Effect of CO$_2$ exposure on the chemical stability and mechanical properties of BaZrO$_3$-ceramics

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Abstract

The reactivity of BaZrO$_3$ with CO$_2$ has been addressed as one of the major challenges with BaZrO$_3$-based electrolytes in proton ceramic fuel cells. Here, we present a study of the effect of CO$_2$ exposure of BaZrO$_3$-materials at elevated temperatures. Dense BaZr$_{1-x}$Y$_x$O$_{3-\delta}$ ($x =$ 0, 0.05, 0.1, 0.2) and BaCe$_{0.2}$Zr$_{0.7}$Y$_{0.1}$O$_{2.95}$ ceramics were prepared by conventional sintering of powder prepared by spray pyrolysis. The Vickers indentation method was used to determine the hardness and estimate the fracture toughness of pristine materials as well as the corresponding materials exposed to CO$_2$. Formation of BaCO$_3$ on the surface of exposed ceramics was confirmed by X-ray diffraction and electron microscopy. The reaction resulted in formation of Ba-deficient perovskite at the exposed surface. The reaction with CO$_2$ was most pronounced at 650 °C compared to the other temperatures applied in the study. The reactivity was also shown to depend on the Y-content and the grain size and was most pronounced for BaZr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$. The reaction with CO$_2$ was observed to have a profound effect on the fracture toughness of the ceramics, demonstrating a depression of the mechanical stability of the materials. The results are discussed with respect to the chemical and mechanical stability of BaZrO$_3$ materials, with particular emphasis on the composition and grain size.

Keywords: BaZrO$_3$, CO$_2$-reactivity, mechanical properties, stability

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Introduction

Solid oxide fuel cells (SOFC) have during the last decades gained considerable attention in relation to power generation or combined heat and power devices due to their high-energy conversion efficiency.\(^1\)\(^-\)\(^4\) Recent advances of SOFCs have resulted in reduced operation temperatures, which has enabled the use of metallic interconnects and improved the stability as well as the durability.\(^3\), \(^4\) Protonic ceramic fuel cells (PCFC) based on proton conducting electrolytes with superior ionic conductivity, may lead to even lower operating temperatures and improved performance since in this configuration the exhaust water is produced at the air electrode and thereby not diluting the fuel at the fuel electrode side.\(^4\) SOFCs can also be operated as electrolysers by reversing the voltage, and the prospects of electrolysers based on SOFC technology has become an important research field.\(^5\)\(^-\)\(^7\)

The most promising proton conducting electrolytes are BaCe\(_{1-x}\)Y\(_x\)O\(_{3-\gamma/2}\) (BCY),\(^4\)\(^-\)\(^11\) and BaZr\(_{1-x}\)Y\(_x\)O\(_{3-\gamma/2}\) (BZY),\(^12\)\(^-\)\(^16\) which exhibit high proton conductivity at intermediate temperatures (~500 °C).\(^17\) Despite the encouraging proton conductivity of these materials, there are several issues addressed related to their chemical stability, mechanical properties and difficulties in sintering of BZY.\(^15\), \(^17\) BCY has a low chemical stability due to the reactivity with CO\(_2\)\(^18\) resulting in formation of barium carbonate,\(^19\)\(^-\)\(^25\) while BZY is proposed to exhibit sufficient chemical stability in CO\(_2\)-containing atmosphere.\(^12\), \(^24\)\(^-\)\(^29\) The reactivity with CO\(_2\) will result in degradation, which precludes applications in electrochemical devices such as fuel cells based on hydrocarbon fuels. The stability of Ba(Zr,Ce)\(_{1-x}\)Y\(_x\)O\(_{3-\gamma/2}\) in CO\(_2\) atmosphere is increasing with increasing Zr content according to thermodynamic data,\(^25\), \(^27\) and can be rationalized by the higher acidity of ZrO\(_2\) relative to CeO\(_2\).\(^13\), \(^21\), \(^22\), \(^27\) Finally, although decomposition of BaZrO\(_3\) is expected below ~530 °C in pure CO\(_2\) (1 atm),\(^22\) BaZrO\(_3\) has been reported to be stable below this temperature due to slow kinetics of the reaction with CO\(_2\).

Here we report on the effect of CO\(_2\) exposure on the chemical stability and mechanical performance of BaZr\(_{1-x}\)Y\(_x\)O\(_{3-\gamma/2}\) (x = 0, 0.05, 0.1, and 0.2) and BaCe\(_{0.2}\)Zr\(_{0.7}\)Y\(_{0.1}\)O\(_{2.95}\). Modifications in the microstructure and formation of carbonates at the surface of the ceramics were investigated by electron microscopy and X-ray diffraction. Vickers indentation was for the first time applied to investigate the degradation of the mechanical performance due to reaction with CO\(_2\). Degradation associated with BaCO\(_3\) formation was demonstrated, and the consequences for the mechanical stability of BaZrO\(_3\)-based electrolytes are discussed.
Experimental

Sample preparation and exposure to CO₂

Fine ceramic powders with composition BaZr₁₋ₓYₓO₃₋ₓ/₂ (x = 0, 0.05, 0.1, and 0.2), denoted as BZ, BZY5, BZY10, and BZY20 respectively and BaCe₀.₂Zr₀.₇Y₀.₁O₂.₉₅ (BCZY27) were prepared by aqueous nitrate solution spray pyrolysis (CerPoTech AS, Trondheim, Norway). The as-pyrolyzed powders were calcined at 950 °C for 12 h in air and ball milled with yttria stabilized zirconia (YSZ) balls in isopropanol for 72 h, dried at 200 °C for 24 h in ambient air, ground and sieved (150 μm). Green cylindrical pellets with 10 mm diameter and ~3 mm thickness were made by uniaxial pressing at 100 MPa with subsequent cold isostatic pressing (CIP) at 200 MPa giving final green densities of 55–56 % of theoretical. Sintering of the pellets was performed in a muffle furnace at 1600 °C for 10 h in ambient air with a heating rate of 600 °C/h. The samples denoted BZY10_1700 and BCZY27_1700 were in addition thermally annealed at 1700 °C for 10 h after sintering at 1600 °C. Samples denoted BZY10_1600* and BCZY27_1600* were sintered using sacrificial powder at 1600 °C for 10 h in air. The sacrificial powder consisted of BZY20, prepared from stoichiometric amounts of oxides via solid state reaction at 1400 °C for 10 h, and ~10 wt% of BaCO₃ (ACS Reagent, ≥99 %, Sigma-Aldrich). The surface of the sintered specimens was polished with SiC papers and diamond suspensions down to 1 μm to obtain smooth surfaces for Vickers indentation. The sintering conditions for the different samples are summarized in Table 1. The polished samples were exposed to CO₂ (< 50 ppm H₂O) at constant flow (~1 atm) for 10 or 20 h in an alumina tube furnace (Entech ETF 50/17-S) at temperatures from 500 to 750 °C. The heating and cooling rates were 300 °C/h. Corresponding heat treatment of all the materials was also performed at 650 °C for 10 h in dry synthetic air.

Materials characterization

X-ray powder diffraction (XRD) of calcined powders and sintered materials was performed on a D8 Advance DaVinci diffractometer using CuKα₁. The diffraction patterns were recorded in the range 20° ≤ 2θ ≤ 60° with a scanning rate 0.7° min⁻¹. Rietveld refinement of the XRD patterns for powders was carried out using the TOPAS V4.1 using a cubic structure model (Pm₃m) for all the materials. Grazing incident XRD (GIXD) was performed using D8 Advance DaVinci diffractometer using CuKα₁ and parallel beam optics.
The density of the materials was measured by the Archimedes method using isopropanol. The microstructure before and after Vickers indentation were investigated with Hitachi S3400N and Hitachi FEG Zeiss Ultra JEOL840 scanning electron microscopes (SEM) on gold coated samples. The average grain size of the ceramics was estimated by the linear intercept method of 50-60 grains from SEM images of polished and thermally etched (0.25 h, 1400 °C) surfaces. BZY5 and BZY10 samples were etched at 1450 °C for 15 min. The chemical composition of phases was investigated by Energy dispersive spectroscopy (EDS) with Oxford Instruments AZtec Energy analysis software.

Mechanical properties of dense and polished ceramics were investigated by the Vickers micro-indentation technique (Leica VMHT MOT) using loads of 0.1, 0.15, 0.25, 0.5, 1, 2 and 5 N. Distance between each indentation was kept more than 5 times the diagonal of the indent and load holding time was set to 10 s. The Vickers hardness was calculated applying geometrical measurements of indent size from SEM images at each load using equation (1),

\[ H_v = 1.8544 \frac{P}{d^2} \]  

(1)

where \( P \) is the applied load (kg) and \( d \) is the mean length of diagonals (mm). The fracture toughness of the materials was estimated using normalized Niihara’s equation (2),

\[ K_{IC} = 9.518 \left( \frac{c}{a} \right)^{-1.5} (H_v^{0.6})(a^{0.4}) \]  

(2)

where \( K_{IC} \) is the fracture toughness (MPa·m\(^{1/2}\)); \( a \) is 1/2 of indentation diagonal length (m); \( c \) is 1/2 of radial crack length (m) and \( H_v \) is the measured Vickers hardness (MPa). The choice of using Niihara’s equation (eq. 2) was based on the criteria \( c/a > 2.5 \) where \( c \) is the radial surface crack radius and \( a \) is the half diagonal of the Vickers indent. It is important to note that the Vickers indentation test does not provide fracture toughness data sufficient for a reliable test, but gives a good estimate of relative changes in the fracture toughness.
Results

Pristine materials

The powders calcined at 950 °C for 12 h in air were all phase pure according to XRD, revealing that this temperature was sufficient to remove traces of BaCO₃ in the as-prepared powders. This calcination temperature is lower than applied in a previous study using similar powders prepared by spray pyrolysis. In the previous study the particle size was ~100 nm after calcination at 1000 °C, inferring that the present particle size in this study was lower than 100 nm due to the lower calcination temperature. The sintering temperature and time were varied in order to obtain high density of the ceramics, and the optimized sintering conditions are given in Table 1. All the materials achieved densities higher than 94 % relative to the theoretical density calculated from the unit cell parameters found by Rietveld refinements (Table 1). Increasing the heating rate from 200 to 600 °C/h had a profound effect on the final density, while no significant improvement in the relative density could be obtained by increasing the sintering time from 10 h to 16 h or using sacrificial powder. The final relative density and grain size of the materials using 600 °C/h heating rate are included in Table 1.

SEM images of the polished and thermally etched surface of BaZrO₃, BaZr₁₋ₓYₓO₃₋ₓ/₂ and BCZY27 pellets sintered at 1600 °C for 10 h in air are shown in Fig. 1. The Y-doped barium zirconates have smaller grains than pure BaZrO₃, while the grain size is increasing with Y-content in BZY. BZY5 had the smallest grain size of 0.18 µm. The grain size of BZY10_1600 and BCZY27_1600 was around 0.25 µm, while grain growth to 0.6 µm was induced after thermal annealing at 1700 °C (Table 1). The average grain size increased on sintering using sacrificial powder (Table 1).

The BZY10 and BZY20 ceramics conventionally sintered at 1600 °C for 10 h in air contained a minor amount of cubic Y₂O₃ phase detected by XRD due to loss of BaO. The Y₂O₃ content in BZY10 and BZY20 was estimated to 1.0 and 2.0 wt%. Y₂O₃ was not present in these two materials sintered with sacrificial powder, but only BZY10* was investigated with respect to reaction with CO₂.
**Vickers micro-indentation method**

A SEM image of a typical indent in pristine BCZY27 is shown in Fig. 2, demonstrating clearly the cracks propagating from the four corners of the indent. In all the pristine materials the crack propagated by an intergranular mode both in the initial and final part of the crack.

The Vickers hardness of BZY10 as a function of the load is shown in Fig. 3. The hardness converged towards a constant value with increasing load in line with theory\textsuperscript{34-37}. Loads higher than 5 N induced lateral cracks and could not give reasonable measurement of the Vickers hardness and cracks with well-defined lengths. A similar trend as shown in Fig. 3 was observed for all other compositions (not shown). Based on these observations a load of 2 N was observed for all the following measurements on all the materials. Ideally, hardness should be measured using a load which would not give radial cracks, but this was only obtained for low loads (<0.25 N) resulting in strongly distorted indents. Vickers hardness for all the pristine materials measured using 2 N load is summarized in Table 1.

The effect of the indentation load on the estimated fracture toughness of pristine BZY10 using Eq. 2 is also shown in Fig. 3 (insert). The fracture toughness was not changing significantly with variation in the load above 1 N. The fracture toughness could not be calculated at 0.1 and 0.15 N loads because the crack lengths were too small. The same trends were observed for all materials. The fracture toughness for the pristine ceramics measured using 2 N load is summarized in Table 1.

The Vickers hardness and fracture toughness of the pristine BZY materials are decreasing with the Y-content accompanied with increasing lattice parameters and oxygen vacancy concentration (Table 1). Moreover, the grain size of the BZY materials was slightly increasing with increasing the Y-content. Vickers hardness was marginally improved for BZY10 by increasing the grain size (BZY10\_1700), while the opposite effect was observed for BCZY27 (BCZY27\_1700). On the other hand, fracture toughness of both compositions decreased after annealing at 1700 °C. There was an apparent reduction in Vickers hardness and fracture toughness of the samples sintered using sacrificial powder (BZY10\_1600* and BCZY27\_1600*). BaZrO\textsubscript{3} ceramics with the largest grains (~1 μm) possess moderate hardness and fracture toughness compared to the BZY materials.
Chemical and mechanical stability of BaZr$_{1-x}$Y$_x$O$_{3-x/2}$ and BaCe$_{0.2}$Zr$_{0.7}$Y$_{0.1}$O$_{2.95}$ in CO$_2$

SEM images of indents in pristine BZY10 and BZY10 exposed to CO$_2$ for 10 h at different temperatures are shown in Fig. 4. Relatively large crystals with average size ~3 μm (see inset Fig. 4c) are evident on the surface of the exposed material. EDS confirmed that the crystals consisted of Ba, C and O, and XRD confirmed that the crystals were BaCO$_3$ (Fig. 5). No additional crystalline phase could be observed using grazing incidence XRD (Fig. 5). The formation BaCO$_3$ on the surface took place from 550 to 750 °C (Fig. 4), while the maximum amount of BaCO$_3$ was observed at 650 °C.

A polished cross section of BZY10 after exposure to CO$_2$ is shown in Fig. 6. EDS line scans of Zr, Ba and Y revealed a gradient in the element content towards the surface exposed to CO$_2$. A clear decrease in the Ba-content is evident at the surface, while the Zr and Y-contents are increasing. The data point to changes in the Ba/Zr ratio in the perovskite towards the surface exposed to CO$_2$.

SEM images of the surfaces of BaZr$_{1-x}$Y$_x$O$_{3-x/2}$ (x = 0, 0.05, 0.1, 0.2) and BaCe$_{0.2}$Zr$_{0.7}$Y$_{0.1}$O$_{3-\delta}$ after exposure to CO$_2$ at 650 °C for 10 h are shown in Figs. 4, 7 and 8. These images demonstrate that the size and number density of the BaCO$_3$ crystals on the material surfaces depended on both the microstructure and the composition of the ceramic. A larger amount of smaller BaCO$_3$ crystals were formed on BZY20 compared to BZY10. The reaction with CO$_2$ with BCZY27 resulted in a few relatively large BaCO$_3$ crystals, inferring that the rate of nucleation of BaCO$_3$ is low compared to the growth rate. The images of the surface of BZY10_1600* and BCZY27_1600* ceramics demonstrate that the use of sacrificial powder during sintering reduces the amount of BaCO$_3$ crystals formed in CO$_2$ at 650 °C (Fig. 8). Formation of BaCO$_3$ could not be observed by SEM in case of pure BaZrO$_3$ but was confirmed by gracing incident XRD (not shown), and the Vickers indent in the exposed materials was altered relative to indent in the pristine material (Fig. 7a). Finally, the cracks in samples exposed to CO$_2$ (Fig. 4, 7 and 8) propagated both along grain boundaries as well as throughout the grains (transgranular mode).

The Vickers hardness and the fracture toughness of BZY10 and BCZY27 with CO$_2$ exposure temperature are shown in Fig. 9. The Vickers hardness of BZY10 and BCZY27 did not change significantly due to exposure to CO$_2$ (Fig. 9a and 9c). On the other hand, fracture toughness of
the BZY10 is clearly decreasing with increasing exposure temperature (see Fig. 9b). The reduced toughness was most pronounced for BZY10_1700 with the largest grain size. The fracture toughness of BCZY27 clearly decreases with increasing exposure temperature in line with the corresponding data for BZY10 (Fig. 9d). The Vickers hardness and fracture toughness of BZY10_1600* and BCZY27_1600* sintered at 1600 °C with sacrificial powder and exposed to CO₂ at 650 °C (Fig. 9) are lower relative to the samples sintered without sacrificial powder. The reduction in the fracture toughness does not reflect the amount of BaCO₃ crystals formed at the surface (see Figs. 4, 7 and 8).

The dependence of the Vickers hardness and the fracture toughness of BaZr₁₋ₓYₓO₃₋ₓ/₂ and BaCe₀.₂Zr₀.₇Y₀.₁O₂.₉₅ on the heating temperature in pure CO₂ are shown in Fig. 10. The hardness of the materials remains relatively constant and was not greatly affected by the formation of BaCO₃. The lengths of the lateral cracks were observed to increase with exposure temperature for all the compositions and consequently the fracture toughness of the materials decreased. Fig. 10 implies that BZY5 with the smallest grains show the most profound reduction in fracture toughness among the acceptor doped materials. The fracture toughness of BaZrO₃ was also shown to be strongly reduced by exposure to CO₂.

The Vickers hardness and fracture toughness of all materials exposed to synthetic air at 650 °C for 10 h are summarized in Table 1 and Fig. 10. The Vickers hardness and fracture toughness of these materials did not deviate from the properties of the pristine materials, which demonstrated that solely the thermal treatment does not influence the hardness and fracture toughness. We can therefore conclude that the observations reported for the materials exposed to CO₂ are truly an effect of the chemical reaction with CO₂.

**Discussion**

*Formation of BaCO₃ and chemical stability of BZY-materials*

The reaction taking place at the surface, using pure BaZrO₃ as an example, has previously been proposed to be

\[
\text{BaZrO}_3(s) + \text{CO}_2(g) = \text{BaCO}_3(s) + \text{ZrO}_2(s)
\] (3)
Despite substantial efforts by diffraction and microscopy we could not detect any evidence for the formation of ZrO$_2$. In contrast a concentration gradient towards the surface exposed to CO$_2$ could be observed by EDS (Fig. 6). An alternative reaction could therefore be established where the formation of Ba resulted in the formation of Ba-deficient BaZrO$_3$. The reaction taking place at the surface during CO$_2$ exposure, using pure BaZrO$_3$ as an example, is then proposed to

$$\text{BaZrO}_3(s) + x\text{CO}_2(g) = x\text{BaCO}_3(s) + \text{Ba}_{1-x}\text{ZrO}_{3-x}(s) \quad (4)$$

Alternatively, reaction (4) can be formulated using point defects as

$$\text{Ba}^{\ast\ast}_{\text{Ba}} + \text{O}^{\ast\ast}_0 + \text{CO}_2(g) = \text{v}^{\ast\ast}_{\text{Ba}} + \text{v}^{\ast\ast}_0 + \text{BaCO}_3(s) \quad (5)$$

The energetics of vacancy formation BaZrO$_3$ has been studied first principle calculations, showing Ba-vacancies has the lowest formation energy relative to the other point defects supporting reaction (4). An illustration of the reaction is shown in Fig. 11. BaCO$_3$ crystals grow on the surface due to mobility of Ba$^{2+}$, while Zr (Y) with inferred lower mobility, remains in the crystal structure forming Ba$_{1-x}$ZrO$_{3-x}$. Rietveld refinement of the conventional XRD patterns of the ceramics after exposure to CO$_2$ did not show any change in the lattice parameters of the BZY materials. Gracing incident XRD of BaZrO$_3$ and BZY10 after CO$_2$ exposure reviled however a minor shift the cell from 4.193 to 4.190 and 4.198 to 4.196, respectively (the uncertainty in the unit cell parameters obtain from GIXRD is larger than conventional XRD). The downshift in the unit cell parameter give supporting evidence for the formation of Ba-deficient BZY at the surface. The Ba-deficiency induced by the reaction with CO$_2$ could in principle result in segregation of Y$_2$O$_3$ or Y incorporation into the Ba-site. Formation of Y$_2$O$_3$ due to the reaction is not likely based on the EDS data on the surface (Fig. 6), while Y on Ba site cannot be proven nor disregarded based on the data provided in this study. Based on the estimated amount of BaCO$_3$ crystal on the surface on BZY10 the Ba-deficiency was estimated to be Ba$_{0.92}$Zr$_{0.9}$Y$_{0.1}$O$_{2.87}$ assuming that the reaction influenced only a ~1 μm layer of the material (x ~ 0.08 for reaction (4)).

Formation of BaCO$_3$ on the surface of the BZY and BCZY27 ceramics (Fig. 4, 7 and 8) reduced clearly the fracture toughness (Figs. 9 and 10). Reaction (4) was most pronounced at 650 °C
where the surface morphology was also most strongly modified by growth of large crystals of BaCO$_3$, which was most likely nucleated at the grain boundaries. The effect on the fracture toughness was even more pronounced above 650 °C (Fig. 10). The reaction with CO$_2$ is therefore also likely even at temperatures as high as 750 °C.

Assuming reaction (3) to be dominant the reaction between BaZr$_{1-x}$Y$_x$O$_{3-x/2}$ and CO$_2$ can be expressed as

$$\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-x/2}(s) + \text{CO}_2(g) = \text{BaCO}_3(s) + \text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}(s) \quad (6)$$

The Gibbs energy of reaction (6) can be estimated in terms of the Gibbs energy of reaction (3) and the following hypothetical reaction

$$\text{BaYO}_{2.5}(s) + \text{CO}_2(g) = \text{BaCO}_3(s) + \text{YO}_{1.5}(s) \quad (7)$$

where $\Delta G^\circ\{6\} = (1-x)\Delta G^\circ\{3\} + x\Delta G^\circ\{7\}$. $\Delta G^\circ\{3\}$ and $\Delta G^\circ\{7\}$ can be estimated from literature data. $^{18,19,40,41}$

The Gibbs energy can be expressed as a function of the partial pressure of CO$_2$ through the expressions

$$\Delta G^\circ\{6\} = \Delta H^\circ\{6\} - T\Delta S^\circ\{6\} = -RT\ln K_5 = -RT\ln(p\text{CO}_2)^{-1} \quad (8)$$

The relationship between $p\text{CO}_2$ and the temperature at equilibrium is then given by

$$\ln(p\text{CO}_2) = (\Delta H^\circ\{6\}/R)(1/T) - \Delta S^\circ\{6\}/R \quad (9)$$

The stable region for BZY materials can be calculated from equation (9). The result is shown in Fig. 12a. The lines represent boundaries separating the stable and unstable regions with respect to reaction with CO$_2$. The thermodynamic stability of BZY decreases with increasing Y-content as particularly shown in Fig. 12b. Although reaction (3) does not represent the true reaction with CO$_2$, Fig. 12 illustrates how the relative stability of BaZrO$_3$ changes with respect to Y-doping. Moreover, it is known that the introduction of Ce$^{4+}$ in BaZrO$_3$ attenuates the thermodynamic stability. $^{22,25}$ Corresponding thermodynamic data for other dopants than Y would be very interesting with respect to the thermodynamic stability of BaZrO$_3$ with respect to doping.
We infer that kinetics of the reaction with CO$_2$ also plays an important role. The effects which could influence on the heterogeneous phase equilibria are acceptor doping (vacancy concentration), cerium content as well as grain size of the ceramics. It is inferred from reaction (4) that the kinetics of the reaction is also related to the cation mobility in BaZrO$_3$-materials. The chemical reaction is most likely to occur at the grain boundaries because the cations are usually more mobile on the grain boundaries than in the bulk.$^{42}$

The reactivity of BZY-based materials with CO$_2$ reported in this study is novel with regards to previous attempts to study the reaction with CO$_2$.\textsuperscript{4, 12, 22, 27} The reaction proposed in this study is also new and does involve the formation of Ba-deficient perovskite. In these studies BZY-ceramics were concluded to be chemically stable in CO$_2$ atmosphere, in contradiction with the data provided in this study. It is noteworthy that the experiments were conducted in 1 atm CO$_2$ and should be considered as harsh. Lower partial pressures of CO$_2$ will increase the stability region of the BZY materials (see Fig. 12b).\textsuperscript{4, 22, 25, 27} This work is also the first study demonstrating the effect reaction with CO$_2$ on the mechanical performance.

\textit{Methodology (Vickers micro-indentation)}

The mechanical performance of ceramics can be revealed by the Vickers micro-indentation method based on the size of indents and radial cracks.\textsuperscript{34, 35} A typical indent on a solid is illustrated in the inset in Fig. 2. Both the indentation fracture load and load holding time can be varied. A previous report on Vickers indentation in zirconia demonstrated that 10 s holding time was sufficient to obtain stable indent,\textsuperscript{35} and this time was adopted this study. The loads were varied in the range 0.25–5 N. Low loads (< 0.25 N) resulted in distorted indent shape and the loads < 1 N resulted in higher Vickers hardness values, whereas high loads (> 5 N) induced lateral cracks. Most of the data reported here was therefore measured using 2 N where the indent was both, symmetrical and with radial cracks propagating from all four corners. The fracture toughness calculated using eq. 2\textsuperscript{31, 32} does not provide the same accuracy as methods like SEVNB.\textsuperscript{36} However, the method gives a good measure of the relative changes in the fracture toughness and provides insight in the change in the mechanical performance of the materials due to exposure to CO$_2$.

The presence of relatively large BaCO$_3$ crystals on the surface will affect the uncertainty in the measured hardness and apparent increase in hardness was estimated from the indents. The reason for this is that the surface morphology is modified from the initial smooth flat surface
due to the reaction with CO$_2$. During indentation these BaCO$_3$ crystals were crushed, reducing the indentation diagonal length resulting in an apparently increasing hardness. We have not made any attempts to correct for this systematic error in the hardness.

*Hardness and fracture toughness of pristine BZY-based materials*

Hardness of a material depends on the bonding strength, Young’s modulus, grain size, porosity, surface roughness, and possibly also mechanically induced stress on the surface of the materials after polishing.\(^{37}\) The hardness as a function of applied load has a softening effect at low loads, which is a well-known effect in ceramics.\(^{37}\) According to our results, there is no systematic variation in the Vickers hardness with regards to the grain size and acceptor dopant concentration for the pristine materials. The Vickers hardness of the BZY10 and BCZY27 samples sintered with sacrificial powder is lower compared to the samples sintered by conventional sintering. This is most likely related to the presence of minor amount of Y$_2$O$_3$ in the conventionally sintered ceramics. Finally, the reported hardness of materials reported in this study is in good agreement with the hardness reported for similar materials.\(^{43-50}\)

The fracture toughness of the conventionally sintered pristine materials does not have a systematic variation with regards to the grain size or the acceptor dopant level. It is noteworthy, that the fracture toughness decreased in the BZY10 and BCZY27 ceramics containing larger grains after sintering with sacrificial powder (Table 1). Possible explanations for these observations are the increased grain size and suppression of formation of Y$_2$O$_3$ secondary phase due to a lower BaO loss by using the sacrificial powder.

*Mechanical stability of BaZr$_{1-x}$Y$_x$O$_{3-x/2}$ and BaCe$_{0.2}$Zr$_{0.7}$Y$_{0.1}$O$_{2.95}$ in CO$_2$*

The cracks propagated by an intergranular mode in the pristine materials. However, when the samples were heat treated in pure CO$_2$, the cracks propagated along grain boundaries as well as throughout the grains (see Fig. 6). The reaction with CO$_2$ does therefore indeed change the mechanical properties of the materials.

In the following a qualitative discussion of the chemical and mechanical stability of the BZY-based materials is given. The significant change in phase composition due to the reaction with CO$_2$ may induce mechanical stress at the surface. A considerable strain induced stress during chemical expansion due to hydration/dehydration was recently addressed for BZY-materials.\(^{51, 52}\)
in the concentration of the water or protons as they diffuse from the surface to the interior of a material. The stress induced at the surface during reaction with CO$_2$ is reflected by the reduced fracture toughness reported here. Reduction in fracture toughness reveals reduction in fracture strength of the materials.\textsuperscript{53} We therefore argue that chemical stability of proton conductors like BZY is most critical with respect to mechanical failure due to decomposition at elevated temperatures. The chemical reaction with CO$_2$ was significant in the temperature interval 550–750 °C. This will lead to microstructural changes at the interface between electrolyte and electrodes in fuel cells. The reduced fracture toughness is most likely related to the weakening of the grain boundaries due to the reaction with CO$_2$. In coarse-grained ceramics chemically induced stress induces micro-cracking, reduced mechanical strength, and possibly catastrophic failure. Some of the problems with low mechanical performance of proton-conducting oxides\textsuperscript{4} may therefore be related to micro-cracking induced by reaction with CO$_2$. Consequently, care must be taken if BZY-based materials will be applied in environments containing significant vapor pressures of CO$_2$.

**Conclusions**

Dense and phase pure Y$^{3+}$- and Ce$^{4+}$-doped barium zirconate ceramics, BaZr$_{1-x}$Y$_x$O$_{3-\delta}$ ($x = 0, 0.05, 0.1, 0.2$) and BaCe$_{0.2}$Zr$_{0.7}$Y$_{0.1}$O$_{2.95}$, were successfully prepared from powders prepared by spray pyrolysis. The stability of these ceramics was investigated by exposing the materials to pure CO$_2$ atmosphere. Clear evidence for the formation of BaCO$_3$ was provided by X-ray diffraction and microscopy for all materials. The reaction with CO$_2$ resulted in formation of Ba-deficient perovskite at the exposed surface. Significant reduction of the fracture toughness was observed for all the materials due to CO$_2$ exposure in the temperature range 550–750 °C. The reaction of BaZrO$_3$-based materials with CO$_2$ is discussed in relation to application of proton conducting materials based on BZY as electrolytes in intermediate temperature proton conducting fuel cells.

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References

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A. K. Eriksson Andersson, S. M. Selbach, T. Grande, and C. S. Knee, "Thermal evolution of the crystal structure of proton conducting BaCe$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ from high-resolution neutron diffraction in dry and humid atmosphere," *Dalton Transactions*, **44**, 10834-46 (2015).

### Table 1. Sintering temperature, density, cell parameters, average grain size, Vickers hardness and fracture toughness of BaZr$_{1-x}$Y$_x$O$_{3-δ}$ and BaCe$_{0.2}$Zr$_{0.7}$Y$_{0.1}$O$_{2.95}$ ceramics. Sintering time was 10 h. *Italic*: Vickers hardness and fracture toughness after exposure to synthetic air at 650 °C for 10 h.

<table>
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<tr>
<th>Compound</th>
<th>T$_{\text{sintering}}$ (°C)</th>
<th>Density (%)</th>
<th>Cell parameter (Å)</th>
<th>Average grain size (μm)</th>
<th>Vickers Hardness ($H_v$)</th>
<th>Fracture toughness (MPa·m$^{1/2}$)</th>
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<td>BZ</td>
<td>1600</td>
<td>97±1</td>
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Figure captions

Fig. 1. SEM micrographs of barium zirconate materials conventionally sintered at 1600 °C for 10 h in air: a.) BZ; b) BZY5; c) BZY10; d) BZY20; e) BCZY27.

Fig. 2. SEM image of a typical indent on pristine BCZY27 with the insets of indentation scheme, crack-start and crack-end.

Fig. 3. Effect of the indentation load on the Vickers hardness of pristine BZY10. Inset: effect of indentation load on the fracture toughness of pristine BZY10.

Fig. 4. SEM images of the indents on BaZr_{0.9}Y_{0.1}O_{2.95} (BZY10) samples, (a) pristine and exposed to flowing CO_{2} atmosphere for 10 h at (b) 550 °C, (c) 650 °C and (d) 750 °C. Insets: BaCO_{3} crystals formed on the surface and crack-ends after indentation on the ceramics exposed to CO_{2}.

Fig. 5. XRD patterns of BaZr_{0.9}Y_{0.1}O_{2.95} (BZY10) before and after exposure to flowing CO_{2} atmosphere at 650 °C for 10 and 20 h. The XRD source is not completely monochromatic and the diffraction line at ~29° is due to W radiation. Diffraction pattern of Au is due to sputtered Au on the surface prior to electron microscopy. Inset: left - (111) diffraction peak of BaCO_{3}; right – GIXD of BZY10 exposed to CO_{2} at 650 °C for 10 h.

Fig. 6. SEM image of the cross section of BZY10 and EDS line scans of elements Zr, Ba, Y across from the surface exposed to CO_{2} towards the bulk. The line scan was performed in parallel to the direction of the Vickers indent.

Fig. 7. SEM images of indents on (a) BZ, (b) BZY5, (c) BZY20, and (d) BCZY27 with BaCO_{3} formed after exposure to pure CO_{2} at 650°C for 10 h. Insets: crack-ends after indentation on exposed ceramics.

Fig. 8. SEM images of indents on (a), (b), (c), (d) BaZr_{0.9}Y_{0.1}O_{2.95} (BZY10) and (e), (f), (g), (h) BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95} (BCZY27) samples before (left column) and after (right column) exposure to pure CO_{2} at 650 °C for 10 h. Samples: (a), (b), (e), (f) sintered at 1600 °C and additionally annealed at 1700 °C; (c), (d), (g), (h) sintered with sacrificial powder at 1600 °C. Insets: crack-ends, crack-starts after indentation and BaCO_{3} crystals on the surface.

Fig. 9. Effect of CO_{2} exposure temperature on Vickers hardness and fracture toughness of (a), (b) BaZr_{0.9}Y_{0.1}O_{2.95} (BZY10) and (c), (d) BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95} (BCZY27) samples sintered at 1600 °C, annealed at 1700 °C and sintered at 1600 °C with sacrificial powder before and after exposure to pure CO_{2} and synthetic air for 10 h.

Fig. 10. Effect of exposure temperature in pure CO_{2} for 10 h on (a) Vickers hardness and (b) fracture toughness for BaZr_{1-x}Y_{x}O_{3-3/2} and BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95} specimens conventionally sintered at 1600 °C.

Fig. 11. An illustration of the microstructural changes on the surface of BZ-ceramics due to reaction with CO_{2}.

Fig. 12. (a) Stable region plot of some BZ-materials at different CO_{2} partial pressures and temperatures obtained by thermodynamic calculations; (b) The equilibrium reaction temperature of different BaZr_{1-x}Y_{x}O_{3-3/2} with CO_{2} as a function of composition and CO_{2} partial pressures; CO_{2} partial pressure in atm as indicated. The data for calculations is taken from literature. 18, 19, 40, 41