaction to silver coat ceramic powders, its much lower price relative to Pd or Pt, and its high electronic conductivity. Finally, the method employed here has been previously used to successfully fabricate mixed conducting oxygen separation membranes with an unprecedented low silver content of <10 vol% using ultrafine samaria-doped ceria as the ionic conductor [8].

The most common method to fabricate metal ceramic composites for gas separation is the mixing of metal and ceramic powders, followed by sintering at high temperature [16,17]. A major challenge in this approach is the high content of the metal needed (>30 vol%) [5,17] to achieve percolation in the electronically conductive phase. Most composites used for oxygen separation therefore contain high levels of the electronically conductive phase [18]. Noble metals with a high melting point such as palladium and platinum are also frequently used due to the high sintering temperature needed for the densification of the cermet. Nickel has also been used, but it cannot be used in air and/or carbon containing atmospheres [19].

This article describes the synthetic route to obtain BCZY, and the characterization of the precursor powder by SEM, XRD and dilatometry. The method to coat the precursor powder with silver is described in detail and the sintering conditions tested are presented. The second part of the work concentrates on the transport properties of a dense composite of the materials from room temperature to 600 °C. This work is part of our efforts to manufacture a metal ceramic composite with a low level of metal to be used as hydrogen separation membrane. To the authors’ knowledge, there is no other work other than our own [8] related to the use of Tollens’ reaction to fabricate dense mixed conducting membranes for gas separation.

**Experimental section**

**Precursor synthesis**

The starting materials were Ba(NO3)2 (Alfa Aesar 99.95%), Ce(NO3)3.6H2O (Aldrich 99.5%), Y(NO3)3.6H2O (Aldrich 99.9%), Zr(NO3)4.6H2O (Aldrich 98%) and Zirconium acetyl-acetonate: Zr(acac)4, (98% Aldrich). The nitrates were dissolved in de-ionized water by stirring and heating. Zr(acac)4 was dissolved in a hot mixture of ethanol and water in a 2:1 volume ratio. The solution containing Zr was added to the solution of nitrates, followed by concentrated ammonium hydroxide (Aldrich, 28–30%) to induce precipitation. The precipitate was then dehydrated overnight under constant stirring on a hot plate. Finally, the precipitate was heated to 350 °C to undergo spontaneous combustion. The remaining powder was calcined at 800 °C for 1 h. The agglomerates of this precursor powder were broken down using a planetary mill with isopropyl alcohol as the dispersing medium and zirconia balls as the milling media. The resultant powder was used as the precursor powders for all subsequent studies. The BCZY phase formation was followed by annealing the powder at different temperatures and times in air, and then analyzing with XRD at room temperature.

The sintering behaviour was studied by dilatometry (DIL 402C Netzsch) using BCZY precursor pellets. The precursor powder was uniaxially pressed and then cold isostatically pressed at 207 MPa for 1 min to produce the green bodies used for dilatometry. The heating rate was 3 °C min-1 up to 1250, 1200, 1300 or 1350 °C. The expansion of the alumina sample mount was taken into consideration by using a standard Al2O3 pellet of similar dimensions.

**Silver coating**

A mixture of water/ethanol was used as the solvent to improve wettability. In a typical experiment 0.51 g of AgNO3 (Aldrich) were dissolved in 30 ml of solvent, then a few drops of concentrated NH4OH were added until the black precipitates (Ag2O), which formed after the initial additions, disappeared. Then 15 ml of 0.1 M KOH solution were added, with additional NH4OH to re-dissolve the black precipitates if they reappeared. In this basic solution, the complex ion [Ag(NH3)2]+, the basis of the Tollens’ reaction, is formed. The BCZY powder was then suspended in the solution with the aid of an ultrasonic bath for 20 min. Finally, 3 ml of 0.25 M dextrose as reducing agent were added to the mixture and left under constant stirring at room temperature. The deposition of silver began after 1 min and finished within 5 min. The
mixture was left to settle, the solution was decanted and then de-ionized water was added to the precipitate followed by stirring and then centrifugation. This procedure was repeated at least five times to eliminate the remaining salts. For this work, the initial composition was 30 w% silver and 70 w% BCZYZ.

**Sintering of the composite powder**

The black/brown powder was then dried at 200 °C for 1 h and then compressed using a uniaxial press followed by cold isostatic pressing at 207 MPa for 1 min. A variety of sintering conditions were tested searching for a dense percolating composite: a) sintering from 1200 to 1300 °C, at 5–15 °C min⁻¹ and b) fast sintering i.e. the sample was introduced in the furnace at high temperature and kept there for a limited time before quenching to room temperature. To minimize silver loss the samples were covered with extra BCZYZ powder, and after sintering the pellets were polished with grinding paper.

**Characterization**

Electron microscopy. A field emission gun scanning electron microscope (FEG-SEM Gemini 1525) was used to image the precursor powders and fractures surfaces of the membranes. X-Ray diffraction was used for phase identification if the precursor powders and consolidated samples using an X'Pert PRO MRD X-ray diffraction system.

Conductivity. Impedance spectroscopy (Autolab PGSTAT302) with an FRA module was used to measure the bulk and grain boundary conductivity in air between 100 °C and 600 °C. The impedance response was measured from 0.1 or 1 Hz to 1 MHz with a potential of 20 mV.

Open circuit voltage (OCV). A dense sample was mounted at the end of an alumina tube and sealed with a ceramic adhesive (Aron D). One of the sides was fed with moist (3% H₂O) hydrogen (10%) diluted in nitrogen while the other side was in an atmosphere of static air (2% H₂O). Silver paint and wire were used on both sides to function as electrodes. The OCV was measured from 150 to 600 °C at a rate of 3 °C min⁻¹. Three impedance spectra were taken at 150, 400 and 600 °C.

**Results and discussion**

**Precursor**

The BCZYZ precursor powders consisted of two perovskite phases similar to BaZrO₃ and BaCeO₃. Although, the precursor is not initially a single phase, the powder was chosen for further studies since it gives excellent results as a precursor for tape casting membranes [10,14]. The phase formation was followed by XRD and although BaCO₃ was not detected by XRD above 800 °C there was always a weight loss after sintering. Therefore, CO₂ and H₂O may still be released upon complete formation of the single phase at 1100 °C.

A micrograph of the precursor powders obtained after treatment at 800 °C is seen in Fig. 2a. The observed cube-shaped crystallites are a characteristic feature in this precursor. Fig. 2b shows the same precursor after coating with silver and it also shows cube-shaped crystallites coated with a very thin layer of silver.

The XRD pattern of the coated precursor and of a final sintered pellet is shown in Fig. 3. The silver does not react with BCZYZ, as expected from a metal that is stable against oxidation at high temperatures. The composite pellet has a high content of silver but it is not dense (see Table 1); it is shown to emphasize the absence of reaction between the components. Some small peaks (49, 58 in 2theta) might be related to the presence of BaCO₃ and have been observed before in BCZYZ in contact with organic pore formers [15] and the shoulders in the main reflections of BCZYZ may indicate an incomplete formation of a single phase, as the sample was exposed to high temperatures only briefly. It was also found that silver was consistently lost at high temperatures although this could be minimized by covering the sample with BCZYZ powder. The amount of silver detected by XRD in samples with open porosity was significantly affected by the polishing; silver was probably spread over the surface of the harder ceramic matrix during polishing; such that larger contents of silver were observed in XRD than those expected from density measurements. Measurements of dense samples by XRD were not affected by polishing.

![Fig. 2 – a) BCZYZ precursor after annealing at 800 °C. b) BCZYZ precursor powder coated with silver.](image-url)
The densities of the green bodies were commonly up to 70% of the theoretical value and after sintering they exhibited a weight loss of ca. 5%, associated to CO2 or H2O release. There are three features common to all the sintering studies of BCZYZ. Fig. 4 shows that at 1100 °C there is an expansion most likely associated with elimination of remaining BaCO3 and the transformation into a single phase. The onset at 1180 °C marks the beginning of a dramatic shrinkage. After reaching a maximum contraction at 1300 °C the pellet expands slightly to a stable volume within less than 3 h. When cooling, the material shrinks as expected and a thermal expansion coefficient of 2.18 × 10⁻⁵ K⁻¹ can be obtained from the linear region between 1300 °C and 900 °C. This value is comparable to 1.12 × 10⁻⁵ K⁻¹ for BaCeO3 and 7.13 × 10⁻⁶ K⁻¹ for BaZrO3 [20], although the values may depend upon the degree of hydration [21]. At lower temperatures there is a clear and continuous expansion: between 800 °C and 600 °C the expansion is such that it neutralizes the shrinkage associated with thermal contraction and below 600 °C it even outweighs the shrinkage. This expansion can be associated with water absorption into the crystal lattice as observed in doped barium zirconates [22] and doped barium cerates [21,23]. Surprisingly, the expansion continues towards lower temperatures. It is also possible that a phase change is responsible for the changes in volume [21,24].

Similar sintering profiles were observed at a heating ramp of 5 K min⁻¹ and at temperatures of 1300 °C and 1350 °C. In all these cases the final densities were above 93%. Sintering at 1250 °C led to a dense sample although this treatment was not always reproducible. Sintering at 1200 °C did not yield a dense (>93%) sample.

These results were used as a guide for the manufacture of Ag/BCZYZ composites. No dilatometry studies were undertaken of the composite precursor powder because some of the silver would melt, and because silver evaporates at higher temperatures, risking contamination in the equipment. During densification there are two processes that compete against each other: high temperatures favour sintering of BCZYZ but increase the undesired loss and exudation of silver. As silver melts at 961.8 °C, if the sintering is not fast enough, the silver drains out of the ceramic before being trapped inside the ceramic matrix. An optimal sintering profile is needed owing to the two key features of an ideal separation membrane: gas tightness and sufficient electronic conductivity. It is the onset of the sintering profile (i.e. between 1180 °C and 1300 °C, in Fig. 4) that allows a window of opportunity to co-sinter silver and BCZYZ without considerable metal losses. Sintering has been successful in the case of ultrafine doped ceria and silver, leading to a dense composite with a percolating silver network [8]. However, there are two critical differences between the sintering behaviour of these the two ceramics; firstly, the ultrafine Ce₀.₈Sm₀.₂O₂₋₄ can be sintered easily at 1200 °C while BCZYZ requires 1300 °C, and secondly, the doped ceria does not release gases while BCZYZ releases CO2 and H2O before sintering completely.

Table 1 displays selected data on the sintering conditions used, the final density and open porosity. The density of pure BCZYZ is 6.08 g cm⁻³, therefore any sample with a higher density indicates that silver, with a density of 9.32 g cm⁻³, is present in the composite. The results can be summarized as follows: in all cases, even sintering at 1300 °C for 4 h, left small amounts of silver trapped in the ceramic matrix that was detectable by XRD and SEM; faster sintering led to the highest contents of silver but the open porosity was large in most cases.

![Fig. 3 – XRD of a powder coated with silver and sintered Ag/BCZYZ (Sample Y-27 in Table 1). Only the main reflections are labelled.](image-url)
The largest amount of silver was found when the sample was fast sintered (Y-27 in Table 1) and the density of $6.39 \text{ g cm}^{-3}$ is equivalent to a content of 9.5 vol% silver. More than half the initial content of silver (21.5 vol%) was lost during the densification process, either through evaporation or polished away from the outermost surface after sintering.

The sample with an undetected level of porosity was a compromise between heating rate and dwell time (Y-17) but the low content of silver was not sufficient to achieve percolation.

Fig. 5 shows a micrograph of a cross section of a composite with open porosity $>10\%$ (Y-27). There is good contact between silver and BCZYZ in the composite (Fig. 5a) while the silver formed droplets in the interior of open pores (Fig. 5b) and on the uppermost surface of the samples.

Conductivity

For application in separation membranes the composites should be dense so the conductivity studies were carried out on sample Y17 (See Table 1) which had an undetected level of porosity and a density $\rho = 6.18 \text{ g cm}^{-3}$, higher than that of pure BCZYZ ($\rho = 6.08 \text{ g cm}^{-3}$). From the density value, the estimated silver content was 2 vol%.

The impedance spectra at 150 °C and at 500 °C in air for a composite and pure BCZYZ are shown in Fig. 6. As is usual for BCZYZ, the semicircle corresponding to the bulk conductivity is only observed at very low temperatures (<250 °C) and high frequencies (>100 kHz) as seen in Fig. 6a. The equivalent circuit used to fit the data is shown. The bulk capacitances were calculated according to [25] and the values for BCZYZ and for the Ag/BCZYZ composite were 51 pF and 223 pF respectively. These values are given as a guide to assign the responses to the different elements (the bulk in this case) and are not necessarily an accurate measurement of the real capacitance. Nonetheless, it can be noted that if the dielectric constant $\varepsilon$ is estimated using the area to thickness ratio of each individual sample, values of 50 and 157 are obtained for pure BCZYZ and for Ag/BCZYZ respectively; an increase in $\varepsilon$ has been observed for silver dispersed in an insulating matrix [26]. At higher temperatures only the grain boundary and the electrode response are detected and this is shown in Fig. 6b and consequently a different equivalent circuit has been used to estimate R. The semicircles of the composite are clearly smaller than those of pure BCZYZ, indicating that the composite consistently exhibited higher conductivity. The bulk conductivity of the Ag/BCZYZ composite shows a thermally activated behaviour, and the activation energy was the same as that of the nominally-pure ceramic, as shown in the Arrhenius plot in Fig. 7. The contribution from protons and electrons to the bulk conductivity requires further analysis, however, it is clear, that in this composite the silver does not form a percolating network.

The most dramatic change is seen in the grain boundary resistance: while BCZYZ has a large semicircle (>MΩ) associated with the grain boundary resistance, the composite has a smaller semicircle, as shown in Fig. 6. The large grain boundary resistance in zirconate-based materials is brought about by a space charge that blocks charge transfer [27]. The trend in the Arrhenius plot for grain boundary conductivity (Fig. 8) indicates that when silver is present, the grain boundary conductivity increases. The activation energy for grain boundary conductivity in pure BCZYZ is 1.09 eV, a value within the range of BaZrO$_3$ materials [27], but when silver is
introduced the activation energy changes to a lower value (0.63–0.64 eV), which is similar to the energies observed in pure BCZYZ in hydrogen atmospheres [14]. This suggests that the inclusion of silver grains in a dense BCZYZ ceramic can diminish the blocking effect of the grain boundaries, a problem which has been known for some time. It is clear though, that there has been an improvement in the overall conductivity in particular in the grain boundary. Furthermore, if silver has introduced a significant electronic component to the total conductivity then the material can work as a passive hydrogen separation membrane. OCV measurements were therefore conducted to further explore the nature of the conductivity enhancement.

Measurement of open circuit voltage

We measured the OCV in fuel cell mode of the same sample (Y17) to determine the nature of the conductivity. Typically pure BCZYZ displays OCVs higher than 1 V using the same conditions as those described here and the same sealant as in previous reports [10,14]. Fig. 9 shows an OCV considerably lower than 1 V, indicating that the composite is not a pure ionic conductor: there is a significant electronic component that reduces the ionic transport number. It is noteworthy that a high ionic number is seen between 300 and 400 °C but as the temperature increases, the OCV decreases sharply. Provided that the sealing was not compromised, as in previous experiments [10,14], the drop in OCV may be related to an increasing hydrogen permeation leading to a local decrease of the pO2 on the air side.

To complement the OCV measurement, the impedance spectra of the fuel cell at three temperatures (150 °C, 400 °C and 600 °C) are shown in Fig. 10. All three impedance plots display semi-circular responses characteristic of resistive and capacitive elements typical of ionic conductors. The impedance values were normalized by multiplying by the area and dividing by the thickness of the sample to allow comparison to Fig. 6. It is thus shown that the composite exhibits mixed electronic protonic conductivity in this range of temperatures. The presence of electronic conductivity in proton conductors is not a rare phenomenon and the best example is SrCe0.95Yb0.05O3 with cerium as a mixed valence ion [28]. Future work will focus on the measurement of the hydrogen permeability of the composite.

Fig. 6 – Impedance spectra for pure BCZYZ and a composite with silver at a) 150 °C and b) 500 °C. The numbers indicate the log10 of the frequency. The equivalent circuit shown was used to fit the data. R1, R2 and R3 correspond to bulk, grain boundary and electrode response respectively. To compare both spectra, the data have been multiplied by the area and divided by the thickness of the specimens.

Fig. 7 – Arrhenius plot for bulk conductivity of BCZYZ and Ag/BCZYZ composite in air.

Fig. 8 – Arrhenius plot for grain boundary conductivity of BCZYZ and Ag/BCZYZ composites in air.
We can estimate a very rough value for the hydrogen flux in a membrane separating two chambers for the simplest case: we assume a fixed proton concentration determined by the acceptor-dopant compensation and considering negligible oxygen mobility in operating conditions; both assumptions reasonable in high temperature proton conductors [29,30]; let us assume too for the sake of simplicity that the electronic conductivity is far higher than the protonic conductivity. The proton flux \( j_{H^+} \) is then given by Ref. [4].
\[
 j_{H^+} = \frac{-2.303RT\sigma_{H^+}}{2p_{H_2}^I} \left( \log p_{H_2}^II - \log p_{H_2}^I \right) (3)
\]
where \( R \) is the gas constant, \( F \) Faraday’s constant, \( L \) the membrane thickness, \( T \) the temperature, \( p_{H_2} \) is the partial pressure of hydrogen in chamber I or II, and \( \sigma_{H^+} \) is the proton conductivity. At 873 K the conductivity is 2.1 mS cm\(^{-1}\) and a thickness \( L \) of 50 \( \mu \)m is easily achieved by tape casting [10]; the factor affecting the logarithm is 0.376 m mol s\(^{-1}\) cm\(^{-2}\). The factor in brackets in Eq. (3) will depend upon the working conditions, but let us assume a \( p_{H_2} = 0.5 \) atm on one chamber and a smaller value on the second chamber: \( 1 \times 10^{-5} \) atm. Finally, using a molar gas volume of 24466 ml per mol at 25 °C and 1 atm we can obtain a possible value of molecular hydrogen flux \( j_{H_2} = 1.28 \) ml min\(^{-1}\) cm\(^{-2}\) at 600 °C.

**Conclusions**

A new method to the fabrication of high temperature proton conducting-silver composites has been presented. A highly sinterable precursor powder of BCZYZ was coated with silver and then a variety of sintering conditions were tested between 1200 °C and 1300 °C, including fast sintering. No reaction between silver and BCZYZ during sintering was observed by XRD. In general, the higher temperatures led to lower silver contents in the resulting composites, but even at the higher sintering temperatures silver remained trapped within the ceramic matrix. It was possible to manufacture a dense sample with 2 vol% silver. The conductivity of this sample was higher than the conductivity of the nominally pure BCZYZ. The conductivity increase was registered in both bulk and grain boundary but most notably in the grain boundary; this suggests that silver may be preventing the build-up of charge on the grain boundaries that is normally found in zirconate-based materials. The composites have the potential to be used for hydrogen separation as there is a significant electronic contribution in addition to the protonic conductivity in BCZYZ. Further work is needed to quantify the contribution from each charge carrier and to evaluate the permeability of hydrogen.

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