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# Elaboration of $CO_2$ tolerance limits of $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ electrolytes for fuel cells and other applications

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## Abstract

The carbonation and decarbonation behaviour of $BaCe_{0.9}Y_{0.1}O_{2.95}$ (BCY10) powder has been investigated as a function of gas composition and temperature by thermogravimetric analysis and X-ray powder diffraction. The results obtained have been used to establish stability limits, which seem to indicate long-term stability for BCY10 under certain conditions.

BCY10 powder is stable in pure $CO_2$ above 1150 °C. In atmospheres containing up to 9% $CO_2$ in argon, BCY10 is stable above 750 °C. Carbonated powders loose $CO_2$ above 700 °C when heated in air, or oxygen and at 620 °C in 5% hydrogen. BCY10 partly decomposes on ageing in pure $CO_2$ at 500 °C. The onset of the reverse water–gas shift reaction changes to lower temperatures in the presence of BCY10 powder.

These results were obtained for powder samples and should be viewed as an accelerated ageing test. Overall these results imply that under fuel cell conditions BCY10 should be resistant to carbonation even in a hydrocarbon fuelled fuel cell at temperatures above 750 °C. In the worst case scenario with 100% hydrocarbon oxidation, no added water and assuming no localised benefit from the gas shift reaction carbonation could occur up to 925 °C. Fully densified electrolytes, especially with an electrode coating, should be much more resistant to carbonation, at least when there is no exolved alkaline earth rich phases at the grain boundary, something that can occur with unoptimised sintering or inappropriate choice of stoichiometry.

*Keywords:* Perovskite; Yttria-doped barium cerate; Carbon dioxide; Stability; Thermogravimetry

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## 1. Introduction

It was found as early as 1981 that barium cerates show a high protonic conductivity at elevated temperatures [1]. Kreuer et al. studied the conductivity of $BaCeO_3$-based compounds in 1994 [2] investigating the influence of water uptake on the concentration of oxygen vacancies and ultimately conductivity as well as the relationship between the diffusion of protonic charge carriers and local oxygen dynamics. The conductivity mechanism in doped perovskites was discussed by Haile et al. [3] and Ma et al. [4]. Bonanos carried out an examination of the requirements for proton conduction in perovskites in 2001 [5], including oxygen deficiency, ready incorporation of water and rapid transport of protons. It was however noticed that in barium cerates, a transition from protonic to oxide ion conduction can be observed between 600 and 1000 °C [6,7]. This transition was suggested to be related to the temperature dependent phase transitions occurring in these materials in which the two crystallographically and energetically non-equivalent low-temperature oxygen sites become equivalent at high temperatures [8]. Oxide ion transport is known to be facilitated between equivalent oxygen sites because low activation energy paths between the sites translate into a higher mobility and corresponding higher conductivity of the ions [9] and were found to decrease with increasing distortion of the lattice [10].

In 1995, Bonanos et al. attributed the variance between maximum conductivities and corresponding doping levels of perovskites published by different authors to different preparation procedures, in particular sintering temperatures [8]. This paper also argues that highly doped materials produced at high sintering temperatures are meta-stable and could decompose when left to age at lower temperatures.

In 1994, a paper on the investigation of structural phase transitions in $BaCeO_3$ by neutron powder diffraction was published by K.S. Knight [11]. This paper also contains a

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review of previous work on the structure determination of barium cerate. Later publications on the structure of barium cerates include an investigation into phase transformations and the distribution of oxide ion vacancies in BCY10 [8], as well as the influence of doping levels and annealing conditions on phase transitions and space group symmetry respectively in yttrium-doped barium cerate at room temperature [12]. In 2001, Knight published a detailed review and study of the structure, phase transitions, oxygen vacancy ordering and protonation in undoped and doped barium cerate, which also clarify some previous problems concerning the setting of the axes in barium cerates [13].

Stability problems in atmospheres containing water and carbon dioxide are generally suspected because of the typical thermodynamic instability of barium containing oxides towards these gases. Kreuer [14] did however point out that the disadvantages with respect to the reaction with gases such as carbon dioxide and water are balanced by a positive influence of the basic character of the oxides on the formation of protonic charge carriers. He explained this from the equilibrium constant for the reaction of oxygen ion vacancies with absorbed water. This is an acid/base reaction that results in a negatively charged OH group on a lattice oxygen position. The reaction is favoured by basic oxides that form strong OH bonds. He furthermore said that the stability of a perovskite in carbon dioxide depends both on the compatibility of the cation with the perovskite structure and the stability of the carbonate with respect to the oxide of the A-site cation. The latter depends on the basicity of the oxide, i.e. a strong base has a deeper potential for reacting with carbon dioxide than a weak base.

Shima and Haile [15] found that any excess of barium oxide in barium cerates will react with atmospheric carbon dioxide, which leads to a loss of mechanical integrity of the materials. Therefore, great care is necessary in the preparation of stoichiometric compounds. Haile et al. [3] also point out that the stability of perovskites ($AMO_3$) increases with increasing perovskite tolerance factor, i.e. when the distortion from the cubic structure due to the difference in the A–O and M–O bond lengths for different materials decreases. However, there are ambiguities for $BaCeO_3$ because the results obtained by different groups and methods lead to opposing results.

At very high temperatures Barium is easily lost from BCY10. This leads to the formation of Ba-deficient phases and BaO (Eq. (1)). The existence of Ba-deficient phases and their defect chemistry is discussed in various papers [3,4]. G. Ma et al. highlight [4] that Ba-deficient BCY10 is more stable in the presence of carbon dioxide and steam than the stoichiometric compound or samples containing excess barium. Higher Ba losses do however cause decomposition of the perovskite, resulting in BaO, $CeO_2$, and $Y_2O_3$ (Eq. (2)). The barium oxide can then react with carbon dioxide and water, resulting in barium carbonate [3] (Eq. (3)) and barium hydroxide (Eq. (4)), respectively. Similar mechanisms for the decomposition of $BaCeO_3$ in $CO_2$ (Eq. (5)) and $H_2O$ (Eq. (6)) can also be broken up into two steps, and were proposed earlier by Gopalan and Virkar [16], and Tanner and Virkar [17] respectively. The instability towards water is a consequence of the high solubility of protons in barium cerates [17]. Dense specimens may be kinetically stable in $CO_2$ because the reaction with carbon dioxide is interfacial [18].

$$BaCe_{0.9}Y_{0.1}O_{2.95} \Leftrightarrow Ba_{1-x}Ce_{0.9}Y_{0.1}O_{2.95-x} + xBaO \tag{1}$$

$$BaCe_{0.9}Y_{0.1}O_{2.95} \Leftrightarrow BaO + CeO_2 + Y_2O_3 \tag{2}$$

$$BaO + CO_2 \Leftrightarrow BaCO_3 \tag{3}$$

$$BaO + H_2O \Leftrightarrow Ba(OH)_2 \tag{4}$$

$$BaCeO_3 + CO_2 \Leftrightarrow CeO_2 + BaCO_3 \tag{5}$$

$$BaCeO_3 + H_2O \Leftrightarrow CeO_2 + Ba(OH)_2 \tag{6}$$

A theoretical examination of the stability of barium cerate and related compounds as determined by their Madelung energies was carried out by Bhide and Virkar [19]. Yamaguchi et al. probed a correlation between the hydroxyl capacity of a barium cerate and the solubility of water in the material [20]. Thermodynamic data for the decomposition and subsequent carbonation of undoped barium cerate can be found in a publication by Haile et al. [3]. They also compared the standard Gibbs free energy obtained for the decomposition of barium cerate depending on the measurement method. In accordance with this, Gopalan and Virkar predicted from galvanic measurements that $BaCeO_3$ is unstable below 1090 °C in the presence of 1 atm $CO_2$ [16]. For the reaction $BaO + CeO_2 \rightarrow BaCeO_3$ they gave the values for standard enthalpy and entropy as 95.3 kJ $mol^{-1}$ and 105.402 J $mol^{-1}$ $K^{-1}$ respectively. That means that barium cerate is thermodynamically unstable with respect to its oxides below 631 °C, although it is kinetically stable. The equilibrium pressure of $CO_2$ for the coexistence of barium oxide and barium carbonate was given by $p_{CO_2} = 1.4967 \times 10^8 \exp[-31490/T]$ atm. Furthermore it was noted in this paper that $BaCeO_3$ decomposes in molten salt under ambient air between 390 and 500 °C, i.e. that it is not thermodynamically stable under the experimental conditions. As a result of sintering experiments in $CO_2$ they also found that $BaCeO_3$ was not stable with respect to barium oxide and carbonate at or below 900 °C. However, their data were extrapolated far outside the range of measurements.

A discussion of the Gibbs free energy for the formation of undoped barium cerate as published by different authors is available from a paper by Schmutzler et al. [21]. The standard Gibbs energy for the reaction of barium cerate with water (Eq. (6)) was calculated by Tanner et al. [17] as well as Chen et al. [18]. To the best of the authors' knowledge there are no thermodynamical data such as the free enthalpy published on the carbonation of BCY10.

## 2. Experimental

BCY10 was prepared from barium nitrate, cerium nitrate and yttria in stoichiometric ratio (Eq. (7)). The starting materials used in the reaction were $Ba(NO_3)_2$ (BDH, 99.5%), $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.5%), $Y_2O_3$ (Alfa Aesar,