TA OF NON-STOICHIOMETRIC CERIA OBTAINED VIA HYDROTHERMAL SYNTHESIS

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Abstract

Doped ceria was studied in the last 20 years as a solid electrolyte capable of replacing stabilized zirconia in fuel cells. Nevertheless, one of the problems concerned with the application of this material is the joint presence of the Ce(III) and Ce(IV) in the ceria sublattice, mainly under low partial pressure of oxygen. TG and DTA measurements were performed in order to verify non-stoichiometric character for cerias hydrothermally treated under reflux and in autoclave. X-ray powder diffraction was used to observe long-range structural evolution varying time and temperature of reaction and the type of hydrothermal synthesis. Finally, scanning electron microscopy (SEM) gave the temperature influence for powder morphology. Those techniques pointed out that: *i*) reaction temperature is not important for converting Ce^{3+} to Ce^{4+}; *ii*) testing the reaction time parameter, it is observed quite complete oxidation for the 2–12 h range; and *iii*) the type of hydrothermal synthesis parameter influences the crystallinity and non-stoichiometric character of products.

Keywords: DTA/TG, hydrothermal synthesis, non-stoichiometric ceria

Introduction

Doped ceria was investigated in the past twenty years as an alternative to stabilized zirconia to be used as an electrolyte in solid-oxide fuel cell (SOFC) devices [1].

Fuel cells produce electrical energy from indirect electrochemical reaction between hydrogen (or natural gas) and oxygen. Both gases are fed externally to the anode (fuel) and to the cathode (oxygen) separately; then there is no combustion and the process has higher energetic efficiency than those for the conventional generators, having water as a product. Fuel cells also produce heat which may be used in raising/lowering temperature cycles, acting as a co-generator.

Some of the fuel cells applications are in: *i*) Spatial vehicles, where the water produced by the cell are used for the crew; *ii*) Hospitals, where blackouts cause seri-

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ous problems; water and heat produced may also be used in the local laundry service; *iii*) Residences, as an alternative form of energy production; the heat produced may be used in water heating for bathing and cooking; *iv*) Vehicles, contributing significantly to the pollution abatement.

Ceria is a promising material for SOFC solid electrolyte due to its outstanding performance as ionic conductor, which allows a lowering of the operation temperature from 1000 to 800°C. The main advantage is that cheaper components may be used in the device [2]. Cerium dioxide (or ceria, CeO_2) has cubic crystalline system, with fluorite structure, belonging to the Fm3m spatial group [3]. Stoichiometric ceria has a cell parameter of 5.41134 Å [4]; but, under non-stoichiometric form, it presents a higher cell parameter value due to the greater ionic radius of Ce(III) in relation to the Ce(IV) (128.3 and 111 pm, respectively) [5, 6].

Being a bad ionic conductor [7], cerium dioxide is doped with metallic ions having a valence less than four, aiming to create anionic vacancies, which are its main point defect [5]. Besides other factors (as the ionic mobility), high vacancy concentration improves the ceria performance as an ionic conductor, making it a fast ion conductor, which also includes stabilized zirconia [8] and Bi_2O_3-V_2O_5 system [9]. Nevertheless, if ceria is under its non-stoichiometric form, electronic conductivity is introduced due to the pair Ce(III)/Ce(IV), minoring the electrolyte activity. This happens mainly after a long period of time above 1000°C, mainly under low oxygen partial pressure [10], producing oxygen gas and Ce(III); and in the 700–800°C range under reducing atmospheres (as hydrogen), producing water and Ce(III) [5, 11]. Those processes are detected using thermal analysis under the conditions presented.

Among the various methods applied for ceria synthesis, sol–gel and oxides mixture calcination are still the main [1, 12]; however, hydrothermal treatment has gained a lot of attention recently for producing nanocrystalline powders without the need of organic elimination or the use of high synthesis temperatures and milling steps. This method also described greater morphological control and homogeneity of produced powders.

High temperature non-stoichiometry of ceria has already been subject of work [13]. The aim of the present report is to study the thermal behaviour and long-range structure of ceria produced by hydrothermal synthesis under mild conditions varying the following parameters: the temperature and time of treatment and the kind of the hydrothermal system.

Experimental

The gels were prepared from dropping the concentrated NH_4OH (Merck 25%), until pH=9, into a stirred 0.1 M Ce(III) solution, which was obtained from an aqueous suspension by adding HNO_3 (Merck) until complete dissolution of $CeCl_3 \cdot 7H_2O$ (99% Aldrich) precursor. They were then submitted to hydrothermal treatment: *i*) under reflux at 100°C for 12, 18 and 24 h; and *ii*) in an Inconel 600 autoclave with teflon bottle for 10 h at 100, 125 and 150°C. For a 2 h time, samples were produced under reflux and in autoclave, both at 100°C, to study the systems available for the
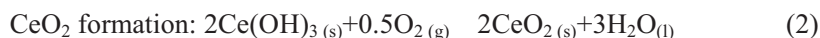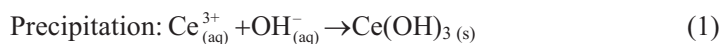
treatment. After synthesis, the mixtures were centrifuged, filtered, washed using distilled water, and dried at 120°C.

X-ray diffraction (XRD) was applied to evaluate the crystallite size, calculated from the Scherrer formula [14] of the highest intensity peak of the X-ray pattern, using a sample of high crystallinity as a standard. Data were collected at room temperature in a Rigaku Miniflex diffractometer with $CuK_{\alpha 1}$ radiation, using as acquiring conditions 0.05°/step and 1 s/step. To estimate the cell parameters, a, from the diffraction patterns, a least-squares program, Eracel, was used. Scanning electron micrographs (SEM) of powders were obtained by using a Zeiss DSM 940 A electron microscope.

Thermal analysis was performed in Shimadzu DTA 50 and TG 50 analyzers, respectively. The applied heating rate was 10°C min^{-1}, in air atmosphere with a rate flow of 30 mL min^{-1}. DTA and TG graphs were obtained using about 50 and 3 mg, respectively, of each sample in platinum crucibles. The temperature range performed was 20–650°C.

Results and discussion

In the course of precipitation process there was a color change from white (cerium(III) hydroxide) to violet (cerium(IV) hydroxide), this result agrees well with the previous Abrăo's findings [15]. The entire process for CeO_2 synthesis may be represented as follows:

$$\text{Precipitation: } Ce^{3+}_{(aq)} + OH^{-}_{(aq)} \rightarrow Ce(OH)_{3\ (s)} \tag{1}$$

$$\text{CeO}_2 \text{ formation: } 2Ce(OH)_{3\ (s)} + 0.5O_{2\ (g)} \quad 2CeO_{2\ (s)} + 3H_2O_{(l)} \tag{2}$$

However, the presence of a brown suspension during hydrothermal treatment (specially for the material obtained after 24 h under reflux) and during washing and drying (more specifically for samples produced after 2 and 18 h under reflux) was a strong evidence of non-stoichiometric ceria (CeO_{2-x}) [5]. The samples treated in autoclave presented a pale yellow color, characteristic of the stoichiometric form. Then, it can be assumed that although cerium(IV) hydroxide is formed, there could be a low Ce(III) content remained in some samples.

For the compounds synthesized after 2 h at 100°C, it can be verified by the observation of their XRD patterns (Fig. 1) that the sample obtained under reflux has thinner and more intense peaks, mainly $2\theta = 28.9, 33.4, 47.75$ and 56.6°; its higher crystallite size (Table 1) confirms that it is more crystalline than the compound obtained in autoclave. Also it can be seen in Table 1 that the cell parameter value of sample treated under reflux is higher, which implies greater non-stoichiometry. Those differences are based on the fact that in autoclave there is pressured oxygen (once it is a 'closed' system), making the oxidation process of Ce(III) faster (making the a value for this sample statistically the same as the one for stoichiometric ceria [4]). On the other hand, the system under reflux presents a slower oxidation, once the oxygen pressure is the same as that of the atmosphere (it's an 'opened' system); this
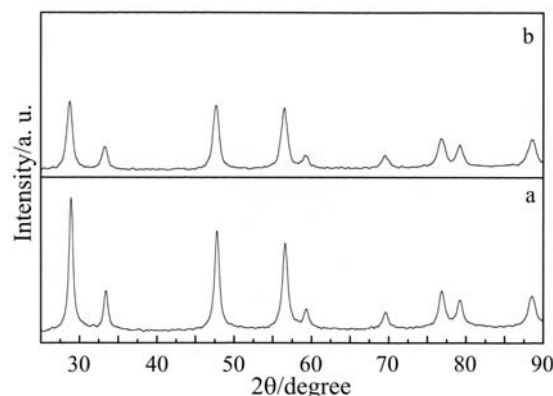
Fig. 1 X-ray diffraction patterns for ceria samples obtained from two hydrothermal systems: a – under reflux and b – in autoclave

condition leads to a stronger interaction between the dispersed material and ammonia, which acts as a mineralizing agent, favouring ceria crystallization.

Table 1 Crystallite size and cell parameter for ceria samples obtained from two hydrothermal systems

Hydrothermal system	Crystallite size D/nm	Cell parameter a/nm
Autoclave	12	0.542(0)
Reflux	17	0.543(1)

The TG and DTA lines of the samples treated for 2 h at 100°C (Fig. 2) complement the information obtained from the long-range structure study (XRD). It can be seen in the DTA graph an intense and thin exothermic peak centered at 230°C for the compound synthesized under reflux (Fig. 2b); however there is no correspondent mass loss (which is expected for an oxidation process) for this process, as can be verified in the TG line (Fig. 2a). The same is valid for the sample obtained from autoclave, only differing from the position and format of the exothermic peak (a less intense and broader peak at 320°C, Figs 2c, e, d). Those exothermic events may be related to a process represented below:

$$2CeO_{2-x\,(s)} \rightarrow 10.5x CeO_{1.81\,(s)} + (2-10.5x)CeO_{2\,(s)} \qquad (3)$$
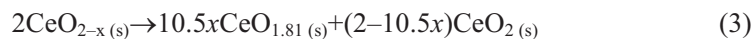
where $x < 0.2$.

As can be verified, the proposed reaction in which the non-stoichiometric form generates the well determined compounds of ceria, without mass gain agrees with experimental results. The fact that the peak for the sample produced in autoclave is displaced to higher temperatures, in relation to that of the reflux system, may be explained by differences in crystallinity. On the other hand, the fact that it is broadened and less intense may correspond to a greater stoichiometry for this phase.
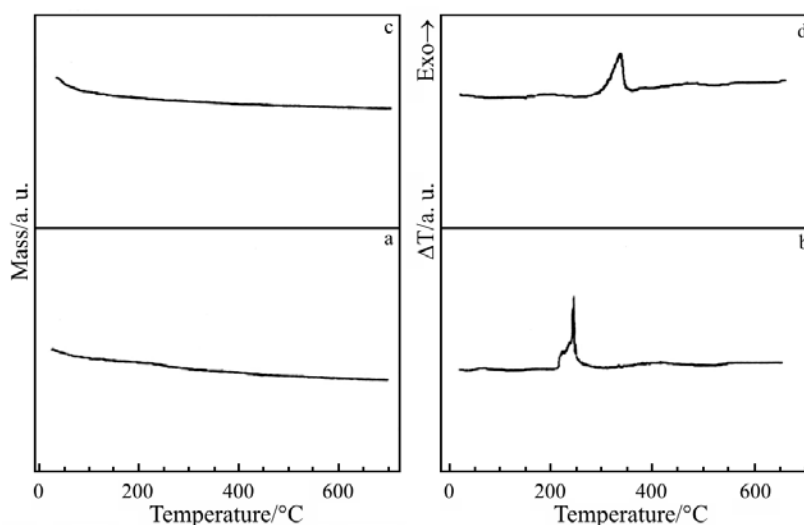
Fig. 2 a – TG and b – DTA for compound synthesized after 2 h at 100°C under reflux;
c – TG and d – DTA for compound synthesized after 2 h at 100°C in autoclave

Aiming to study the influence of synthesis time on ceria production, the gels precipited were submitted to 12, 18 and 24 h of hydrothermal treatment at 100°C under reflux. Their values of crystallite size and cell parameter obtained from the XRD patterns (Fig. 3) are in Table 2.

It can be verified that all samples obtained with variation of residence time under reflux presented the same values of cell parameter (Table 2). However those values cannot be distinguished from that for stoichiometric ceria [4], although the colors presented for those phases were characteristic of the non-stoichiometric form, as already discussed. It can be said in general that they are more stoichiometric than the compound synthesized after 2 h under reflux, due to the progressive reaction of the dispersed medium with oxygen (Table 2).

The X-ray patterns (Fig. 3) and crystallite size values (Table 2) suggested that the compound synthesized with 12 h residence time was less crystalline than the others, mainly if reflections (111) are compared. Then it can be said that in the 12–18 h residence time interval there is a crystallization step of the dispersed material by the dissolved ammonia, alternate to the former oxidation process by oxygen in the 2–12 h interval. This fact also supports the hypothesis of having ammonia as a mineralizing agent for ceria.

To study the influence of temperature in ceria formation, some experiments were carried out in autoclave for 10 h, at 100, 125 and 150°C. Their XRD patterns are in Fig. 4 and the values of crystallite size and cell parameters are in Table 3.

Table 2 Crystallite size and cell parameter for ceria samples obtained under reflux at 100°C dur-
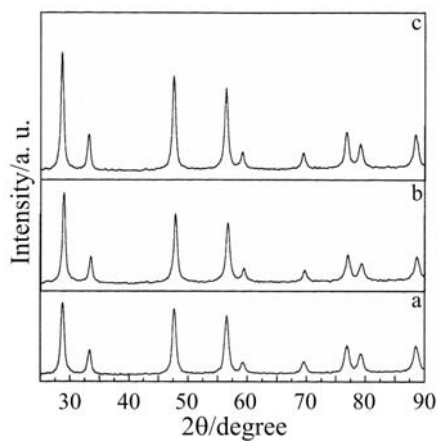ing different hydrothermal treatment time

Treatment time/h	Crystallite size D/nm	Cell parameter a/nm
2	17	0.543(1)
12	13	0.542(2)
18	20	0.542(5)
24	21	0.542(2)

It can be observed that there is no apreciable modification in the cell parameters
and crystallite size values for the compounds obtained with variation of synthesis tem-
perature (Table 3). Also it can be said that the samples have the same stoichiometry as
those produced under reflux with variation of time in the range 12–24 h.

Table 3 Crystallite size and cell parameter for ceria samples obtained from autoclave hydrother-
mal treatment for 10 h at different temperatures

Treatment temperature/°C	Crystallite size D/nm	Cell parameter a/nm
100	11	0.542(1)
125	12	0.542(5)
150	13	0.542(4)

It can be observed in both hydrothermal systems tested that the oxygen potential
of the aqueous solutions is diminished by the dissolved ammonia secondly to the fol-
lowing reaction, obtained from the database of HSC Chemistry for Windows 4.1 pro-
gram (Outokumpu Oy – Finland), in its licensed form to PEMM/COPPE/UFRJ.

Fig. 3 X-ray diffraction patterns for ceria samples obtained under reflux at 100°C dur-
ing different hydrothermal treatment time: a – 12 h; b – 18 h; and c – 24 h

$$2NH_{3\ (aq)} + 3/2O_{2\ (aq)} \rightarrow N_{2\ (aq)} + 3H_2O_{(l)} \tag{4}$$

Under reflux, the use of atmospheric partial pressure of oxygen contributes to the disposal of ammonia in the medium, which produces the increase of powder crystallinity, mainly for the 2 h time sample. Also this reaction represents lowering of the pressure of oxygen associated to an opened system, which makes the oxidation of the ceria a slow process.

In autoclave, the pressured oxygen is rapidly consumed (about 2 h), by reactious (2) and (4), giving rise to a quite stoichiometric form (Table 1), with no further oxidation for bigger residence times (Table 3). This also explains the lower crystallinity of the ceria produced for 2 h in autoclave (Table 1), once ammonia is not available as a mineralizing agent.

Then the use of high pressure of O_2 in the autoclave for hydrothermal treatments described in [7] is entirely justified for a better stoichiometry achievable.
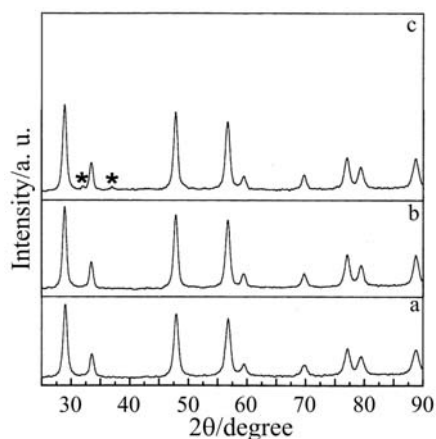
Fig. 4 X-ray diffraction patterns for ceria samples obtained in autoclave for 10 h at different temperatures: a – 100°C; b – 125°C and c – 150°C (with peaks of a second phase indicated)

The presence of a second phase for the sample obtained in autoclave at 150°C was noticed, with low intensity peaks at $2\theta = 32.05$ and $36.95°$ (Fig. 4c). DTA graphs for this sample (Fig. 5) show the presence of two exothermic events, centered at 431 and 492°C, both being very broad and intense. Those peaks are related to a mass loss of 14% as the TG line shows (Fig. 5), with a band beginning at 363°C and ending at 547°C, not differentiating the two processes. The occurrence of those events surely supports that a second phase is present in the sample. Table 4 shows each mass loss in percentage obtained from each process in the DTA curve.

The second phase may be related to a by-product of the interaction of dispersed material and nitrate ion, once nitric acid was used to aid the dissolution process of cerium(III) chloride. The compound $Ce(OH)_2(NO_3)_2$, for example, can be considered, once it would be the product of the following reaction:

$$Ce(OH)_{4\,(s)}+2NO_{3\,(aq)}^{-}\rightarrow Ce(OH)_2(NO_3)_{2\,(s)}+2OH_{(aq)}^{-} \qquad (5)$$

This reaction is only considered to happen at 150°C, once the raise of treatment temperature tends to produce secondary reactions. Also the acid medium due to the Ce^{4+} hydrolysis turns the reaction equilibrium to the right, producing $Ce(OH)_2(NO_3)_2$.
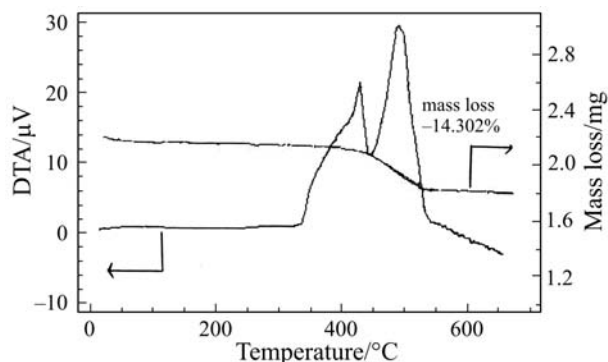

Fig. 5 DTA and TG for compound synthesized for 10 h at 150°C in autoclave

A theoretical mechanism for the thermal events observed can be divided into two steps and they would be:

$$\text{Step 1: } Ce(OH)_2(NO_3)_{2\,(s)}\rightarrow CeO(NO_3)_{2\,(s)}+H_2O_{(g)} \qquad (6)$$

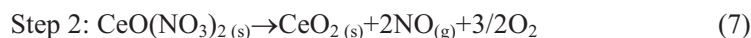$$\text{Step 2: } CeO(NO_3)_{2\,(s)}\rightarrow CeO_{2\,(s)}+2NO_{(g)}+3/2O_2 \qquad (7)$$

Table 4 shows the experimental results and the calculated mass losses from reactions (6) and (7). It can be observed that the theoretical mass losses are about 2–3 times higher than the experimental ones. Then, the set of reactions presented is representative of the system, once CeO_2, which does not contribute to this process, is present in much greater quantity than the second phase (Fig. 4c). Then, this proposal can be considered a good approach.

Table 4 Correlation between experimental and theoretical mass losses for the two exothermic events presented in Fig. 5

	Step 1	Step 2	Overall mass loss
Experimental mass loss/%	3	11	14
Theoretical mass loss/%	6	36	42

Besides the formation of by-products verified by the structural and thermal studies, the effect of an increase in treatment temperature was also studied by SEM analysis. The micrographs, with two different resolutions, for the samples synthesized in autoclave for 10 h at 100 and 150°C are in Figs 6 and 7. They show that the latter powder visually has smaller agglomerates (Figs 6a and 7a) and is more dispersed
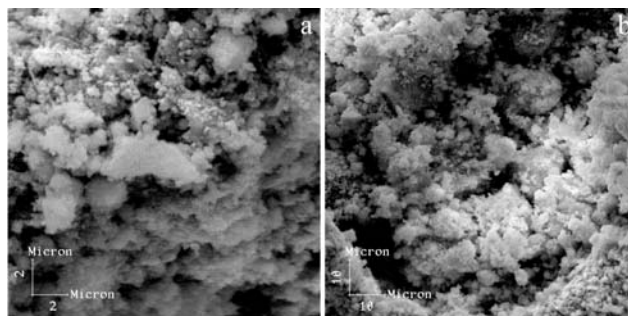
Fig. 6 SEM micrographs for the compound synthesized in autoclave at 100°C for 10 h, with: a – 1000× and b – 5000×
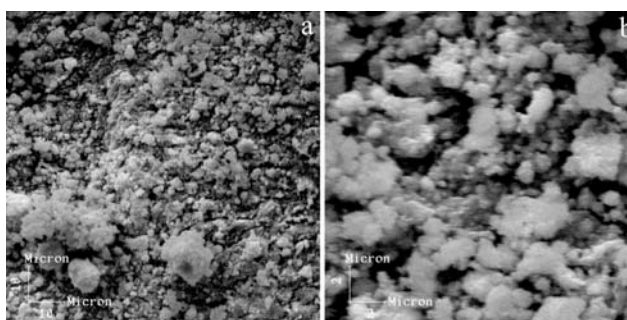
Fig. 7 SEM micrographs for the compound synthesized in autoclave at 150°C for 10 h, with: a – 1000× and b – 5000×

(Figs 6b and 7b) than the former one. This fact may have some relation to the formation of a by-product, which disables the powder agglomeration, in the higher temperature sample. In this case, it can be concluded that the increase of treatment temperature leads to a less agglomerated powder.

Conclusions

It was verified the non-stoichiometric character of both samples by thermal analysis for the residence time of 2 h. The observed color for the compound obtained under reflux matched the interpretation by the correspondent calculated cell parameter.

Under reflux, in the 2–12 h range there was an oxidation process of non-stoichiometric ceria, with lowering of crystallinity. On the other hand, for the 12–18 h interval, the mineralizing behaviour of ammonia was verified. In general, it can be said that the oxidation process is more effective in autoclave, once oxygen is pressured.

The temperature study showed that the treatment at 150°C, during 10 h, leads to the formation of a second phase, confirmed by the XRD and thermal analysis. The compound $Ce(OH)_2(NO_3)_2$ was shown to be a good approach as in the second phase. In general, it can be said that the degree of powder agglomeration decreases with the increase in the treatment temperature, for the conditions presented.

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