New Insights into the Dynamics that Control the Activity of Ceria-Zirconia Solid Solutions in Thermochemical Water Splitting Cycles

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ABSTRACT

The reactivity of a ceria-rich $Ce_{0.85}Zr_{0.15}O_2$ solid solution towards the thermochemical water splitting process (TWS) was studied over repeated H_2/H_2O redox cycles. The structural and surface modifications after treatment at high temperature under air or N_2 atmospheres were characterized by High-Resolution Transmission Electron Microscopy (HRTEM), X-ray diffraction (XRD), Raman spectroscopy, X-ray Photoemission Spectroscopy (XPS) and Positron Annihilation Lifetime Spectroscopy (PALS). Samples treated under nitrogen resulted more active due to phase segregation with formation of a zirconyl oxynitride phase in catalytic amount. Insertion of N^{3-} into the structure contributes to increase the numbers of oxygen vacancies that preferably arrange in large clusters, and to stabilize Ce^{3+} centers on the surface. In comparison, treatment under air resulted in a different arrangement of defects with less Ce^{3+} and smaller and more numerous vacancy clusters. This affects charge transfer and H-coupling processes, that play an important role in boosting the rate of H_2 production. The behavior is found to be only slightly dependent on the starting ceria-zirconia composition and it is related to the development of a similar surface hetero-structure configuration, characterized by the presence of at least a ceria-rich solid solution and a (cerium-doped) zirconyl oxynitride phase, which is supposed to act as a promoter for TWS reaction. The above findings confirm the importance of a multi-phase structure in the design of ceria-zirconia oxides for water splitting reaction and allow a step forward to find an optimal composition. Moreover, the results indicate that doping with nitrogen might be a novel approach for the design of robust, thermally resistant and redox active materials.

INTRODUCTION

The necessity to increase the sustainability of the modern societies requires the development of a circular economy based on an increasing use of renewable resources for the production of energy services. Solar energy and water are winner ingredients for improvement of the energy conversion chain, which would be based on the use of hydrogen or bio-fuels. Among the technologies that exploit the sunlight to produce ~~energy and~~ fuels, solar thermochemical processes have a good potentiality in terms of efficiency and there are excellent reviews that summarize the main outcomes in the field.[1-3] In these processes the solar resource is used directly to drive endothermic chemical reactions such as the splitting of water (WS) and/or of CO_2 (CDS). Water spontaneously decomposes into elementary O_2 and H_2 only at temperature higher than 3800 °C.[3] This condition, along with the necessity of separating O_2 from H_2 makes the direct thermolysis of water impractical. However, the reaction is possible through multi-steps thermal cycles using specific compounds as promoters. Reducible metal oxide redox couples such as SnO_2/SnO, ZnO/Zn, Fe_3O_4/FeO, CeO_2/Ce_2O_3 have been shown suitable to split water in two steps: an endothermic step at high temperature (~1200-2000 °C) in which the oxide is reduced in inert atmosphere and a subsequent exothermic step at lower temperature in which water oxidizes the metal oxide producing H_2 (~400-1300 °C).[3] The working temperature of each step, O_2 and H_2 yields, and the fuel purity strongly depend on the type of metal oxide involved. Among many metal oxides proposed in literature, ceria is one of the most promising candidates.[4] CeO_2 can be reduced to Ce_2O_3[5] or to $CeO_{2-\delta}$ (reaction 1)[4,6] with the aid of solar energy in an inert atmosphere and at high temperature (1300-1800 °C). Then it can be promptly oxidized by water (reaction 2) at intermediate temperature (500-800 °C) producing pure H_2 on demand without purification, storage and transport complications, as conversely encountered in other metal oxide based cycles.

$$CeO_2\,(s) \rightarrow CeO_{2-\delta}\,(s) + \delta/2\ O_2\,(g) \qquad (1)$$

$$CeO_{2-\delta}\,(s) + \delta H_2O\,(g) \rightarrow CeO_2\,(s) + \delta H_2\,(g) \qquad (2)$$

Thermodynamic studies of this cycle suggest that solar to fuels efficiency approaching 30% could be achievable, when a complete heat recovery is accomplished.[7,8] Several experimental and theoretical studies have identified in the reduction step the main limits of ceria based cycles.[3,9] At a temperature higher than 1800 °C, which is necessary for a full reduction of CeO_2 to Ce_2O_3, CeO_2 starts to sublimate, consequently the yield of cycles has been observed to decrease over the time. At lower temperatures ceria cannot be fully reduced and H_2 production depends on the degree of reduction achieved. Therefore, many studies on ceria-based systems have been focused on decreasing the reduction temperature of the Ce^{4+}/Ce^{3+} redox couple, while maintaining the high reactivity of reduced Ce^{3+} species towards water.[3,10] The addition of Zr^{4+} into the ceria lattice resulted effective in increasing the thermodynamic driving force of CeO_2 reduction at lower temperatures[11,12], while aliovalent dopants have been found less effective.[13,14] New synthesis strategies to control the morphology and the sintering processes of ceria have also been adopted with success.[15] Most recently other solutions allowed to obtain a high and stable production of H_2, such as the addition of rhodium to ceria lattice as catalyst[16] or the use of a composite of CeO_2 and SnO_2 that under reducing conditions forms a stoichiometric pyrochlore phase more reactive than the non-stoichiometric $CeO_{2-\delta}$.[17]

The effect of zirconium content in the two steps water splitting reaction has been widely studied[13,18-21]; a linear increase of the reduction yields as a function of zirconium content was observed up to a content of 25 mol%, while at higher contents a stabilization of the released O_2 was recorded. On the other hand, ceria-zirconia based materials showed a slow kinetics of oxidation.[3,13,21] The oxidation rate seems to be controlled by intergranular gas–phase diffusion in the material layer. In this case, improving morphological and textural properties of the mixed oxides via co-doping[22] or by using different synthesis approaches[13,23] resulted beneficial due to the possibility of tuning the crystalline size, porosity structure and composition at the nanoscale.[24] Most of the research has been focused on ceria rich compositions, which were supposed to be structurally stable to the high temperatures adopted in the reduction step and the attention of scientists was mainly drawn on kinetic and thermodynamic issues of the cycle. Only a few studies investigated the correlations between water

splitting performance and structural/compositional modification undergone during the redox steps,[23,25] despite it is well known that the redox properties of the materials are markedly affected by the thermal and redox history.[26] In a recent communication, we showed that also zirconia-rich ceria-zirconia mixed oxides can be suitable for the WS process.[27] In that study, it appeared clear that phase segregation and nitridation processes, which were induced by the thermal redox cycles, might play a major role in determining the high activity. The present study investigates in more detail the WS behavior of $Ce_{0.85}Zr_{0.15}O_2$ over more cycles and compares the results with previous outcomes with the aim to find some commonalities governing the overall behavior of ceria-zirconia in thermochemical water splitting reactions. Through the use of positron annihilation life time spectroscopy (PALS) and other complementary techniques we are able to describe for the first time, not only the characteristics of phases but also the arrangement of defects on the surface of material when treated at high temperature under air or nitrogen-containing atmospheres. This allows to put forward a conceivable mechanism that explains the significance of nitridation in the WS activity of ceria-zirconia oxides.

EXPERIMENTAL

Materials. $Ce_{0.85}Zr_{0.15}O_2$ was prepared with a surfactant assisted precipitation method as reported elsewhere.[28] Briefly, proper amounts of $Ce(NO_3)_3 \cdot 6H_2O$ salt (Treibacher Industrie AG) and $ZrO(NO_3)_2$ liquid gel (Treibacher Industrie AG) were dissolved in demineralized water obtaining a 0.2 M solution; concentrated H_2O_2 (35% Sigma-Aldrich) was then added according to the molar ratio $[H_2O_2]$/[tot metals ions] equal to 3. After 45min of continuous stirring at ambient temperature concentrated $NH_3 \bullet H_2O$ (28% Sigma-Aldrich) was added to obtain a pH value of 10.5. Finally, lauric acid (Sigma-Aldrich), using a molar ratio ([tot metal ions]/[lauric acid]) equal to 0.25, was directly added and maintained under continuous stirring for 4h. The precipitate was then filtered and washed three times with 0.5L of de-mineralized water and the resulting cake was dried at 100 °C overnight. The dry precipitate was calcined in air at 500 °C for 4h. This method allows to obtain highly

homogeneous starting materials, which ensures a reproducible phase segregation. In order to simulate the aging effect undergone during the strongly endothermic step of TWS cycle, the oxide was treated at 1300 °C in nitrogen or air for four hours. Other thermal treatment in air were made at 800 °C/4h, and at 1100 °C. All the samples were cooled down in the atmosphere of treatment and exposed to air at room temperature before of the reactivity tests.

Reactivity tests. The experimental conditions have been chosen on the basis of previous studies.[20,23] The activity of $Ce_{0.85}Zr_{0.15}O_2$, calcined at 1300 °C/4h either in N_2 (CZ85_N_2) or in air (CZ85_air) was evaluated towards a two steps water splitting thermal cycle using two different setups. Reduction degree of the material in N_2/air atmosphere was measured in a thermogravimetric analyser (Q600-TA Instruments). The thermally aged samples (25mg) were heated at 10°C/min in N_2 flow (100 ml/min) up to 1300°C. The oxygen released from the oxide was evaluated from the weight loss observed during 80 minutes of isotherm at 1300 °C. The water splitting (WS) activity was evaluated in a Micromeritics apparatus using the same method as described by Pappacena et.al.[27] Each sample (50 mg) was previously reduced to obtain the same reduction degree achieved in the first endothermic step by using a 5% H_2/Ar flow and a heating ramp of 10 °C/min up to 700 °C. These conditions have been established through a thermogravimetry analysis (TGA, Q500-TA Instruments) in 5%H_2/Ar flow by reducing the sample up to 900 °C. The reduced sample was evacuated in He and oxidized by 20 pulses of water vapor (30% in Ar flow) at 800 °C. H_2 consumption and production were monitored with a thermal conductivity detector; the total H_2 production was measured by calculating the H_2 outcome from the first twenty water vapor pulses. At the end of the WS reaction the sample was oxidized with air for 10min to complete the oxidation and cooled down to ambient temperature in He atmosphere. The cycle was repeated six times. The same experiment was carried out also without completing the oxidation with air in order to verify whether the oxidation conditions may affect the reaction of water splitting.

158 **Characterization**. Structural and surface properties of all materials were investigated through
159 the use of several techniques. X-ray Diffraction analysis (XRD) were performed using a Philips
160 X'Pert diffractometer operated at 40 kV and 40 mA equipped with a nickel-filtered CuK_α radiation.
161 All spectra were collected using a step size of 0.02 2θ degrees and a counting time of 40s per angular
162 abscissa in the range of 20–145 2θ degrees. The Philips X'Pert HighScore software was used for
163 phases identification. The mean crystalline size was estimated from the full width at the half
164 maximum (FWHM) of the X-ray diffraction peaks using the Scherrer's equation[29] corrected for the
165 instrument line broadening. Rietveld refinement of XRD spectra was performed by means of
166 GSASEXPGUI program.[30.31]
167 Raman spectra have been recorded with a LABRAM HR800 equipped with a solid-state laser (Laser
168 XTRA, Toptica Photonics) operating at 785 nm and a Peltier cooled CCD detector. The laser radiation
169 was filtered by an interference filter and was focused on the sample through an Olympus BX41
170 microscope. A 50X Olympus objective (NA = 0.75) has been used. The Rayleigh radiation was
171 rejected using Notch filters. In order to ascertain the absence of artifacts the spectra have been
172 obtained also using excitation radiations, at 512 and 633 nm and two different grids (600 lines/mm;
173 1800 lines/mm).
174 High resolution transmission electron microscopy (HRTEM) was accomplished with a JEOL J2010F
175 instrument equipped with a field emission electron source and operated at 200 kV. Samples were
176 dispersed in alcohol and a drop of the suspension was placed over a grid with holey-carbon film.
177 Specific surface area (SA) and porosity of oxides were measured by nitrogen adsorption/desorption
178 isotherms at 77 K, following the BET and BJH method respectively[32], using a Tristar 3000 gas
179 adsorption analyzer (Micromeritics). The pore size distribution was calculated from the desorption
180 branch of the isotherm.
181 XPS was used as the main tool to assess the surface chemical composition of the samples before and
182 after the catalytic process. Analyses were performed on a Perkin-Elmer Φ 5600-ci spectrometer using

non-monochromatized Al Kα radiation (1486.6 eV). The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f7/2 line at 83.9 eV with respect to the Fermi level. The standard deviation for the BEs values was ± 0.2 eV. Survey scans were obtained in the 0−1300 eV range (187.8 eV pass energy, 0.4 eV $step^{-1}$, 0.05 sec $step^{-1}$). Detailed scans were recorded for the C1s, O1s, Zr3d and Ce3d and N1s regions (23.5 eV pass energy, 0.1 eV $step^{-1}$, 0.1 sec $step^{-1}$). The BE shifts were corrected by assigning to the C1s peak associated with adventitious hydrocarbons a value of 284.8 eV.[33] The analysis involved Shirley-type background subtraction, non-linear least-squares curve fitting adopting Gaussian-Lorentzian peak shapes, and peak area determination by integration.[34] The atomic compositions were evaluated from peak areas using sensitivity factors supplied by Perkin-Elmer, taking into account the geometric configuration of the apparatus.[35] The experimental uncertainty on the reported atomic composition values does not exceed ± 5%.

Positron annihilation lifetime spectroscopy experiments (PALS) were carried out with a fast-slow coincidence system which has a resolution of 230ps. The scintillation detectors are plastic scintillator coupled with photomultipler tubes. A 40μCi ^{22}Na source of positron was sandwiched between two pieces of identical samples. For each spectrum about $2x10^6$ coincidence counts have been recorded to ensure the repeatability of the measurements. The positron lifetime data were analyzed by the lifetime9 program with the necessary source corrections.

RESULTS

Reactivity results. The endothermic step corresponding to the thermal reduction was evaluated via thermogravimetry by measuring the weight loss of the sample treated at 1300 °C in N_2 or air. O_2 released during the thermal treatment was 276 μmol/g and 169 μmol/g respectively for the sample aged in N_2 and air, which corresponds to a degree of Ce^{4+} reduction of 21 mol% and 13 mol%. Similar results were reported in literature, but generally using higher temperature.[19,20]

Figure 1 shows the results obtained in the exothermic water splitting experiment for both the N_2-treated oxide and for the sample aged in air. A total of 6 cycles are reported, and the detail for one

cycle is shown to the right of the image. N_2-treated sample is more active, and the H_2 production increases significantly up to a stable value obtained with the fourth cycle. A comparison with results obtained on $Ce_{0.15}Zr_{0.85}O_2$ indicates that regardless of initial composition H_2 yields reach close values for the two nitrogen-pretreated compositions after a few cycles.[27] To exclude the role of oxygen in the promotion of H_2 production observed from the 2nd cycle, the same experiment was repeated without oxidizing the samples with air at the end of each cycle, and the results are compared in Figure S1.

Characterization results. Table 1 summarizes the textural and morphological properties of $Ce_{0.85}Zr_{0.15}O_2$ after thermal treatment in the range of temperatures 500-1300 °C. The material shows a good thermal stability up to 800 °C; higher temperatures causes a large drop in surface area with values close to 1 m^2/g after calcination at 1300 °C, regardless of the gas type used in the treatment. Correspondingly, an increase of average crystallite size up to 40 nm with loss of porosity is found. The structure of the samples was investigated at the nanoscale through XRD, Raman spectroscopy and HRTEM.

Table 1: Characteristics of $Ce_{0.85}Zr_{0.15}O_2$ after the thermal treatments.

Calcination Temperature (°C)	Treatment Atmosphere	Specific Surface Area (m^2/g)[a]	Pore size (Å)	Crystallite size (Å)[b]
500	Air	94	238	54
800	Air	45	345	99
1100	Air	9	ND	275
1300	Air	1	ND	425
1300	Nitrogen	1	ND	403

a: according to BET method; b: determined with Sherrer equation from XRD analysis,. ND: not determined

Figure 2 shows the corresponding X_ray diffraction profiles of the samples. After calcination at 500°C the sample crystallizes in a cubic fluorite structure with a unit cell value of 5.3652(5) Å. This value is lower than the one measured for a pure ceria sample, 5.4118(1) Å, and indicative of the insertion of Zr^{4+} into the ceria lattice. The application of Vegard law[36] allows us to calculate a molar doping of zirconium equal to 0.167, that is very close to the nominal composition of the starting

material. No large differences exist among the XRD profiles except for the narrowing of the peaks with the increase of the calcination temperature, indicating sintering of crystallites as a consequence of the thermal treatments.[37] However, a careful evaluation of the profiles of samples treated at 1300°C in both air and nitrogen evidences a tiny shift ($2\theta=0.12\pm0.4$) of the most intense peak (111) of CZ85 to higher angles and a small shoulder at $2\theta=28.10$ degrees; thus indicating the occurrence of phase segregation accompanied by small changes in the composition of the cubic CZ85 phase. The small peak at $2\theta=28.10$ is attributable to the presence of a monoclinic zirconia-rich phase, ($Ce_{0.05}Zr_{0.95}O_2$, PDF 88-2392). The XRD profile of the samples sintered in air shows also a small peak at $2\theta=29.83$ which is probably related to a tetragonal zirconia-rich phase ($Ce_{0.18}Zr_{0.82}O_2$, PDF 80-0785) or to tetragonal ZrO_2 (JCPDS 01-080-0785). Such type of segregation is consistent with what is reported in literature for similar compositions.[38]

Figure 3 shows the Raman spectra of samples treated at 1300 °C before and after WS cycles. Figure S2 shows also the spectra collected using excitation lines at 512 and 633 nm. Spectra in the region 180-800 cm^{-1} are characterized by an intense signal at ca. 476 cm^{-1} corresponding to the fundamental vibration mode F_{2g} of the fluorite structure and satellite bands at 300 and 602 cm^{-1}, consistent with a distortion of the cubic structure and the presence of a tetragonal t'' phase.[39] The minority phases are not detectable and the spectra of the samples before and after WS cycles are almost identical. Above 1000 cm^{-1} all the spectra show complex bands which are generally attributable to electronic f-f transitions of Ln^{3+} ions present as impurities in the materials.[38] Alternatively, these bands have been also associated to the presence of Ce^{3+} ions.[39,41,42] It is interesting to note that the intensity of these bands, which is generally related to the asymmetry of the sites, increases after the cycles.

Figure 4A shows a HRTEM image of the sample treated in nitrogen at high temperature. The crystallite labeled "a" corresponds to a single cubic CZ particle oriented along the [110] crystallographic direction. Spots at 3.0 Å correspond to the cubic (111) planes. In contrast, the crystallite labeled "b" shows a FT pattern exhibiting spots aligned at 2.5 and 5.1 Å as well as spots at

2.9 Å. The spots aligned at 2.5 and 5.1 Å are ascribed to the (400) and (200) crystallographic planes of Zr_2ON_2, respectively, whereas those at 2.9 Å correspond to the (222) planes of Zr_2ON_2.

These results are in good agreement with those reported in literature[42], except for tiny differences which could be explained with the insertion of cerium in the structure. This hypothesis is reasonable considering that Ce^{3+} (103 pm) has an effective ionic radius similar to that of La^{3+}, and that the formation of $LaZrO_2N$ has been demonstrated.[44] The HRTEM analysis of sample treated in air (Figure 4B) does not evidence the presence of the oxynitride phase. FT image with spots at 3.0 Å corresponds to the (111) planes of cubic CZ, which is the dominant phase. The effects of WS cycles at the nanoscale are shown in Figure 4C. The TEM image (left) evidences a sample constituted by crystallites measuring more than 100 nm in a compact arrangement, suggesting that the sample sintered during the cycles. Triple junctions are easily recognized, which usually appear upon high temperature calcination treatments. The figure at the right corresponds to a representative HRTEM image of the sample. In this case, only lattice fringes corresponding to the CZ oxide are recognized. In the figure, several lattice fringes are indicated and correspond to the (111), (220) and (222) crystallographic planes of cubic CZ at 3.0, 1.8 and 1.5 Å, respectively.

The composition and defects structure of samples before and after WS cycles are investigated through XPS and PALS techniques. Figures 5A and B show the XPS spectra and the corresponding fitting components of Ce3d and O1s regions for the samples treated at 1300 °C in nitrogen. Similar features were observed for the air-treated sample and for the samples after six WS cycles (see Figure S3 and S4). Figures 5C and D show the N1s region of the sample treated in nitrogen before and after WS cycles.

In Figure 5A, U and V refer to cerium $3d_{3/2}$ and $3d_{5/2}$ spin-orbit components, respectively. U, U'',U''', V, V'', and V''' refer to the final states of Ce^{4+}, while U°,U' and V°,V' refer to those of Ce^{3+} [25]. The fitted peak areas were used to estimate the relative amount of Ce^{3+} and Ce^{4+} (see Table 2). The O1s region is suitably fitted with two components (Figure 5B). The main component (peak 1) at about 529.5 eV is associated with the cerium–zirconium oxide matrix, while the component centered at

531.5 eV (peak 2) can be ascribable mainly to surface hydroxyl groups.[44] The signal N1s at 399.9 eV (Figure 5C) confirmed the insertion of nitrogen into the surface of the CZ85_N_2 and the formation of a zirconyl oxynitride phase[27,46,47] In addition, the evidence of the same nitrogen peak on the CZ85_N2 surface after WS cycles (CZ85_N2_ws, Figures 5D) indicates that the oxynitride phase is stable under WS conditions. No signal corresponding to insertion of nitrogen is observed for samples treated under air.

Table 2 summarizes the surface chemical composition (atomic %) of the samples, determined from the analysis of Ce3d and Zr3d XPS peaks.

Sample calcined at 500 and 1100 °C show a surface composition consistent with the nominal stoichiometry of the $Ce_{0.85}Zr_{0.15}O_2$ solid solution revealing that the starting material was homogeneous and thermally stable up to 1100 °C. After treatment at 1300 °C the value of Zr/Ce ratio increase to 0.26 in agreement with the phase segregation observed by XRD and indicating that zirconia-rich compositions are mainly located on the outer part of the crystallite. The presence of Ce^{3+} in the starting material (500 °C) is due to the nanometric nature of the powder and to the presence of extrinsic defects induced by the zirconium doping.[38] Besides, a small quantity of Ce^{3+} could be generated by the reduction of Ce^{4+} under the X-ray irradiation during XPS analysis.[48] The amount of Ce^{3+} increased after calcination at 1100 and 1300 °C as expected from the state diagrams of CeO_2 in air and N_2 conditions, for which CeO_2 starts reducing above 1000 °C.[4,6] After water splitting cycles the concentration of Ce^{3+} remained the same for the sample treated in nitrogen, while it slightly decreased in the case of the sample pretreated in air. For the N_2 treated sample the extent of surface nitridation, was determined from the N/Ce atomic ratio which resulted similar before and after the WS reaction, with a value of ca. 0.03. However, due to the very low intensity of the N1s peak, this is only a rough estimate.

Table 2. Results of XPS analysis

Sample	Ce[b] [Ce^{3+}, Ce^{4+}][c]	Zr[b]	Zr/Ce	Ce^{3+}/Ce^{4+}
CZ85-500[a]	84.2 [14.3, 69.9]	15.8	0.19	0.20
CZ85-1100[a]	85.4 [22.2, 63.2]	14.6	0.17	0.35
CZ85_air	79.0 [22.1, 56.9]	21.0	0.26	0.39
CZ85_N2	79.1 [24.5, 54.6]	20.9	0.26	0.45
CZ85_air_WS	79.8 [18.4, 61.4]	20.2	0.26	0.30
CZ85_N2_WS	79.1 [24.5, 54.6]	20.9	0.26	0.45

a - the number indicates the temperature of calcination in air; b-the uncertainty on the quantitative values does not exceed ±5%, c - values obtained from fitting of the Ce3d region.

Details into the organization of surface defects were obtained via positron annihilation lifetime spectroscopy (PALS). Figure S5 shows the PALS spectra for some representative sample. All spectra were fitting to three lifetime components (τ_1, τ_2, τ_3) and the corresponding values along with their relative intensity (I_1, I_2, I_3) are summarized in Table 3. As far as we know, this is the first time that PALS technique is applied to the characterization of CZ85 mixed oxides, therefore we used a CZ85 sample calcined at 1100 °C as a reference material for an interpretation of the data. Since the temperature used for treatment is not enough high to cause phase segregation and thermal reduction, such a sample is representative of a homogeneous highly sintered composition.

The longest component τ_3 is attributed to the annihilation of orthopositronium atoms formed in the large voids present in the material.[49] It hardly helps in giving some useful information of defects in the samples because the formation of the orthopositronium atoms are not related to the positron trapping at defects, so it will be neglected in the following discussion. The component τ_1 is generally attributed to the free annihilation of positrons in defect-free crystal. However, for disordered systems it may also be associated to small defects (like mono vacancies) and shallow positrons traps (like oxygen vacancies), which can decrease the average electron density and elongation of τ_1.[50,51]

Table 3: Peak-fitting results of PALS spectra, Spectra fitted with the Lifetime9 software.

sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)	I_1(%)	I_2(%)	I_3(%)
CZ85_air	170.8	310.0	1.09	78.9	20.8	0.35
CZ85_N_2	175.2	358.0	1.02	72.2	26.6	1.20
CZ85_N_2_ws	173.7	351	1.83	83.9	15.5	0.53
CZ85_air_ws	164.4	291	1.4	74.6	25.0	0.44
CZ85-1100	179.1	359	0.95	47.2	51.9	0.88

In many studies on ceria based oxides in form of nano-powders, this first component τ_1 has been related to neutral oxygen mono-vacancies associated to Ce^{3+} ($Ce'_{Ce}V_{O}^{\bullet\bullet}Ce'_{Ce}$) according to Krögel and Vink's defect notation).[52] From Table 3 we can see the τ_1 values are about ~175 ps, which are far lower than that reported in literature, indicating that the small vacancies have higher electron density in our samples. Such a difference might be due to the fact that, in our case, the material has a larger crystal size owing to its sintering at high temperature.[51] The component τ_2 is much larger than the component τ_1, and it arises from positrons trapped by larger size defects. These type of defects mainly locate on the surface or subsurface, thus τ_2 should give useful information on the surface defects of samples.[52,54]

It is worth noting that the values of τ_1 and τ_2 for the reference sample CZ85-1100 are very similar to the respective life times for the sample treated in nitrogen before the test (CZ85_N_2). Conversely, the related intensity I_1 and I_2 are different, the thermal treatment in nitrogen leads to a decrease of the number of large size clusters on the surface with respect to the reference. The sample treated in air (CZ85_air) shows a lower value of τ_2. Taking into account that the electron density is lower in the large size clusters rather than in the small defects, and consequently the positron lifetime increases in the larger size defects, it is inferred that in the air-treated sample the clusters of defects are smaller than in the N_2-treated sample or in the reference. Moreover, by comparing the ratio I_1/I_2 of the two

samples heated at 1300 °C, it is clear that the material treated in nitrogen have a higher clusters density than that treated in air.

After WS cycles, both the samples treated in nitrogen and that treated in air showed lower values of τ_1 and τ_2. The entity of the decrease is more significant for the sample treated in air (CZ85_air_ws) rather than for the sample treated in nitrogen (CZ85_N_2_ws). Opposite trends have been observed for the value of I_2 in the two samples. After cycles the value of I_2 diminished of the 37% for the CZ85_N_2_ws, while increased 20% for the CZ85_air_ws. That implies respectively a less or higher number of defects clusters in the two samples after reaction.

DISCUSSION

The results indicate that thermal treatment either in N_2 or air at high temperature of $Ce_{0.85}Zr_{0.15}O_2$ induces subtle structural changes promoting phase segregation. The material treated under nitrogen shows the formation of a zirconia based oxy-nitride phase located at the outer part of the grains that is beneficial for the water splitting reaction. The active phase is composed by this oxynitride phase which is present in catalytic amount and by a pseudo-cubic oxide rich in ceria ($Ce_xZr_{1-x}O_{2-\delta}$, $0.7 \leq x \leq 0.9$) as a major phase. This study uses XPS and PALS to obtain more details into the defects organization of these heterogeneous structures to see how the structure and quantity of oxygen vacancies can help in developing more stable and robust WS catalysts.

In agreement with previous observations, our findings confirmed that the main surface defects in ceria–zirconia oxide are polarons, which are related to Ce^{3+} centers, and oxygen vacancies.[55] XPS analysis accounts for the number of Ce^{3+} (Table 2) while PALS technique gives information on the organization of oxygen vacancies (Table 3). The material treated in nitrogen shows a higher concentration of Ce^{3+} and larger oxygen vacancy clusters at its surface in comparison to the sample treated in air. Moreover, the configuration of these defects remains almost the same after redox cycles (the same amount of Ce^{3+} and the same dimensions of cluster, even if clusters number decreased). Conversely, the sample treated under air shows a new arrangement of defects with the presence of

smaller and more numerous vacancy clusters and a decreased amount of Ce^{3+} at the surface. Since the thermal treatments in nitrogen or air caused similar structural and compositional changes in the oxide material, the different configuration of vacancies in air and N_2 treated materials has to be related with the nitridation process and the initial reduction degree of the two materials. Assuming that charge neutrality has to be preserved, the substitution of O^{2-} anions with N^{3-} must be balanced by the introduction of oxygen vacancies.[56] The addition of these extra vacancies along with the necessary vacancies to balance Ce^{3+} charges, (more numerous in the sample treated in nitrogen because more reduced) may justify the formation of larger vacancy clusters in the sample treated in nitrogen. Defects configurations after testing are related to samples oxidized with water, and the differences observed for the two materials suggest that water splitting proceeded through different pathways. We can put forward some hypotheses on basis of recent theoretical and experimental studies regarding the stability and behavior of reduced CeO_2(111) surface when interacting with water.[57] It is reported that large surface vacancy clusters are formed and stabilized via a "hydroxyl-vacancies model".[58] The coexistence of hydroxyl groups and vacancies at the subsurface of CeO_{2-x}(111) favors the stabilization of vacancy dimers or trimers at the surface. Large clusters at the surface in turns favor the mobility of H in the bulk and a higher concentration of Ce^{3+} at the surface.[59] The formation and presence of subsurface hydroxyl groups favor the H transfer between neighboring top-surface O and subsurface O rather than the direct surface diffusion of H among top surface O, because of the lower energy barrier of the mechanism.[58] The high concentration of Ce^{3+} at the surface, close to vacancy clusters leads to a more significant charge modification of the neighboring surface O pushing more covalent electrons towards O. This would contribute to weaken the H-O bond and, consequently, benefit the process of H coupling, which requires O-H bond breaking, to form H_2.

The water splitting process involves surface reactions (i.e. adsorption/dissociation of water, ion/electron transfer on the surface and association of H atoms and H_2 desorption), and incorporation of ions into the bulk. Recently it has been demonstrated that in ceria-zirconia based materials the surface oxygen-ions transfer, mediated by bulk oxygen vacancies is fast and that the rate determining

step of reaction is related to the reduction of hydroxyl groups, and to the release of H_2, rather than due to the incorporation of ions into the bulk.[60,55]

Our results agree with the idea illustrated in Figure 6. The oxynitride phase contributes to create and stabilize large vacancy oxygen clusters[61] that at the first cycle can be easily hydroxilated (Figure 6 A-C). The co-existence of these large clusters and hydroxyl groups helps maintaining reduced surface through a rapid replacement of vacancies from the bulk and an incorporation of hydroxyl groups into the subsurface layers of the oxide (Figure 6 D). This configuration contributes to boost the rate determining step of water splitting to produce H_2, thus explaining the higher reactivity of the material treated in N_2 from the second cycle. In this view, the material treated under air lacks of suitable centers to induce hydroxylation of subsurface and the reaction will be limited at the surface with a less effective rearrangement of defects over cycles.

This study allows also to clarify and explain the behavior of Zr-rich compositions like $Ce_{0.15}Zr_{0.85}O_2$.[27] Despite this latter composition is less thermally stable and shows a more significant surface segregation under nitrogen flow, the final composition at the outer part of the particles is similar to that observed for $Ce_{0.85}Zr_{0.15}O_2$. Figure 7 summarizes the main steps of the transformation for both compositions trying to elucidate the reasons why ceria-rich and zirconia-rich materials show similar water splitting reactivity after thermal treatment in nitrogen and redox activation. It is worth noting that after thermal treatment we end up with a surface phase arrangement which is characterized by the co-presence of $Ce_xZr_{1-x}O_{2-\delta}$, $0.7 \leq x \leq 0.9$ and Zr_2ON_2, which is formed from the nitridation of segregated zirconia and is stable under redox cycles. The possibility that under our conditions the oxynitride phase might be doped with cerium cannot be excluded, and further investigations are requested to better address the nitridation mechanism and the stability of such phases.

CONCLUSIONS

This study investigates the structural changes occurring on $Ce_{0.85}Zr_{0.15}O_2$ during thermochemical water splitting cycles. It is found that thermal aging in nitrogen atmosphere modifies the surface structure and composition of the materials by promoting the segregation of a ceria-zirconia solid solution rich in ceria along with a zirconia-oxynitride phase, a fate that is similar to that found over zirconia-rich compositions. Positron Annihilation Lifetime Spectroscopy measurements have shown that the oxynitride phase contributes to form large surface vacancy clusters with an appropriate defect configuration which promotes charge transfer and H coupling, thus playing a pivotal role in boosting the production of H_2. Modification in the size distribution and number of structural defects can explain the different behavior when the material is treated under air atmosphere.

All these findings suggest new approaches for the development and design of ceria based materials for the two-step water splitting reaction and highlight the importance of engineering the surface defect structure/configuration of the material to obtain an efficient catalyst. In this regard, the role and the impact of nitridation process need to be further investigated.

ASSOCIATED CONTENT

Supporting Information

Reactivity test, Raman spectra, XPS, HRTEM, PALS spectra

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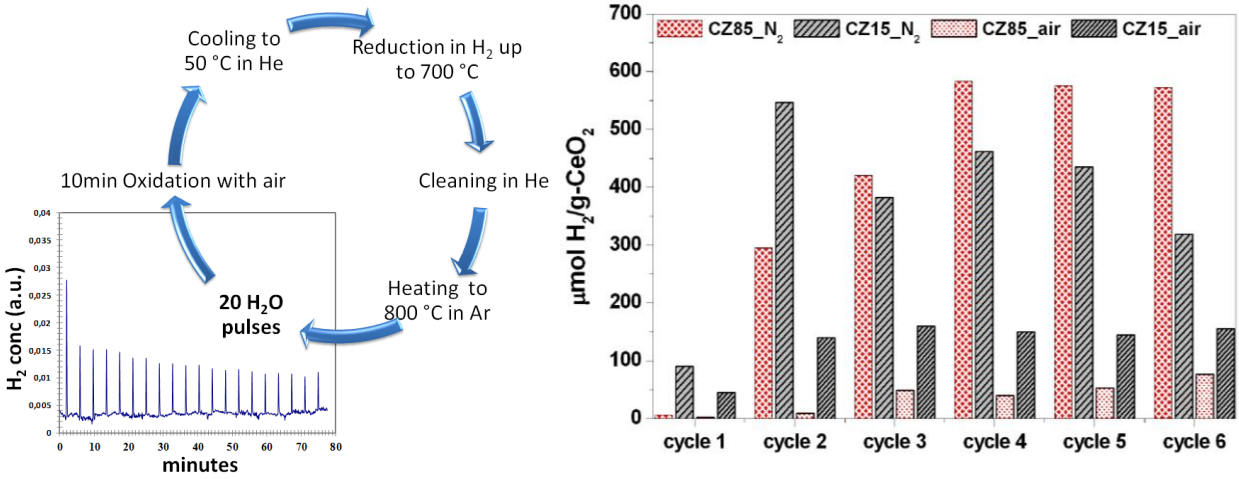

Figure 1: Comparison between water splitting reactivity of CZ85 and of CZ15[27] pretreated in N_2 or Air at 1300 °C/4h. On the right, schematic of one typical cycle.

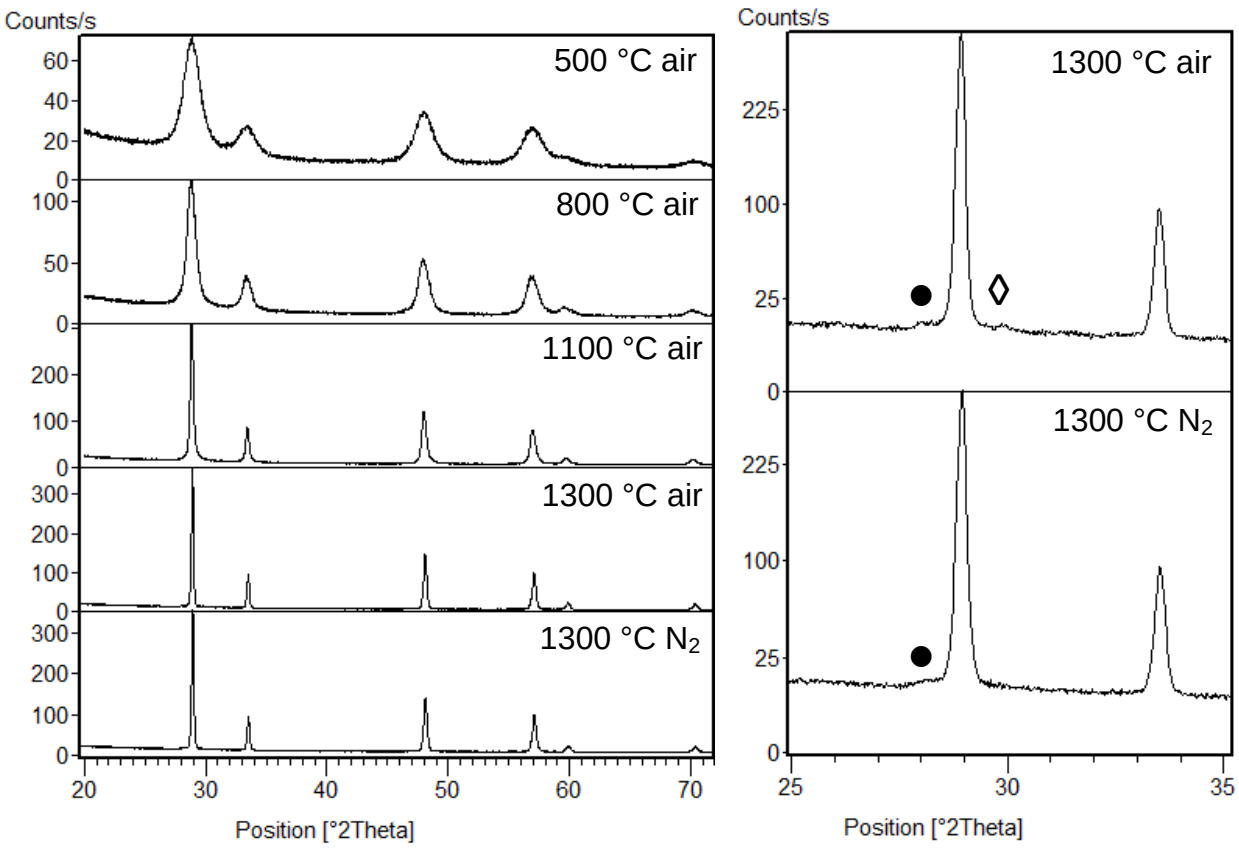
Counts/s
500 °C air
800 °C air
1100 °C air
1300 °C air
1300 °C N2
Position [°2Theta]
Counts/s
1300 °C air
1300 °C N2
Position [°2Theta]

Figure 2: X-ray profiles of $Ce_{0.85}Zr_{0.15}O_2$ calcined at different temperatures in air and at 1300 °C in N_2 flow. To the right: details of samples treated at 1300 °C/4h. Symbols indicate the segregated crystal phases :● $Ce_{0.05}Zr_{0.95}O_2$ (PDF 88-2392); ◊ $Ce_{0.18}Zr_{0.82}O_2$ (PDF 80-0785).

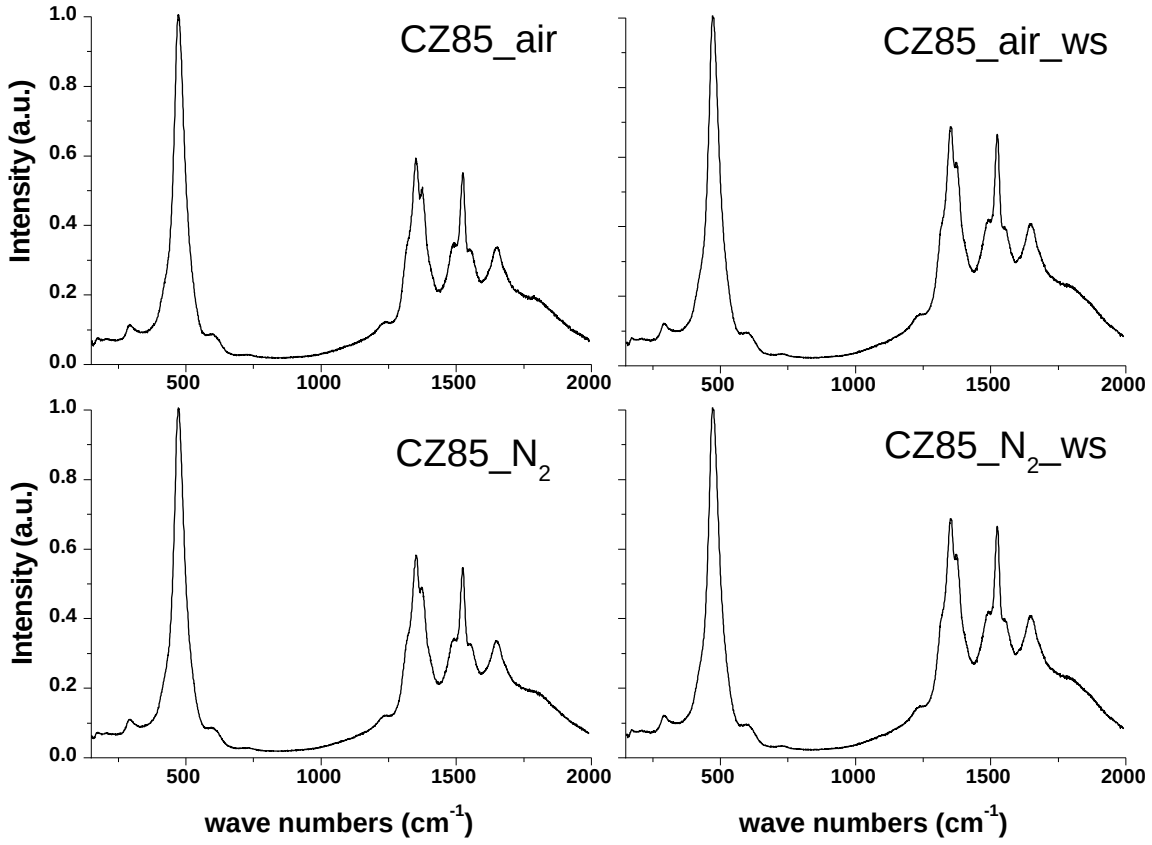

Figure 3: Raman spectra of CZ85 treated in air before(CZ85_air) and after six water splitting cycles (CZ85_air_ws) or in N_2 before (CZ85_N_2) and after six water splitting cycles (CZ85_N_2_ws). Spectra collected using an excitation radiation at 785 nm.

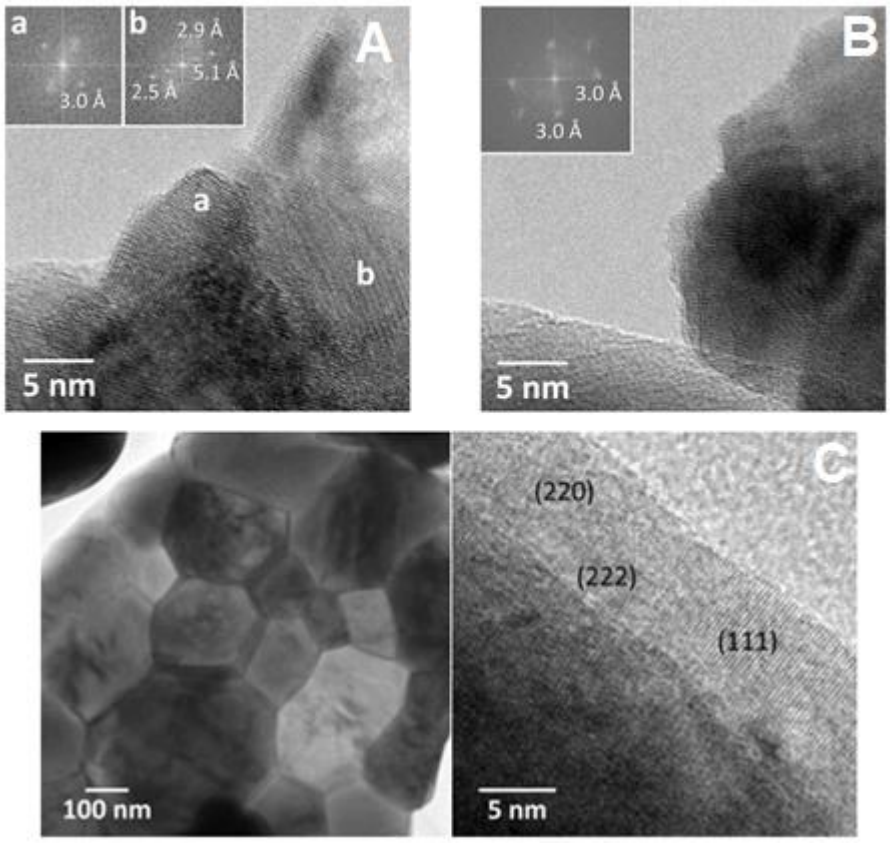

Figure 4: HRTEM of $Ce_{0.85}Zr_{0.15}O_2$ (CZ85) treated at 1300 °C/4h: A) in N_2; B) in air; C) images of the sample treated in N_2 after water splitting test.

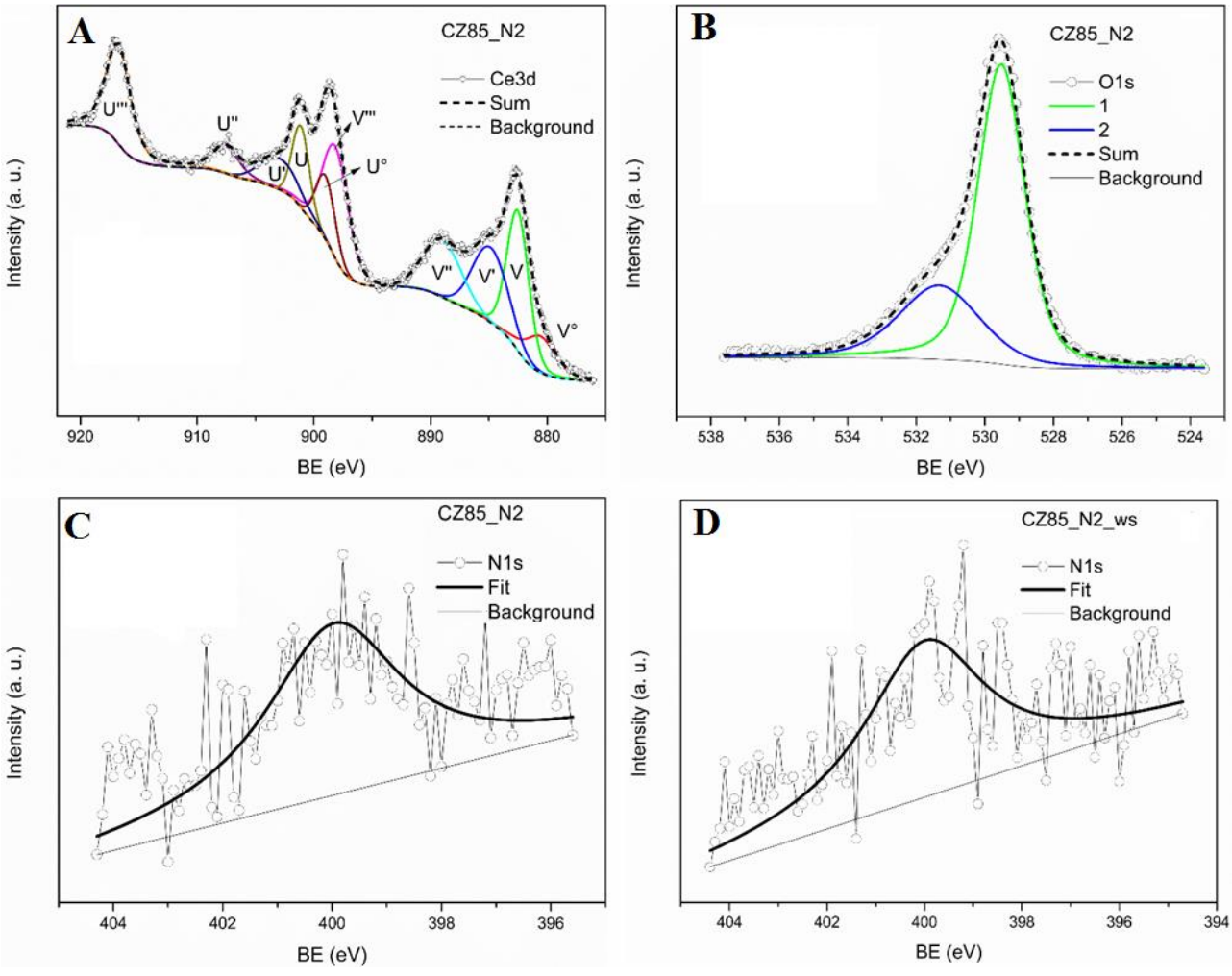
A
CZ85_N2
Ce3d
Sum
Background
U'''
U''
U'
U
V'''
U°
V''
V'
V
V°
Intensity (a. u.)
920
910
900
890
880
BE (eV)
B
CZ85_N2
O1s
1
2
Sum
Background
Intensity (a. u.)
538
536
534
532
530
528
526
524
BE (eV)
C
CZ85_N2
N1s
Fit
Background
Intensity (a. u.)
404
402
400
398
396
BE (eV)
D
CZ85_N2_ws
N1s
Fit
Background
Intensity (a. u.)
404
402
400
398
396
394
BE (eV)

Figure 5: XPS spectra of CZ85 treated in N_2 1300 °C/4h. Figures show Ce3d, O1 and N1s regions and related fitting components.

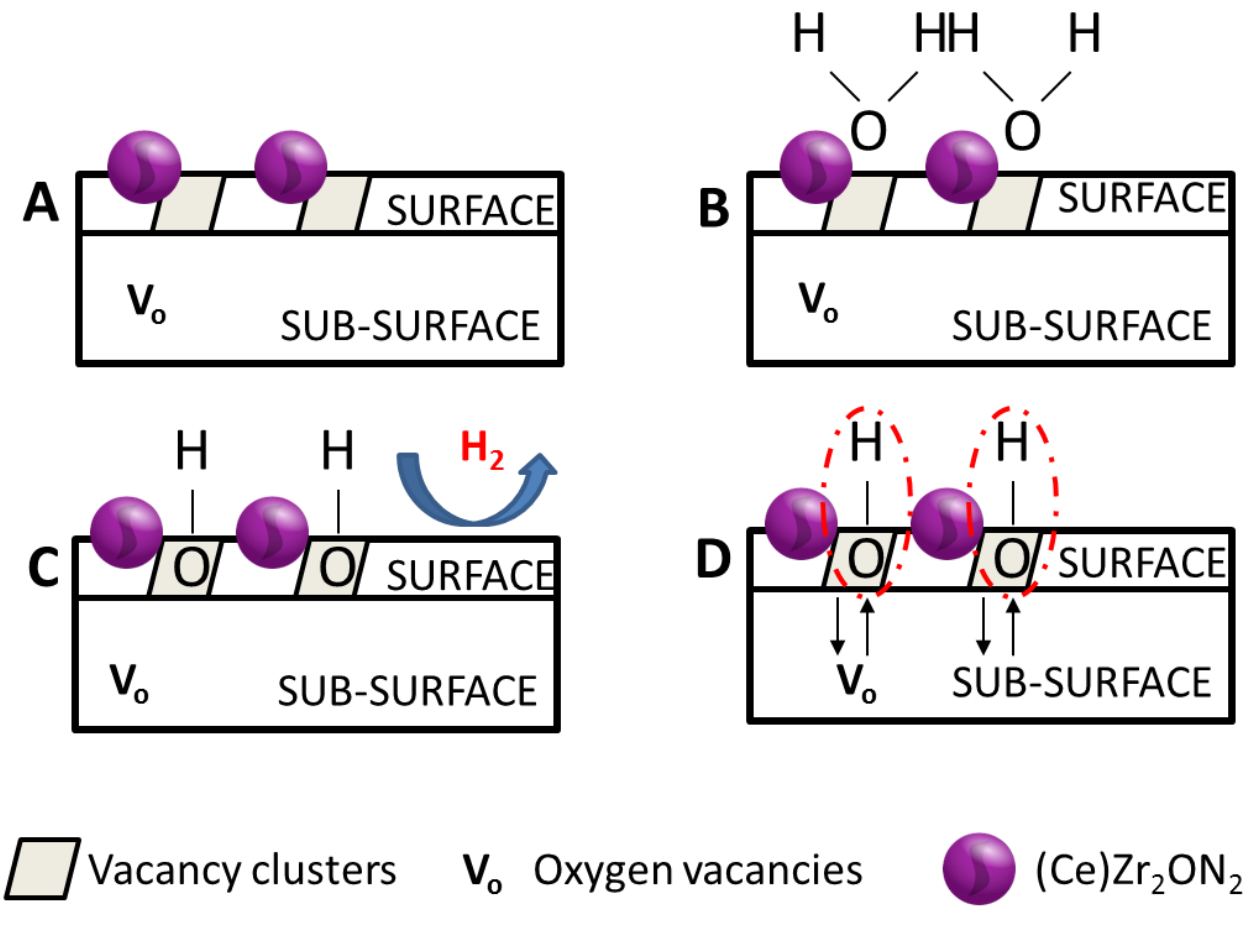

Figure 6: Surface activation mechanism of CZ80 doped with an zirconium oxynitride phase: A) $(Ce)Zr_2ON_2$ contributes to form and stabilize large vacancy clusters (VC) on the surface; B-C) water is adsorbed on VCs forming surface hydroxyl groups (OHs), D) hydroxylated clusters favour the incorporation of OHs into the subsurface layers and oxygen vacancies migration from the bulk, such configuration boosts the production of H_2 from the second redox cycle.

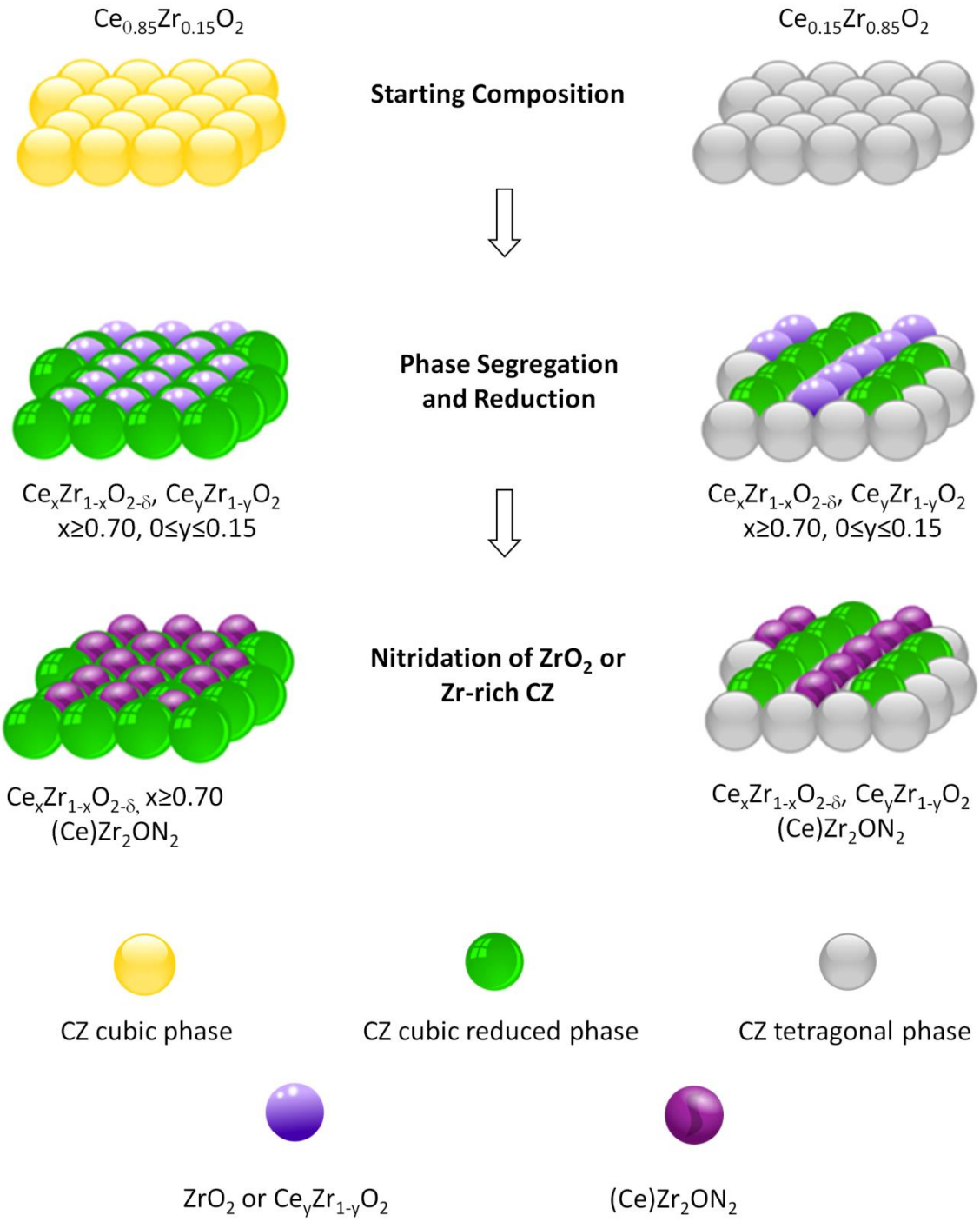

Figure 7: Schematic of segregation processes at 1300 °C in N_2 atmosphere of CZ85 and CZ15.

TABLE OF CONTENTS (TOC) IMAGE