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Study of reduced states of $\text{Ce}_{1-y}\text{Fe}_y\text{O}_2$ and $\text{Ce}_{1-y}\text{U}_y\text{O}_2$ for the thermochemical water splitting to hydrogen

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Solar thermochemical water splitting (TCWS) is a promising approach for sustainable hydrogen production using concentrated solar energy. Cerium oxide (CeO_2) is one of the most studied redox materials for this process due to its fast oxidation kinetics and structural stability at high temperature. However, its practical implementation remains limited by the high reduction energy required to reach significant non-stoichiometry, which restricts hydrogen yields. In this review, key fundamental aspects of ceria reduction and defect formation are discussed, with a focus on strategies to enhance reducibility through partial substitution of Ce cations by transition metals and actinides. In particular, substitution with Fe or U promotes the formation of oxygen vacancies (for different reasons, as discussed) and stabilizes reduced states, thereby increasing the extent of reduction and improving hydrogen production. Experimental and theoretical studies on $\text{Ce}_{1-y}\text{Fe}_y\text{O}_{2-\delta}$ and $\text{Ce}_{1-y}\text{U}_y\text{O}_{2\pm\delta}$ are reviewed, including insights from temperature-programmed reduction, core- and valence-level X-ray photoelectron spectroscopy, and DFT+U calculations. Test reactions show, in line with spectroscopic results, that small fractions of Fe^{3+} or U^{4+} gave highest Ce^{3+} and TCWS reaction yields, while increasing the dopant fraction decreases the reaction yield. The correlations between reduction behavior, oxygen vacancy formation, charge-transfer phenomena, and hydrogen yields are discussed, with emphasis on the need for fundamental understanding of reduction energetics as a key factor for advancing solar thermochemical hydrogen generation.

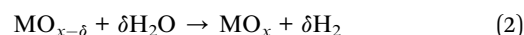
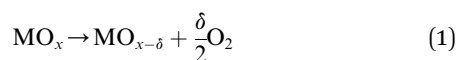
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1. Introduction

The Thermo-Chemical Water Splitting (TCWS) reaction is a solar driven H_2 production from water using a redox type process of suitable materials. This short review's focus is on reducible oxides as the material of choice. The reaction has received considerable attention these last few decades¹⁻³ and the process is a two-step reaction. The first one is endothermic, in which an oxide material in binary or mixed phases is reduced at a high temperature in an inert environment releasing a fraction of its oxygen atoms as O_2 . Temperatures as high as 1500 °C are typically needed to ensure a reduction suitable for studies and with a potential for application (eqn (1)). The second step is exothermic, where the reduced oxide(s) is exposed to H_2O vapor, typically conducted a few hundred degrees lower in temperature. In this second step the reduced oxide is oxidized back and H_2 is released (eqn (2)). Therefore, H_2 and O_2 are produced separately. The following two equations present these two steps.



Where M is a metal cation, x is for the compound stoichiometry (2 in the case of CeO_2 for example) and δ is the extent of reduction, $\delta < x$ (typically a small fraction of x).

This reaction performs similarly for CO_2 to CO reduction. When the energy input is provided from the sun, it uses a large fraction of the solar spectrum making it among of the most efficient^{4,5} known systems for H_2 generation from water with theoretical efficiencies >40%. It is still in the research phase largely because of the cost associated to the solar concentrators needed for the reduction.

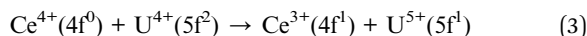
The dynamics of the reduction and oxidation of metal oxides affect their properties and these in turn, dictates their performance in many applications, and that includes other processes beside the TCWS or CO_2 reduction such as in redox-driven reactions in catalysis⁶ and gas sensors.⁷ Cerium oxide ($\text{CeO}_2/\text{CeO}_{2-x}$, $x < 0.5$) stands out as one of the most active and stable reducible metal oxides⁸ and is therefore prone to many fundamental studies largely because of its relatively simple structure (fluorite), simple surface termination dominated by the (111) face, and localized charges upon the creation of oxygen defects; when compared to many other solar materials.



It is worth making a distinction between the TCWS cycle and a hydrocarbon-based catalytic cycle as it is in practice at present. In catalysis, the reduction of an oxide, is conducted by using a chemical compound (providing the chemical energy), such as H₂ (ref. 9) or CO.¹⁰ H₂ and CO are largely generated by steam methane reforming and therefore contribute to CO₂ emission, that is why solar thermal-driven alternatives are desired when looking beyond a hydrocarbon-based energy system. The main challenge for this alternative process is the large input of energy needed for the reduction step. To this end, considerable amount of work addressing the reduction of CeO₂ in order to understand its steps at the fundamental and applied levels is pursued. Many computational studies have indicated that the energy needed to create an oxygen vacancy in the bulk of CeO₂ is about 3 eV,^{11–13} while the energy required for atomic oxygen diffusion¹⁴ is less ≈ 1 eV. Despite the relatively fast reaction kinetics for the redox cycle, which is highly desired for the two steps described by eqn (1) and (2), the high energy cost makes the process unsustainable. At present, estimates of the levelized cost of H₂ [LCOH: the cost of making H₂ before making profit after a number of years, typically 20 years] produced by the TCWS method is close to 10 USD per kg, which is about five times higher than the present cost from fossil fuels.¹⁵ Because the TCWS reaction solely relies on the O-defect density, which is, per mass, low in CeO₂, many approaches have been pursued to mix CeO₂ with other metal cations to decrease the reduction energy and consequently increase the density of the reduced state.¹⁶

Among the few methods used the following two are of focus of this review.

(A) Charge transfer: a fraction of Ce⁴⁺ cations is substituted with metal cations that can donate electrons and themselves be oxidized. For example, the substitution of Ce⁴⁺ with U⁴⁺ was found to enhance the reduction of CeO₂, particularly at low levels, ref. 12 and 13. Upon the removal of an oxygen atom (two electrons are left in the lattice), in a pure CeO₂ two Ce⁴⁺ cations are reduced by these two electrons to Ce³⁺ cations. However, in the presence of U⁴⁺ three Ce³⁺ cations are formed (instead of two), and one U⁴⁺ cation is oxidized to a U⁵⁺ cation, as per the following equation.



For a charge-transfer mechanism to occur between two cations in a mixed oxide, several conditions should ideally be satisfied:

- (i) The substituting cation should have an ionic radius close to that of the host cation,
- (ii) It should possess the same (initial) oxidation state, and
- (iii) The corresponding oxide should have a similar crystal structure to the host material, which increases the likelihood of forming homogeneous solid solutions.¹⁷

Yet, the optimal fractional substitution for the reduction of Ce cations is not straight forward to know because statistical entropy (distribution of U⁴⁺ cations around Ce⁴⁺ cations) affect the electron transfer process, and in addition phase segregation may still occur depending on the environment (oxidizing vs.

reducing). The redox properties of such a system have been experimentally studied in the past.^{18–21} Experimental evidence of charge transfer was found, and the optimal charge transfer between Ce and U cations occurred at low % of U. In these studies, the mixed oxide Ce_{1–y}U_yO_{2±δ} was reduced by H₂ at 973 K to prevent phase segregation or by Ar⁺ sputtering for the core level spectroscopy measurements to monitor the charge transfer. For hydrogen production from water, experimental results showed, in line with spectroscopy, that low levels of U substitutions were better than higher levels, with an experimental optimal of about 10%. Moreover, spectroscopic studies of the Ce and U oxidation states of an epitaxy of the mixed oxide with (111) surface termination have largely confirmed the polycrystalline results.²²

(B) Charge compensation (alio-valency): this is generally viewed as due to lattice distortion because of the difference in the cations' size and charge. The substitution of Ce⁴⁺ with these metal cations, of a lower oxidation state, creates vacancies. These vacancies are not associated to excess electrons and therefore there is no increase/decrease in electron charge. A large number of elements were studied for this, and most showed that indeed Ce⁴⁺ reduction to Ce³⁺ was enhanced. The addition of cobalt (Co) enhanced CeO₂ reduction during the photoreduction²³ of CO₂ to CH₄ and COS hydrolysis²⁴ reactions. Praseodymium (Pr), where Pr³⁺ increases the creation of oxygen vacancies and Pr⁴⁺ increases the oxygen storage capacity.²⁵ Manganese (Mn), enhanced oxygen mobility *via* vacancy formation.²⁶ Computationally, a large body of work has also been conducted to study the creation of oxygen vacancies upon alio-valent cation substitution, Table 1. Among them: Mn (DFT+U and HSE06),²⁷ Cu (DFT+U),²⁸ Ni (DFT+U and HSE06)²⁹ and (DFT+U),³⁰ and Fe (DFT+U). These results indicated that the oxygen vacancy formation energy is lower when compared to ceria alone.^{31,32}

Among the aliovalent systems, solid solutions of CeO₂ containing Fe³⁺ have been studied in some details. In one of these works it was found that substituting a fraction of Ce⁴⁺ by Fe³⁺ cations in CeO₂ led to a decrease of the activation energy for the selective catalytic reduction reaction of NO by half.³⁹ This was attributed to the formation of a distorted Fe–O–Ce structure. DFT calculation and titration *via* pyridine-adsorption indicated that this Fe–O–Ce structure has increased the number of Lewis

Table 1 Representative DFT computed values for oxygen vacancy formation energy of Ce_{1–y}M_yO₂ (*E*) and vacancy migration barrier. M is the element added to CeO₂, and *y* is the element fraction [near and far are with respect to the metal cation used]

Element	<i>E</i> (eV)	Migration barrier (eV)	References
Fe ³⁺	1–1.5	—	33
Zr ⁴⁺	≈ 2 (Ce _{0.875} Zr _{0.125} O ₂)	<1	34 and 35
La ³⁺	1.3 (near) 1.6 (far)	0.7	36 and 37
Nb ⁵⁺	2.3 (near) 2.9 (far)	0.6–0.8	35 and 38
U ⁴⁺	2.7	—	12 and 13



Table 2 Examples of reported performance of CeO₂ and mixed oxide-CeO₂ based systems for the thermochemical water splitting reaction^a

Material	Conditions (<i>T</i> , atm)	δ or O ₂ released	H ₂ yield per cycle	References
CeO ₂ (bulk)	1773 K	$\delta < 0.02$	~10 mL H ₂ per g	45–48
Ce _{0.9} Zr _{0.1} O ₂	1673 K	$\delta \sim 30\%$ vs. CeO ₂	~10 mL H ₂ per g	49
Ce _{0.9} Fe _{0.1} O _{2-δ}	1673–1823 K	Up to 50 μmol O ₂ per g	~20–25 mL H ₂ per g	50
Ce _{0.9} U _{0.1} O _{2$\pm\delta$}	973–1200 K ^a	Ce ³⁺ fraction ^a >50%	~18–22 mL H ₂ per g	20
Ce _{0.8} Pr _{0.2} O _{2-δ}	1773 K	~15 mL O ₂ per g ⁻¹	~4 mL H ₂ per g	51 and 52
Ce _{0.8} Mn _{0.2} O _{2-δ}	1773 K	Fast vacancy migration	~4 mL H ₂ per g	53 and 54

^a Reduced by Ar ions sputtering.

acid sites as well as the charge density around Ce cations when compared to those of pure CeO₂. The authors also found that low Fe fraction ($x < 0.3$) kept the fluorite structure (solid solution) *via* a vacancy compensation mechanism, leading to an increase in oxygen vacancies which was linked to increase of the catalytic performance. Other work has shown the presence of a considerable fraction of Ce³⁺ cations by analyzing the XPS Ce 3d lines (at *ca.* 885 eV and 904 eV (V' and U' lines)) upon the introduction of Fe³⁺ cations into the lattice of Ce_{0.8}Fe_{0.2}O_{2- δ} ^{40,41} (δ : deviation from stoichiometry). Also, other have shown that Fe substitution of less than 30% increased the number of oxygen vacancies⁴² and improved CO conversion to CO₂ the

latter is attributed to the formation of more mobile oxygen atoms in the redox cycle.⁴³ In another study, Fe 5 at% was tested at 1823 K and found to be more active (a higher production rate per unit weight) and faster (a higher rate of release of hydrogen) than CeO₂ alone for the same reaction. Phase segregation, however, occurred due to the very high thermal reduction, 1823 K, temperature.⁴⁴

The performance of pristine and cation substituted CeO₂ in TCWS has been systematically studied, revealing that these metal cation can lower reduction temperatures, increase δ , and improve H₂ yield per cycle. However, trade-offs with stability and phase segregation remain critical (Table 2).

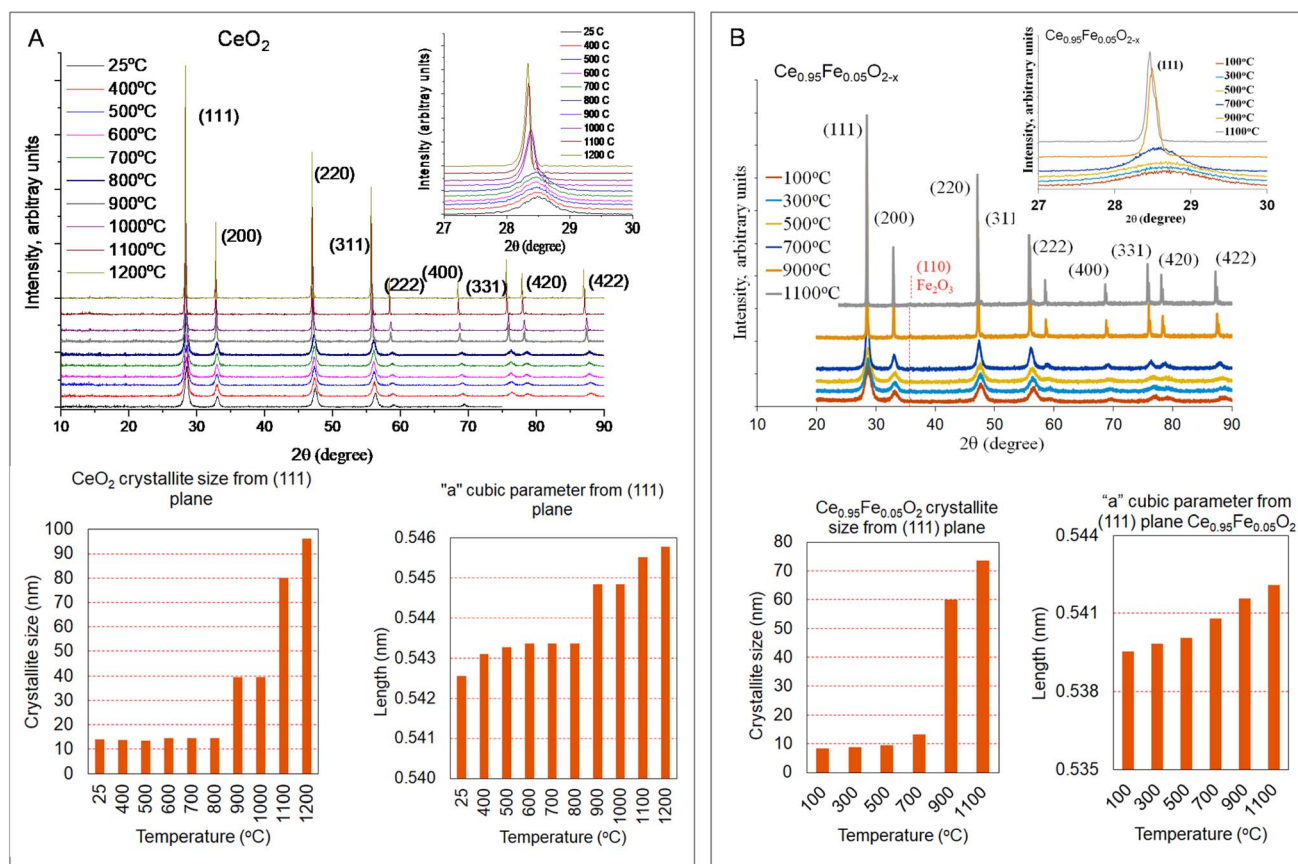


Fig. 1 (A) XRD patterns of CeO₂ together with the extracted crystallite size and cubic parameter from the (111) lines; inset: a zoom on the (111) diffraction line to highlight the shift in angle and narrowing of the Full Width Half Maximum (FWHM) with increasing temperature in ambient environment. (B) Contains similar results for Ce_{0.95}Fe_{0.05}O_{2-x}. From ref. 50, permission License number 6133081449846.



The review focuses on two systems for which complementary information has been obtained using a combination of techniques, including spectroscopy, diffraction, microscopy, and thermochemical performance measurements. This two systems are composed of Fe and U cations used (separately) as substituents to enhance the reduction of CeO₂. A particular attention is given on phase segregation studied by XRD, charge transfer studied by core- and valence-level spectroscopy, and reduction temperature by TPR, all on polycrystalline samples. Also, core level spectroscopy results of single crystals of the mixed Ce_{1-y}-U_yO₂ grown by epitaxy complemented by DFT+*U* computations are presented.

2. X-ray diffraction (Ce_{1-y}Fe_yO₂ and Ce_{1-y}U_yO₂)

Fig. 1 presents XRD patterns of CeO₂, and Ce_{0.95}Fe_{0.05}O₂ that were heated at the indicated temperatures.

The diffraction pattern of CeO₂ shows a nano size dimension ($L \approx$ about 14 nm) for the “as prepared” oxide, with a lattice parameter (a) = 0.543 nm (Fig. 1A). Crystalline CeO₂ gives rise to strong lines at $2\theta = 28.5^\circ, 33.0^\circ, 47.5^\circ, 56.4^\circ$ for the (111), (200), (220) and (311) respectively, whose positions and Full Width Half Maximum (FWHM) being sensitive to its crystallite dimension and degree of crystallinity. No change in these parameters is seen up to *ca.* 900 °C (1173 K). At this temperature L considerably increased to 39 nm (due to sintering) together with an increase of a (0.545 nm) (due to bulk reduction). At 1100 °C, L doubled to 80.2 nm and a further increase of a (0.546 nm) is seen. Hematite Fe₂O₃ gives lines at $2\theta = 33.3^\circ, 35.7^\circ$ and 62.3° for the (104), (110) and (214) lines, respectively. Because Fe³⁺ (0.6 Å) ions are much smaller than Ce⁴⁺ ions (*ca.* 1 Å in octahedral coordination) their incorporation into the lattice can be monitored mostly by a positive shift of 2θ which is associated with a broadening of the lines due to the formation of smaller crystallites.⁵⁵ Therefore, both the shift and the absence of Fe₂O₃ lines are often taken as a strong indication of the presence of a solid solution. Depending on the preparation method this is found to be up to about 0.3–0.4 atomic ratio Fe³⁺/Ce⁴⁺ cations.⁵⁶ The addition of Fe to CeO₂ appears to be substitutional since no other diffraction lines attributed to Fe₂O₃ were seen up to 900 °C or so. Segregation occurred at 1100 °C where diffraction lines corresponding to Fe₂O₃ (110) and (003) are observed. Table 3 compares the parameters of three oxides at 500 °C and 1100 °C.

Fig. 2 presents XRD of as prepared Ce_{0.5}U_{0.5}O₂ and after it has been heated, *in situ* under N₂ atmosphere, at the indicated

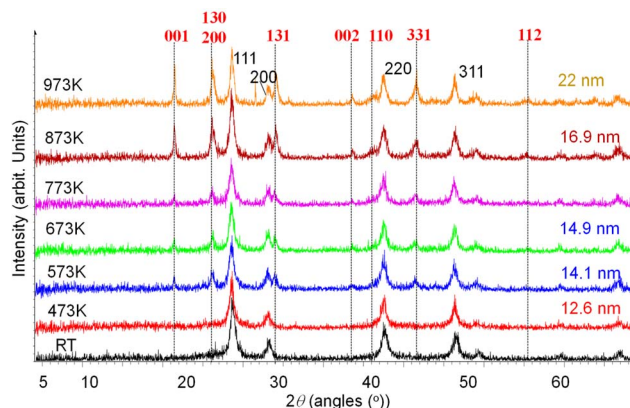


Fig. 2 *In situ* XRD of Ce_{0.5}U_{0.5}O₂ that was heated at the indicated temperatures. The numbers at the right hand side of the figure are those of crystallites size based on the (111) diffraction line of the fluorite structure at $2\theta = 28.54^\circ$ ($d = 3.12$ Å). The numbers (in red) on top of the dashed vertical lines in the figure are the diffraction pattern of α -U₃O₈. From ref. 20, permission license number 6133100874303.

temperatures. XRD patterns related to the fluorite structure are identified with prominent (111), (200), (220) and (311) peaks at $2\theta = 28.54^\circ, 33.11^\circ, 47.58^\circ, \text{ and } 56.39^\circ$, respectively. The crystallite dimension calculated from the (111) diffraction line is found close to 12 nm for the fresh oxide. Upon heating to 300 °C (573 K) other diffraction patterns at $2\theta = 21.38^\circ, 26.16^\circ, 33.95^\circ, 43.58^\circ, \text{ and } 51.68^\circ$ are seen. The patterns are attributed to other uranium oxide phases: orthorhombic α -U₃O₈ or hexagonal α -U₂O₅, or orthorhombic U₂O₅.^{57,58} Previous work has indicated that in the process of oxidation of UO₂ to UO₃, U₃O₈ is formed⁵⁹ as the most stable phase; however, metastable U₂O₅ is also formed that eventually transform to α -U₃O₈. The small crystallite structures and the broadening of the lines did not allow for further analysis. It is clear however, that some U cations in the solid solution segregate forming a more stable higher oxide that is attributed to either α -U₃O₈ (or U₂O₅). Because the process occurs under N₂ environment, it is expected that CeO₂ left in the fluorite structure is reduced to CeO_{2- δ} ; this point will be reviewed in more details below.

3. Transmission electron microscopy (TEM); Ce_{1-y}Fe_yO₂ and Ce_{1-y}U_yO₂

Fig. 3 presents the TEM, Selected Area Electron Diffraction pattern (SAED) and Energy Dispersive X-ray patterns (EDX) of

Table 3 Crystallite size and cubic lattice dimension for CeO₂ and Ce_{1-y}Fe_yO₂ at 773 K and 1373 K. Data extracted from Fig. 1. From ref. 50, permission license number 6133081449846

Oxide	2θ CeO ₂ (111) at 773 K	Crystallite size at 773 K (nm)	Cubic lattice parameter at 773 K (nm)	Crystallite size at 1373 K (nm)	Cubic lattice parameter at 1373 K (nm)
CeO ₂	28.46°	14	0.543	80.2	0.545
Ce _{0.95} Fe _{0.05} O ₂	28.68°	9.5	0.540	73.6	0.542
Ce _{0.75} Fe _{0.25} O ₂	28.84°	6.5	0.540	61.3	0.544



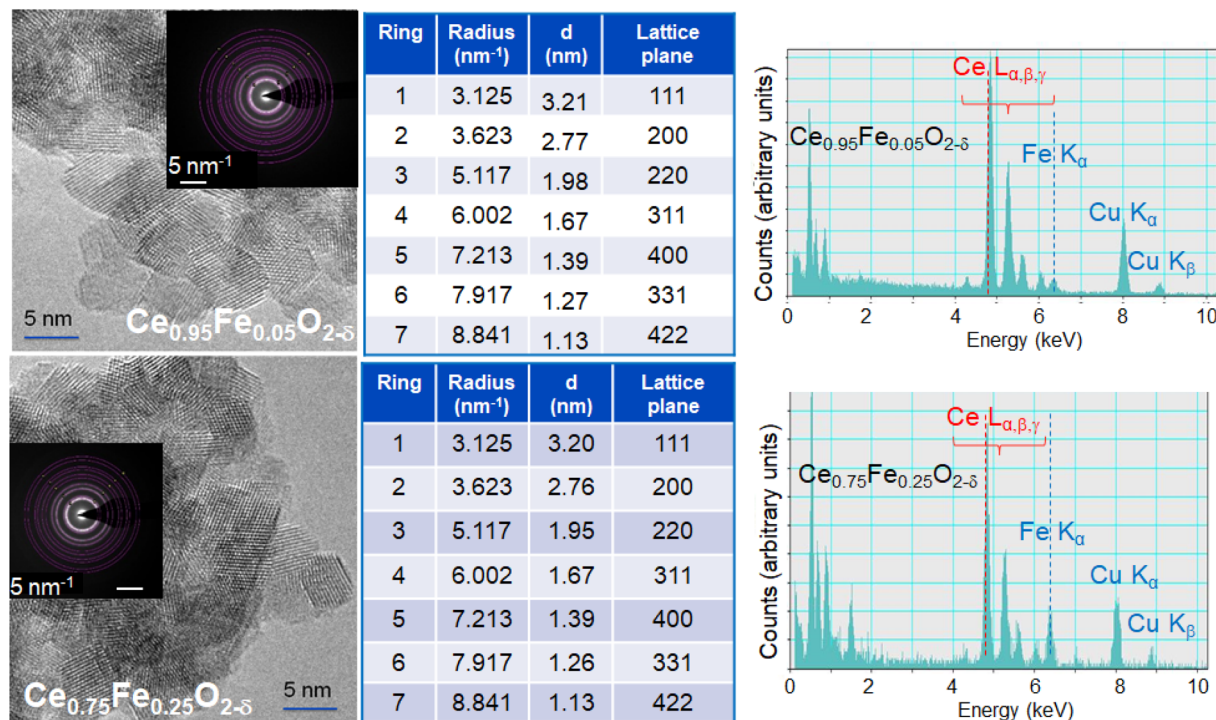


Fig. 3 Transmission Electron Microscopy (TEM), Selected Area Electron diffraction pattern (SAED) and Energy Dispersive X-ray patterns (EDX) of $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ and $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ that were calcined at 773 K. The values in the tables in the middle are extracted from the SAED in the inset of the TEM images and ring numbers starts with the center of the concentric circles (the bright spot of each inset). From ref. 50, permission license number 6133081449846.

$\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$, and $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ that were calcined at 773 K. Like the data of XRD, both presented the fluorite structure of CeO_2 ; no Fe_2O_3 phase is seen. The d spacing shows a slight decrease in the case of $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ when compared to $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$. Therefore, both microscopic and macroscopic diffraction methods indicate that the crystallite size of CeO_2 decreases with Fe substitution. From TEM the average crystallite size of $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ is 8–10 nm while that of $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ is 5–7 nm. The decrease of the crystallite size might be due to a decrease of the surface energy (more stable) when compared to that of CeO_2 . EDX shows the presence of Fe in both mixed oxides with an intensity qualitatively tracking the expected concentration.

A series of polycrystalline $\text{Ce}_{1-x}\text{U}_x\text{O}_{2\pm\delta}$ was synthesized and studied for their thermochemical water splitting to hydrogen. XRD, as shown above for the as-prepared mixed oxides, present a fluorite structure, in line with numerous other studies in which Ce and U cations have high miscibility^{60–62} for the as prepared oxide. Fig. 4A (HR-TEM) indicates that particles are crystalline with a size of about 10 nm. Like in the case of Fe, data indicate a high miscibility of U cations in CeO_2 . For example, while Fig. 4B (STEM) shows no distinction between the atoms while the EELS spectra of the same area, Fig. 4C, shows the presence of both U and Ce; the Ce 3d \rightarrow 4f and U 4d \rightarrow 5f transitions. The lattice fringes obtained from the diffraction pattern (Fig. 4D) related to Fig. 4B are nearly identical to those of CeO_2 .

4. Temperature programmed reduction (TPR) ($\text{Ce}_{1-y}\text{Fe}_y\text{O}_2$ and $\text{Ce}_{1-y}\text{U}_y\text{O}_2$)

Fig. 5 shows TPR results for a series of $\text{Ce}_{1-y}\text{U}_y\text{O}_2$ oxides. The addition of U cations to CeO_2 resulted in lower reduction temperature and higher hydrogen consumption overall. Because the size of U^{4+} is very close to that Ce^{4+} the increase in reduction is not due to lattice compensation but most likely due to the presence of U cations in higher oxidation state than +4 in addition to possible charge transfer. Table 4 shows a summary of the H_2 consumption of the series, together with BET surface areas and the calculated fraction of oxygen removed. The addition of U cations further increases the reduction of CeO_2 (from 9% for CeO_2 alone to 26% of oxygen atoms removed in the case of $\text{Ce}_{0.25}\text{U}_{0.75}\text{O}_2$). There is also a decrease of the “overall” reduction temperatures when compared to CeO_2 or UO_2 alone. The case of the 0.5 fraction of each cation is intriguing as it presents one single large reduction peak; this however was not further investigated.

Next, TPR of $\text{Ce}_{1-y}\text{Fe}_y\text{O}_2$ together with that of Fe_2O_3 is presented, Fig. 6. The four profiles are plotted as monitored without multiplication and with offset for clarity. The weight of the oxide used is given on the left side of each profile and the total amount of consumed hydrogen is given on the right side. The stoichiometry of the oxides, based on their formulae units, is given next to each line. The table in the inset presents the



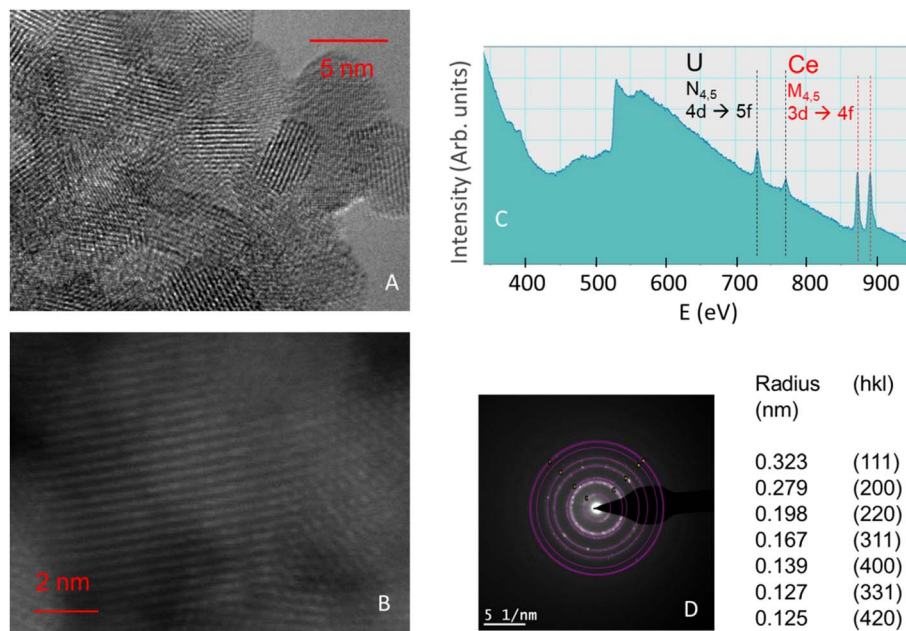


Fig. 4 (A) High-resolution transmission electron microscopy (HRTEM) of $\text{Ce}_{0.75}\text{U}_{0.25}\text{O}_2$ polycrystalline mixed oxide. (B) Scanning transmission electron microscopy (STEM) of a selected area from (A). (C) Electron energy loss spectroscopy (EELS) spectrum of the area shown in (B). (D) Selected area electron diffraction (SAED) of (B). From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License).

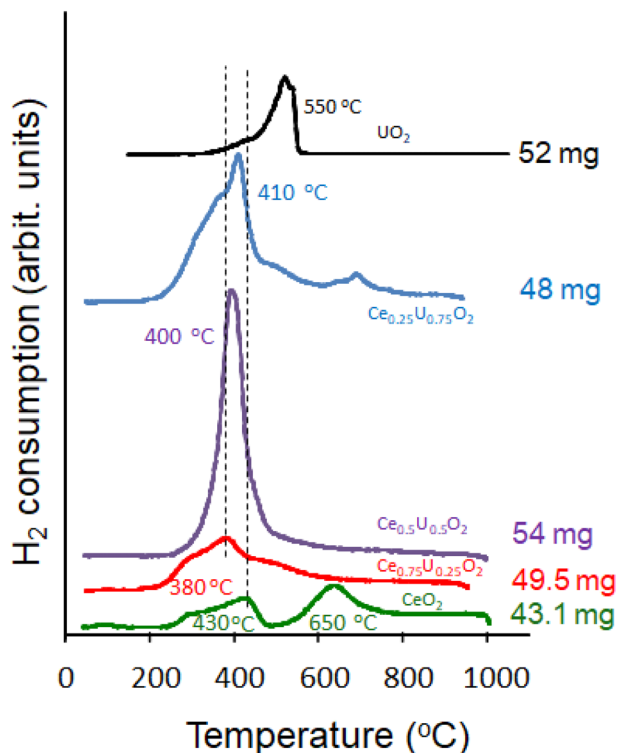


Fig. 5 TPR of a series of $\text{Ce}_{1-y}\text{U}_y\text{O}_2$: CeO_2 , $\text{Ce}_{0.75}\text{U}_{0.25}\text{O}_2$, $\text{Ce}_{0.5}\text{U}_{0.5}\text{O}_2$, $\text{Ce}_{0.25}\text{U}_{0.75}\text{O}_2$ and UO_2 ; ramping rate ($10\text{ }^\circ\text{C min}^{-1}$). The weight used in each run is indicated on the right-hand side of the curves. Adapted from ref. 63, permission license number 6133100874303.

stoichiometry based on hydrogen consumption (loss of oxygen). Fe_2O_3 is expected to be completely reduced to metallic iron. The needed amount of hydrogen to reduce it (*ca.* 420 mL g^{-1}) is about 80% of that observed ($\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$); it may indicate experimental errors of 20% or so but can also, partly be due to excess oxygen (of surface hydroxyls from adsorbed water).

The results of the mixed oxides can be qualitatively explained based on those obtained from the pure ones. The two peaks of CeO_2 labeled I and II may represent surface and bulk reductions. These are qualitatively similar to those reported in Fig. 5, although it is from a different sample batch. Based on XRD (and TEM) results the addition of Fe cations to CeO_2 is substitutional and resulted in decreasing the crystallite size. The decrease in crystallite size would in turn results in increasing the surface to bulk ratio which explains the increase in peak I compared to peak II ratio in the CeFe oxides. Peak III is that of pure Fe_2O_3 ; because it is also present in the case of $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ some Fe cations may have segregated out of the fluorite structure. The increase in peak II of $\text{Ce}_{1-y}\text{U}_y\text{O}_2$ oxides compared to CeO_2 alone might be due to the ease of bulk reduction due to the presence of Fe cations inside the fluorite structure.

The increased reduction of CeO_2 using Fe was studied by Temperature Programmed Reduction (TPR) in other works. Pure CeO_2 was seen to be reduced in two temperature domains at about 773 K and 1073 K.⁶³ The first has been attributed to surface reduction while the second to bulk reduction. The reduction is mild (leads to the removal of a small fraction of oxygen anions typically 10–20%) and the formation of Ce^{3+} cations within the investigated temperatures in TPR (typically up to 1273 K). Only few Thermo-Gravimetric Analysis (TGA)



Table 4 Amount of H₂ consumed and the corresponding computed % of lattice oxygen removed from TPR results (assuming that the as-prepared material has the given stoichiometry)

Oxide	Amount of H ₂ consumed mL g _{oxide} ⁻¹	% of removed O atoms	BET surface area m ² g _{oxide} ⁻¹
CeO ₂	24.3	9	71
Ce _{0.75} U _{0.25} O ₂	21.8	10	33
Ce _{0.5} U _{0.5} O ₂	32.8	16	34
Ce _{0.25} U _{0.75} O ₂	38.9	21	30
UO _{2+x}	27.9	Excess	17

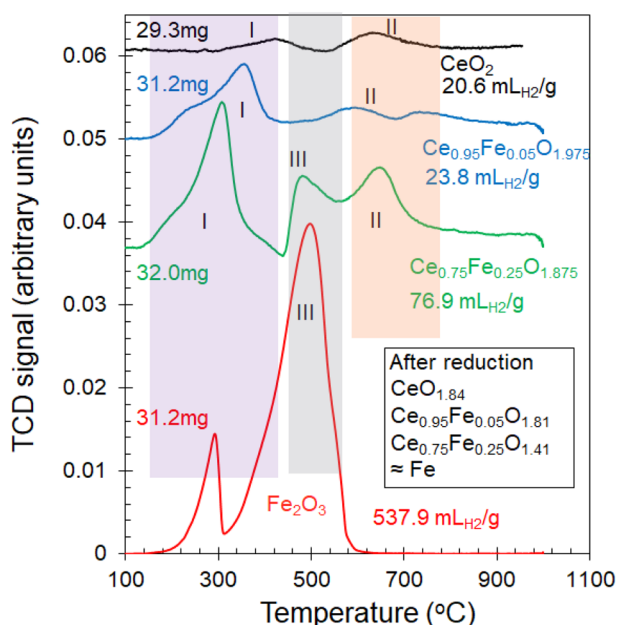


Fig. 6 TPR of CeO₂, Ce_{0.95}Fe_{0.05}O_{2-δ}, Ce_{0.75}Fe_{0.25}O_{2-δ}, and Fe₂O₃. All oxides were pre-calcined at 500 °C. The computed values of 2 - δ are given beside each line in the formulae units. The inset rectangle has the computed formulae units based on the oxygen loss during TPR. The amount of hydrogen used to fully reduce Fe₂O₃ to Fe may give an indication on the errors, about 20%. The highlighted regions I and II are those of surface and bulk reduction of CeO₂ while region III is that of bulk reduction of Fe₂O₃. The first peak in the TPR of Fe₂O₃ might be due to surface reduction. From ref. 50, permission license number 6133081449846.

experiments of doped CeO₂ with Fe cations are available. In a one particular study devoted to the effect of doping CeO₂ with metal cations, it was found that the incorporation of Fe³⁺ increased the mass loss of CeO₂ (due to reduction). In this case for Ce_{0.9}Fe_{0.1}O_{2-δ}, 50.0 μmol of O₂ per g_{material} were removed at each cycle during ten thermochemical cycles in which the thermal reduction step was performed at 1673 K. These were active sites since nearly stoichiometric CO production (by CO₂ reduction) 96.3 μmol g_{material}⁻¹·cycle at 1273 K was seen.⁶⁴

5. Valence band (Ce_{1-y}Fe_yO₂)

Fig. 7A and B presents the valence band and shallow core levels (Ce 5p, O 2s, and Ce 5s) of Ce_{0.75}Fe_{0.25}O_{2-δ} and Ce_{0.95}Fe_{0.05}O_{2-δ} before and after argon ion sputtering for reduction. This

reduction method has advantages and disadvantages when compared to reduction in the presence of H₂ or thermally in inert environment. Thermal reduction of these oxides requires heating to at least 1773 K. The mixed oxide at this temperature largely segregates, and therefore, the analysis may not be conducted. Reduction using H₂ in UHV is not possible because of its very low sticking coefficient on oxides. Argon ion sputtering to reduce oxides relies on the mass difference between M and O and the stability of the reduced phase. Ce³⁺, Fe²⁺, and Fe⁰ are stable in UHV conditions for a few hours because of the low H₂O and O₂ partial pressures. One of the disadvantages of Ar ion sputtering is the loss of surface structure (the formation of an amorphous layer due to the high energy used, 1 kV).

The spectra of the as-prepared oxides (0 min) are dominated by the O 2p, O 2s, Ce 5p and Ce 5s lines, marginal changes are seen between both oxides. There are some, surface hydroxyls (-OH, 3σ) at a binding energy of ca. 10 eV. There is also a minor contribution from reduced Ce cations (Ce 4f, Ce³⁺) and reduced Fe cations (Fe 3d, oxidation state <+3), both have lower binding energies (at 0.5–2 eV with respect to Fe) than that of the O 2p binding energy band.

Upon argon ions sputtering, one notices the following:

- An increase of the signal below the O 2p line due to reductions (due to increased concentrations of Ce³⁺ and Fe^{x+}, x < +3).
- An increase in surface hydroxyls.
- A relative increase in Ce 5p signal with respect to the O 2s signal.

For (i) the increase is expected and is treated in more detail to extract quantitative information below. For (ii) the increase, that has been seen before, is due to the increase in the sticking coefficient of the traces of dissociatively adsorbed water over a reduced metal oxide when compared to its stoichiometric form. Ions bombardment causes a reduction due to oxygen removal (as atoms), and the remaining two electrons, per oxygen atom removed (V_O), are transferred to Ce⁴⁺ (and/or Fe³⁺) to reduce them. The creation of V_Os leads to the preferential dissociative adsorption of H₂O. This results in the formation of two pairs of surface hydroxyls for each oxygen vacancy healed.

For (iii), this observation is treated qualitatively below.

Fig. 8A and B presents the valence band region, in which the signal below the XPS O 2p line was fitted by two peaks: at about 0.4 eV and at ca. 1.5 eV, binding energy. There are no noticeable changes in the large O 2p lines' shapes upon reduction. For both oxides, the signal attributed to the Ce 4f¹ orbital is larger



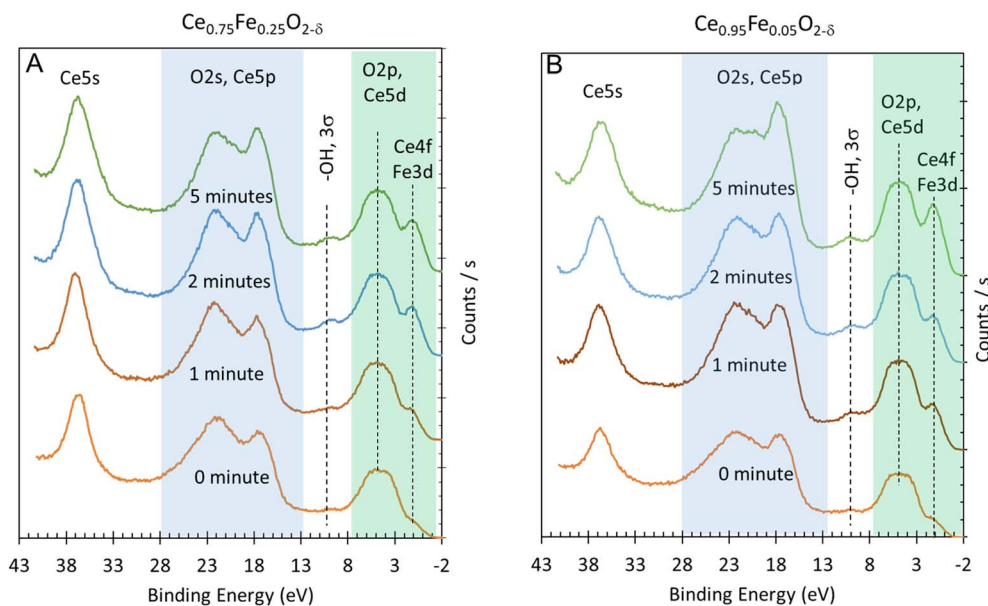


Fig. 7 (A) Valence band XPS (green shaded) and Ce 5p, O 2s (blue-shaded) and Ce 5s spectra of $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ before (0 minute) and after argon ion sputtering (x minutes). (B) Valence band XPS (green shaded) and Ce 5p, O 2s (blue-shaded) and Ce 5s spectra of $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ before (0 min) and after argon ion sputtering (x minutes). From ref. 16 (no permission is needed: Creative Commons Attribution 4.0 License).

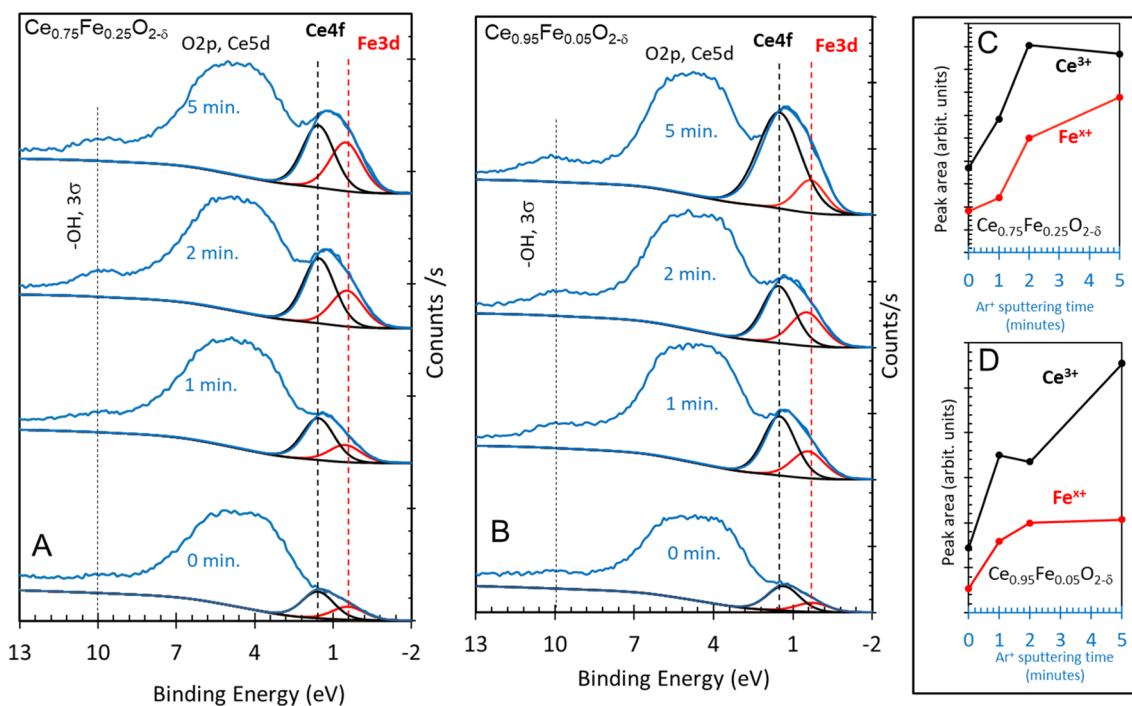


Fig. 8 (A) Valence band XPS of as-prepared $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ after 1, 2 and 5 minutes of Ar ion sputtering. (B) Valence band XPS of as-prepared $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ after 1, 2 and 5 minutes of Ar ion sputtering. (C and D) Computed peak areas of fitted Ce 4f (FWHM = 1.5 eV) and Fe 3d (FWHM = 1.5 eV) signals. From ref. 16 (no permission is needed: Creative Commons Attribution 4.0 License).

than that of the Fe 3d orbitals and is more pronounced for $\text{Ce}_{0.25}\text{Fe}_{0.05}\text{O}_{2-\delta}$ when compared to $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$. This is consistent with core levels measurements and with the TCWS results (see below). For $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$, increasing the reduction time affects mostly the Ce cations, while for

$\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$, it favors Fe reduction. This might be due to the probability of hitting the atoms during bombardment. At a high Fe%, the probability of oxygen removal adjacent to Fe atoms is high, and therefore more Fe is reduced, while at a low Fe%, the



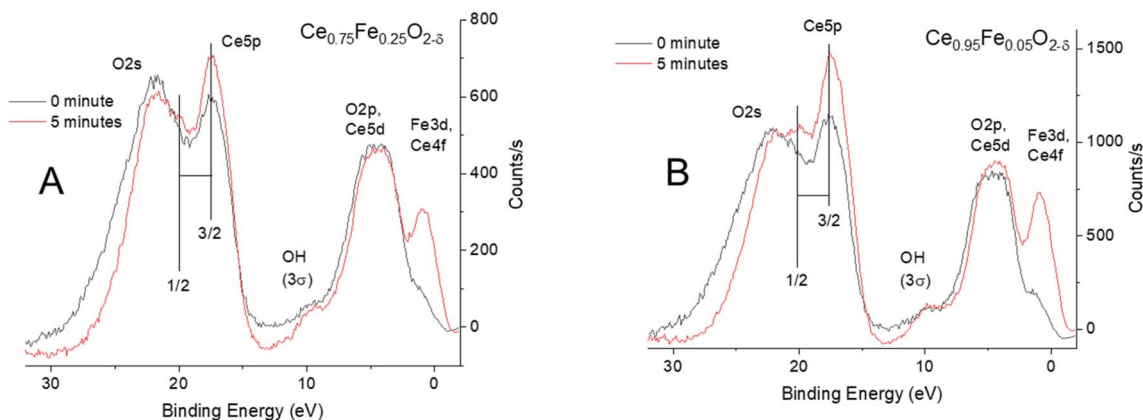


Fig. 9 (A) Normalized valence band XPS and the Ce 5p and O 2s spectra of $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ before (0 minute) and after 5 minutes of argon ion sputtering. (B) Normalized valence band XPS and the Ce 5p and O 2s spectra of $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ before (0 minute) and after 5 minutes of argon ion sputtering. Note the change in intensity of the Ce 5p signal when compared to the O 2s signal.

oxide is more homogeneous and the chemical effect on the reduction is expected to be higher.

Fig. 9A and B presents the valence band and the Ce 5p and O 2s lines. The spectra are baseline-subtracted, then normalized to highlight the differences. Ions sputtering results in a preferential increase in the Ce 5p signal when compared to the O 2s lines. In addition, the O 2s line becomes narrower. There is no noticeable shift in the binding energy before or after ion bombardment. Similar experiments were conducted on CeO_2 , and no change was seen. Some qualitative information may be drawn upon comparisons with previous work conducted by others. In one study also using ions bombardment⁶⁵ of CeO_2 , (Fig. 3a and b of ref. 65), the relative ratio has increased in favor of the Ce 5p orbital, like in this work. The exact position of the O 2s orbital with respect to the Ce $5p_{1/2}$ orbital is not clear. Here, it is put after the Ce $5p_{1/2}$ lines similar to other work, although others have put it in between the Ce $5p_{3/2}$ and Ce $5p_{1/2}$ energy positions based on the relativistic computation of CeO_8 and $\text{Ce}_{63}\text{O}_{216}$ clusters.⁶⁶ The O 2s and Ce 5p lines give information on charge transfer; because of their quasi-degenerate energy positions they are sensitive to the oxidation state of Ce cations. The spectra in Fig. 9 are similar to those reported for a thin film of CeO_2 grown on Rh(111) excited with photon energy equal to 125 eV (Ce 4d–Ce 4f resonance).⁶⁷ The spectra are also similar to those of irradiated (with Xe ions) CeO_2 thin film and bulk [ref. 65]. The authors pointed out to the final state effect ($3d^9 4f^1 \text{OVMO}^{-1}$ (outer valence molecular orbital, OVMO) and $3d^9 5p^5 np^1$ (inner valence molecular orbital, INVO)). The Ce 5p atomic orbitals participate in the formation of both OVMO and IVMO, where a large part of the latter is taken by the filled Ce $5p_{1/2}$, $5p_{3/2}$ and O 2s atomic shells.⁶⁸

The increase in the Ce 5p/O 2s intensity ratio after sputtering reflects the creation of oxygen vacancies and the associated reduction of Ce^{4+} to Ce^{3+} . Removal of oxygen decreases the O 2s contribution to the inner valence molecular orbitals while electrons left by the vacancy populate Ce 4f states. The resulting modification of the Ce–O valence manifold enhances the Ce-derived component of the IVMO. From ref. 16 (no permission is needed: Creative Commons Attribution 4.0 License).

6. X-ray photoelectron spectroscopy (XPS) ($\text{Ce}_{1-y}\text{Fe}_y\text{O}_2$)

Fig. 10 presents XPS Ce 3d lines of Ce cations in the fresh and reduced samples. The presence of both oxidation states of Ce cations is clear. The lines' positions and attributions are shown ($3d_{5/2}$: u , u' and u'' , and $3d_{3/2}$: v , v'' and v''' for Ce^{4+} cations, and $3d_{5/2}$: u_0 and u' and $3d_{3/2}$: v_0 and v' for Ce^{3+} cations). In Fig. 10 and the inset table, a comparison between the fresh and the most reduced samples is made. The presence of Fe at a 5% concentration resulted in a more pronounced Ce^{3+} concentration when compared to the presence of Fe at a 25% concentration. This is in line with the valence band results presented in Fig. 7 and 8. CeO_2 alone showed a very mild increase upon reduction; this is also in line with the virtually no change in the Ce 5p/O 2s lines. While Ar ions sputtering relies on momentum transfer of incoming ions (in this case, 1 keV of kinetic energy), which results in breaking the chemical bonds there should be no difference between CeO_2 and Fe-substituted CeO_2 since the incoming ions have much more energy than the chemical bond, assuming complete energy transfer. However, this is a cascade reaction where the energy transfer occurs consecutively, and therefore the last steps of an incoming ion (before it leaves the material or is implanted in it irreversibly) would be more efficient for weaker bonding.

Based on the Ce 4f/O 2p, Ce 5p/O 2s and Ce 3d (for Ce^{4+} and Ce^{3+}) XPS signals, Table 5 is made to provide an estimate of the reduction of Ce cations.

The XPS core levels of iron oxides are among the most studied of oxide materials.⁶⁹ There are three common oxidation states: Fe^{3+} , such as in Fe_2O_3 , Fe^{2+} , such as in FeO , and Fe_3O_4 , in addition to Fe^0 . The spectra are complicated by the presence of satellites,^{70–72} iron hydroxide (FeOOH)^{73,74} and many multiplets.⁷⁵ The binding energy of the XPS Fe 2p signal is about 707 eV for Fe^0 , 710 eV for Fe^{2+} and 711 eV for Fe^{3+} . In $\text{Ce}_{1-y}\text{Fe}_y\text{O}_2$, a further complication arises from the presence of Ce Auger lines in the Fe 2p region. Although charge neutralization was used to acquire the spectra, the as-prepared oxide always had wider peaks when



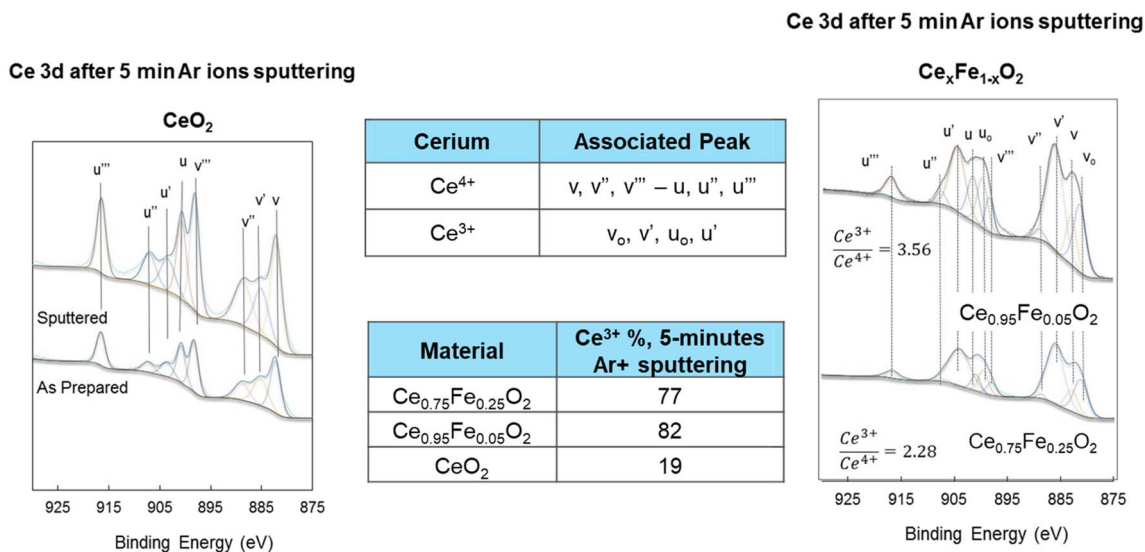


Fig. 10 XPS Ce 3d spectra of CeO₂ (left panel), Ce_{0.75}Fe_{0.25}O_{2-δ} and Ce_{0.95}Fe_{0.05}O_{2-δ} (right panel) after 5 minutes of Ar ion sputtering. Also shown are the computed contributions of the Ce³⁺ cations. From ref. 16 (no permission is needed: Creative Commons Attribution 4.0 License).

Table 5 Quantitative values obtained from XPS Ce 3d, Ce 4f, Ce 5p and Fe 2p lines. The XPS data are those for reduced oxides after 5 minutes of Ar ions sputtering

Oxide	Ce ³⁺ /Ce ⁴⁺ (Ce 3d)	[Ce 4f + Fe 3d ²]/ O 2p	Fe ⁰ /Fe ³⁺ (Fe 2p)	Ce 5p/ O 2s
CeO ₂	0.2	≈ 0	≈ 0	1.1
Ce _{0.75} Fe _{0.25} O _{2-δ}	2.3	0.3	0.5	1.6
Ce _{0.95} Fe _{0.05} O _{2-δ}	3.6	0.4	0.6	1.75

compared to that reduced upon ion sputtering. Therefore, peak areas are to be taken as an estimate and binding energies within a 0.5 eV accuracy. Both oxides show similar spectra and trends upon reduction (Fig. 11). While, the as-prepared oxides contained Fe³⁺ cations, they, however, also contained Fe²⁺ and some Fe⁰. The small % of Fe²⁺ might be formed during the preparation. The presence of metallic iron was not expected and might be due to interstitial atoms formed due to strong lattice distortion. It is also possible that this peak is due to another Auger line of Ce cations. The insets in both figures show the trend during the reduction. In both cases, the amount of Fe²⁺ increases, similar to a previous study,⁷⁶ then decreases to zero, indicating that within the reduction time studied, all reducible Fe³⁺ cations were transformed to Fe⁰. In line with the valence band results, it appears that both Ce⁴⁺ and Fe³⁺ cations are more efficiently reduced when in small amounts (Fe_{0.05}), although the difference is not as pronounced.

7. Epitaxy (Ce_{1-y}U_yO₂)

Growing the mixed metal oxide as an epitaxial film in a controlled environment allows more accurate studies of the charge transfer process. It also offers an alternative prototype material for the reaction because both heat and mass transfer

limitations would be largely removed. Many previous works have shown epitaxial films of CeO₂ on metal single crystals such as Ru(0001)⁷⁷⁻⁷⁹ and Pt(111)^{80,81} surfaces. Here the characterization of a series of Ce_{1-y}U_yO_{2±δ} (111) thin films of about 6 nm thick grown on Ru(0001)/Al₂O₃(0001) templates is presented and discussed.

Fig. 12 shows the Low Energy Electron Diffraction (LEED) pattern of (111)-oriented epitaxial thin films for a series of Ce_{1-y}U_yO_{2±δ}. Samples with low U content present a faint ring associated with a fraction of randomly oriented islands. Increasing the U fraction translates into a blurring of the spots due to a higher disorder and a larger density of structural defects. The absence of Ru(0001) spots indicates a complete coverage of the whole substrate.

In situ XPS measurements of Ce 3d and U 4f regions are presented in Fig. 13A and B for CeO₂ and UO₂ references, respectively. The Ce 3d lines are dominated by the Ce⁴⁺ cations ($v = 882.6$ eV, $v''' = 898.7$ eV, and $u''' = 916.9$ eV) for the UHV annealed film. The small contribution from Ce³⁺ cations (v' ca. 886 eV) disappears upon heating in O₂. For the UHV annealed UO₂ film, XP U 4f spectra indicate the presence of U⁴⁺ cations (U 4f_{7/2} = 380.2 eV and its satellite at 6.9 eV above). Heating in the presence of O₂ resulted in the oxidation of a fraction of U⁴⁺ cations to U⁵⁺ cations (U 4f_{7/2} = 381.1, U 4f_{5/2} = 391.8 and its satellite at ca. 8 eV above; the U 4f_{5/2} component of the U⁴⁺ cations obscures the U 4f_{7/2} satellite of the U⁵⁺ cations).⁸² The UHV annealed films are mostly composed of Ce⁴⁺ (for CeO₂) and exclusively composed of U⁴⁺ (for UO₂).

8. Charge transfer from U⁴⁺ to Ce⁴⁺ cations

8.1. Experimental

A noticeable difference is seen for the mixed oxides samples. Fig. 14A and B presents the same XPS regions as those shown in



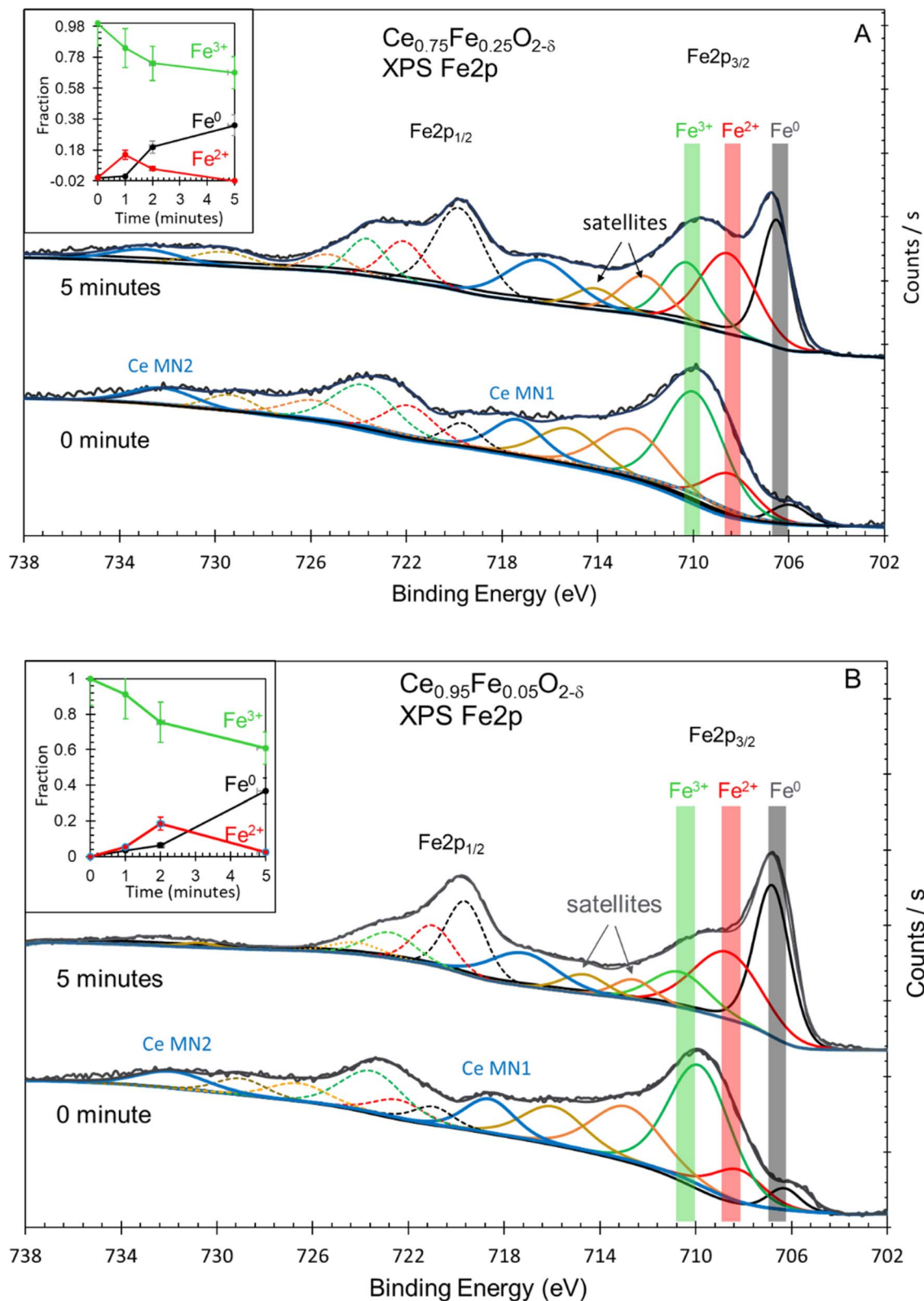


Fig. 11 (A) XPS Fe 2p spectra of as-prepared $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ after 5 minutes of Ar ions sputtering. (B) XPS Fe 2p spectra of as-prepared $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ after 5 minutes of Ar ions sputtering. Insets in (A and B): quantitative analysis of XPS Fe 2p spectra of $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ and $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ before and after sputtering at the indicated time. Data acquisitions were conducted using an Al K_α X-rays. From ref. 16 (no permission is needed: Creative Commons Attribution 4.0 License).



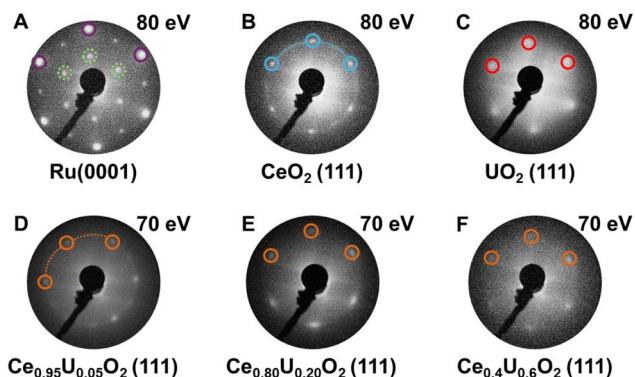


Fig. 12 LEED patterns: (A) clean Ru(0001)/Al₂O₃(0001) substrate. The hexagonal pattern indicated by solid violet circles corresponds to the Ru spots, while the dashed green circles indicate the (2 × 1) reconstruction of adsorbed oxygen. (B) and (C), CeO₂ and UO₂ (111) reference thin films; solid circles (blue and red) indicate their spots in azimuthal registry with the Ru(0001). For the CeO₂ pattern, the dashed blue arc indicates the faint ring associated with a small fraction of randomly oriented islands. (D)–(F) LEED patterns of Ce_{1–y}U_yO_{2±δ} thin films with $y = 0.05, 0.2, \text{ and } 0.6$, respectively. Solid orange circles indicate their spots in azimuthal registry with the Ru(0001). From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License).

Fig. 13 for the Ce_{0.8}U_{0.2}O_{2±δ}. XPS Ce 3d indicates (Fig. 14A) that the UHV annealed film contains a significant fraction of Ce³⁺ (which was not observed for CeO_{2±δ}); the estimated ratio Ce³⁺/Ce⁴⁺ is equal to 2.7. XPS U 4f lines of the same film contain a large fraction of U⁵⁺ (the UHV annealed of UO₂ did not contain U⁵⁺); the U⁵⁺/U⁴⁺ was found equal to 1.5. Similar trends were

obtained for other investigated mixed oxides, yet quantitative differences were observed. In particular, the charge transfer occurs during the annealing process (as indicated by eqn (3)). Heating in O₂ resulted in preferential oxidation back to Ce⁴⁺, yet under these conditions, part of the oxygen consumed for the oxidation was taken or transferred from U⁵⁺–O because the oxidation trend has reversed (Fig. 14B). This indicates that the dynamic of the electron transfer between both metal cations is sensitive to the partial pressure of O₂ in addition to the Ce to U ratio.

8.2. Compositional effect (Ce_{1–y}U_yO₂)

Increasing the percentage of U decreased the fraction of oxidized U cations Fig. 15A and B. Also, the ratio Ce³⁺/Ce⁴⁺ decreased compared to that of the lower U content. This trend indicates that the reduction of Ce⁴⁺ decreases when U cations content is significant and is not solely explained by the charge transfer described in eqn (3). However, Ce³⁺ cations were still present even when heated in O₂, while U cations were oxidized to U⁵⁺ and a small fraction to U⁶⁺. As mentioned above, previous works on polycrystalline Ce_{0.5}U_{0.5}O₂ showed segregation of the uranium oxide upon heating,²⁰ with diffraction lines that are attributed to either/or U₂O₅ and U₃O₈. Taking these observations together and the fact that UO₂ tends to become UO_{2+x}, one may conclude that it may segregate to the top of the thin film, shielding CeO₂ from being oxidized, and that is why Ce³⁺ cations are still present even when the film was annealed in the presence of O₂. While Ce³⁺ cations are formed, when the percentage of U cations is high, the former will not be as active because they are in deeper layers, thus explaining the decrease

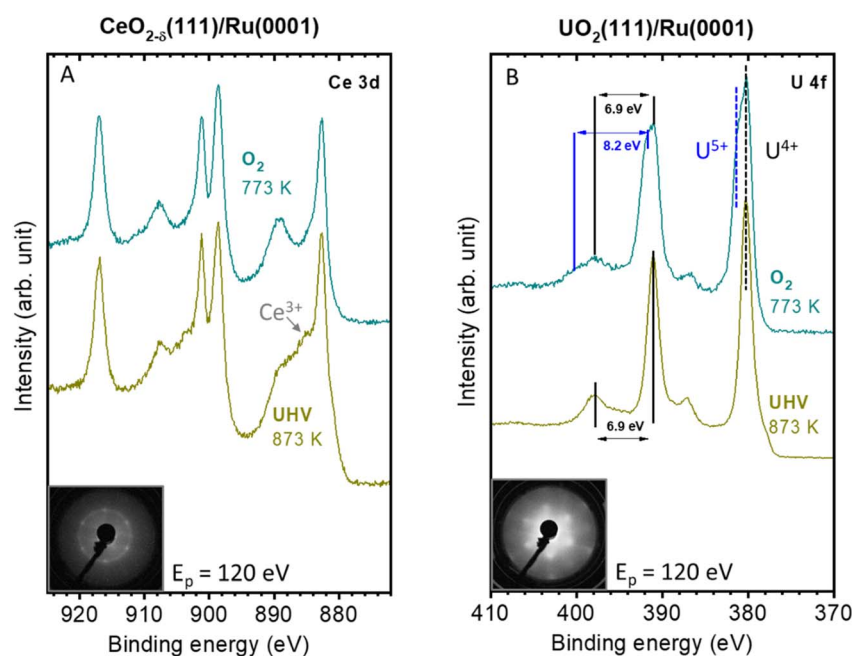


Fig. 13 (A) XPS Ce 3d of CeO₂ thin film after annealing in UHV (bottom) and heating in 5×10^{-7} mbar O₂ for 30 minutes (top). (B) XPS U 4f of UO₂ thin film after annealing in UHV (bottom) and heating in 5×10^{-7} mbar O₂ for 30 minutes (top). The insets show the LEED images of the UHV annealed films. From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License).



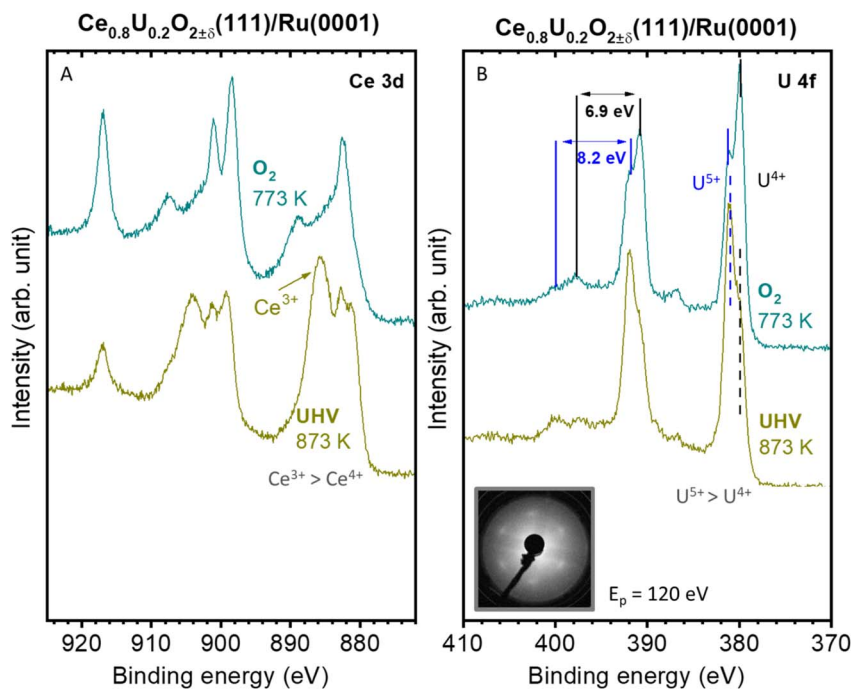


Fig. 14 (A) XPS Ce 3d of $\text{Ce}_{0.8}\text{U}_{0.2}\text{O}_{2\pm\delta}$ after annealing in UHV (bottom) and heating in 5×10^{-7} mbar O_2 for 30 minutes (top). (B) XPS U 4f of $\text{Ce}_{0.8}\text{U}_{0.2}\text{O}_{2\pm\delta}$ after annealing in UHV (bottom) and heating in 5×10^{-7} mbar O_2 for 30 minutes (top). The inset shows the LEED images of the UHV annealed samples. The arrows in (B) point to the ΔE of the satellites (6.9 eV for U^{4+} and 8.2 eV for U^{5+}). From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License).

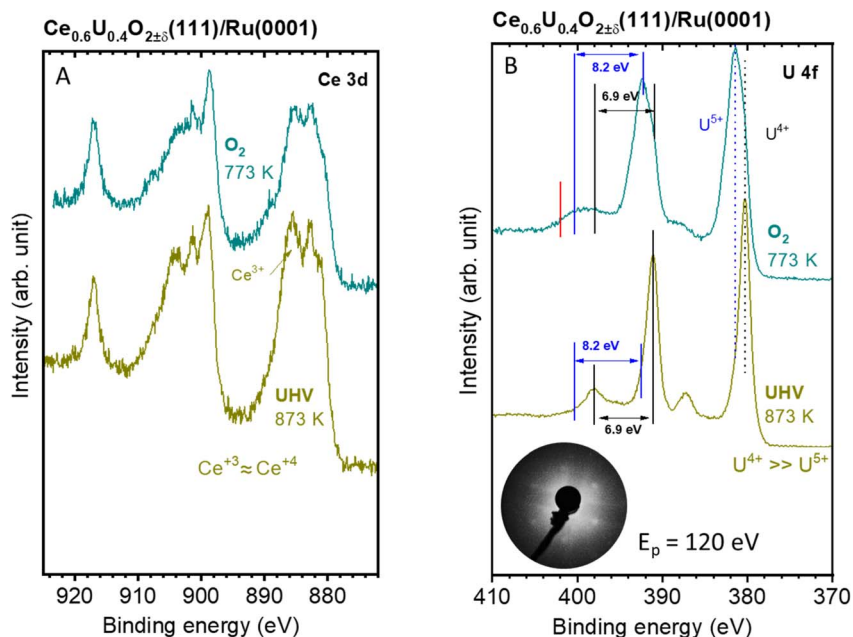


Fig. 15 (A) XPS Ce 3d of $\text{Ce}_{0.4}\text{U}_{0.6}\text{O}_{2\pm\delta}$ after annealing in UHV (bottom) and heating in 5×10^{-7} mbar O_2 for 30 minutes (top). (B) XPS U 4f of $\text{Ce}_{0.4}\text{U}_{0.6}\text{O}_{2\pm\delta}$ after annealing in UHV (bottom) and heating in 5×10^{-7} mbar O_2 for 30 minutes (top). The inset shows the LEED image of the UHV annealed sample. The arrows in (B) point to the ΔE of the satellites (6.9 eV for U^{4+} and 8.2 eV for U^{5+}). The red line is at the position of a U^{6+} satellite; this, together with the large FWHM of the main lines ($\text{U} 4f_{7/2,5/2}$), indicates that U cations have a wide range of oxidation states from +4 to +6. From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License).



of the activity of the mixed oxide for water splitting (as presented below) with increasing U content after the optimal concentration.

8.3. Computation

Fig. 16(A and B) presents the results of the DFT+*U* computation of $\text{Ce}_{31}\text{UO}_{64}$ before and after creating an oxygen vacancy to make a $\text{Ce}_{31}\text{UO}_{63}$ super-cell. There are no Ce 4f electrons before the removal of the oxygen ion, while three electrons on three Ce cations (Ce 4f orbitals) are seen after the creation of the V_{O} . Removing an oxygen ion from the lattice has resulted in the transfer of two electrons towards two Ce^{4+} cations, plus the additional reduction of a third Ce^{4+} to Ce^{3+} due to charge transfer from U^{4+} that becomes U^{5+} . Fig. 16(C and D) presents the bond distances between Ce (U) and oxygen ions and the Bader charge analysis in the presence of V_{O} . Contraction in the U–O bonds and expansions in the Ce–O bonds is observed. Quantitative description is given in Table 6, in which the focus is made on the bonds of seven oxygen anions with Ce and U cations (the oxygen atoms are labeled 1 to 7). Ce^{3+} cations directly adjacent to the vacancy experience an expansion in their bond distance to the nearest oxygen by 2.7%. Also, Ce^{4+} cations

Table 6 Bond distances between Ce (U) and O ions upon the removal of one O atom from $\text{Ce}_{31}\text{UO}_{64}$ super cell. The % changes are from the Ce–O and U–O distances of the stoichiometric cell (Ce–O = 2.372 Å and U–O = 2.342 Å). The alphabetical subscripts in Ce and numerical subscripts in O are displayed on the corresponding atoms in Fig. 7 in the main text. From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License)

Atom	O _{1,2,3}	O _{4,5,6}	O ₇
Ce _{a,b,c}	2.436 (+2.7%)		
U	2.188 (−6.6%)	2.283 (−2.5%)	2.244 (−4.2%)
Ce _{d,e,f,g,h,i}	2.531 (+6.7%)		

adjacent to the nearest oxygen atoms, labeled Ce_{d–i}, experience an even larger bond distance expansion of 6.7%. On the contrary, the U^{5+} cation shows a contraction of its bond distances to the seven oxygen ions. The contraction is, anisotropic and spans from 2.5 to 6.6%.

To study the configurational effect of U cations on the reduction of Ce^{4+} cations, computation of a system in which U cations having the same concentration but in two different positions were conducted. Fig. 17A and B presents results from

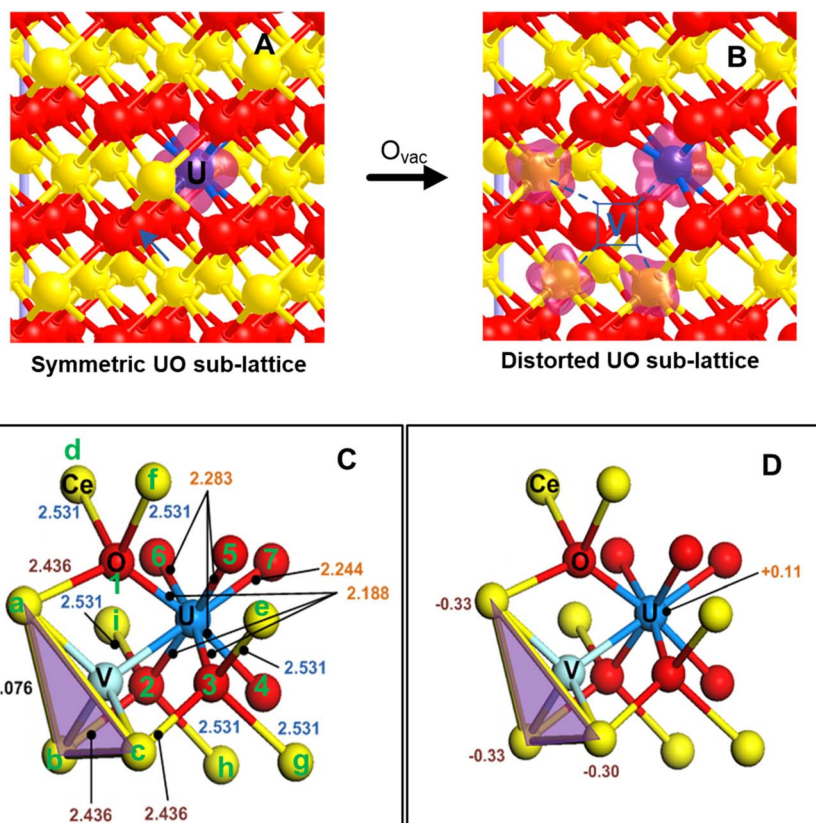


Fig. 16 (A) A section of the super cell ($\text{Ce}_{1-x}\text{U}_x\text{O}_2$; ($2 \times 2 \times 2$) model (31Ce, 1U, and 64O atoms); U% = 3.1%) showing the U cation (purple), Ce cations (yellow) and oxygen anions (red). The arrow points to the oxygen ion to be removed. Note the 5f orbitals of the U^{4+} cation that contain two electrons and the absence of 4f electrons on the Ce^{4+} cations. (B) The same section as in (A) after removing the oxygen anion. Three Ce cations have accommodated one electron each in their 4f states, while the U cation has lost one electron. (C) Bond distances of the Ce and U cations adjacent to the oxygen vacancy (Ce–O and U–O distances of the stoichiometric cells are Ce–O = 2.372 Å and U–O = 2.342 Å). (D) Bader charges on the three Ce cations and U cation in the presence of V_{O} . From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License).



a super cell ($4 \times 2 \times 1$) containing 3 U cations of a $\text{Ce}_{29}\text{U}_3\text{O}_{64}$. In one case (Fig. 17A) they are surrounding a Ce^{4+} cation, representing a high local concentration, while in the second case (Fig. 17B) one of the three cations is moved away, three units to the left on the x -axis and one unit up on the y -axis (a unit is defined as the Ce^{4+} to Ce^{4+} distance, which is equal to 3.86 Å).

No electron transfer occurred in the first configuration, while in the second, in which only two U cations were adjacent to Ce^{4+} , transfer did occur to the Ce cation at equidistance from the two U cations. This occurred in the absence of V_O . Fig. 17C and D presents a specific case of Fig. 17B. The removal of an oxygen ion in this case did not result in the formation of three Ce^{3+} but in two. In this case, the presence of the two U cations adjacent to each other prevented the charge transfer upon the removal of an oxygen ion.

Based on the results on polycrystalline and epitaxial $\text{Ce}_{1-y}\text{U}_y\text{O}_2$ samples, it was observed (in both cases) that charge transfer from U to Ce cations occurs. Its extent, however, has a considerable entropic factor. While low concentrations of U

cations are needed, this is not solely related to a dilution effect. Also, the analysis of model $\text{Ce}_{1-y}\text{U}_y\text{O}_2$ (111) thin films indicates that the fraction of Ce^{4+} reduced to Ce^{3+} is larger than that of U^{4+} oxidation to U^{5+} (or U^{6+}) by a factor far exceeding experimental uncertainties (more details can be found in ref. 22). At high U concentrations, U cations migrate to the shell of the crystallites. Besides the fact that UO_2 is easily oxidized to higher oxidation states, O_2 adsorption on $\text{UO}_2(111)$ is possible (with a computed adsorption energy of -0.24 eV),⁸³ whereas there are no known experimental reports of O_2 irreversible adsorption on $\text{CeO}_2(111)$. Together, these facts would result in a core-shell structure ($\text{UO}_2/\text{Ce}_{1-y}\text{U}_y\text{O}_2$), preventing Ce^{3+} cations from being oxidized in the core of the crystallite. Such element migration and phase separation are not uncommon in metallic nanoparticles; for example, an alloy of RhPd or RhPt particles sees migration of Rh to the surface in an oxidized environment⁸⁴ because it is easier to oxidize Rh when compared to Pt or Pd. The reduction of Ce cation in the presence of U cations, while occurs through charge transfer, is therefore sensitive to the

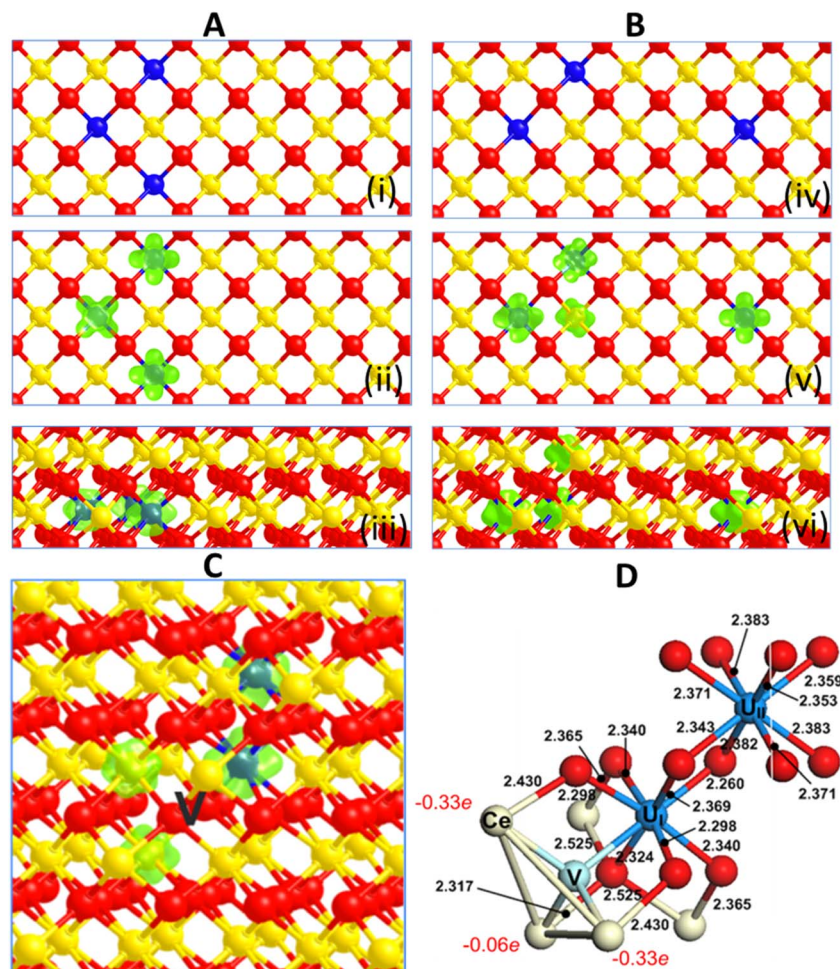


Fig. 17 (A and B) Effect of U arrangement around Ce ions on electron transfer. U concentration is 9.3% of the ($4 \times 2 \times 1$) bulk model ($\text{Ce}_{29}\text{U}_3\text{O}_{64}$ ($\text{Ce}_{0.907}\text{U}_{0.093}\text{O}_2$)). (i) and (iv) U, Ce, and O are in blue, yellow, and red; top view. (ii) and (v) Projected orbitals on U and Ce ions; top view. (iii) and (vi) Projected orbitals on U and Ce ions; side view. (C) U concentration is 6.2% of the ($2 \times 2 \times 2$) bulk model ($\text{Ce}_{30}\text{U}_2\text{O}_{63}$ ($\text{Ce}_{0.937}\text{U}_{0.063}\text{O}_{1.969}$)) in the presence of V_O . (D) Bond distances and Bader charge on Ce in the presence of V_O (from C). From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License).



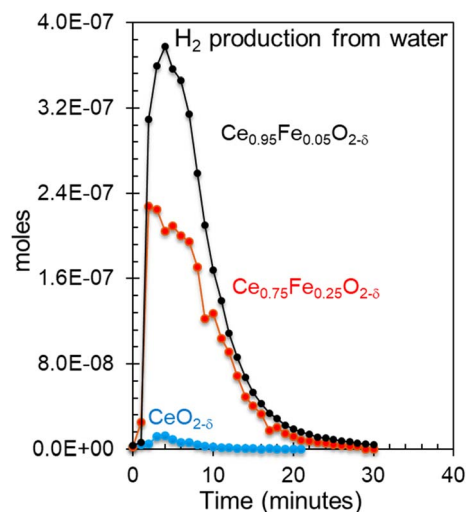


Fig. 18 Hydrogen production from water over CeO_2 , $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ and $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$, which were previously reduced with hydrogen at 973 K at one atmosphere (reaction temperature = 973 K). The total H_2 production was found equal to 0.2, 7.4 and 11.4 $\mu\text{mol g}_{\text{oxide}}^{-1}$ for CeO_2 , $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ and $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$, respectively. From ref. 16 (no permission is needed: Creative Commons Attribution 4.0 License).

configuration of the metal cations, and, as pointed out computationally before (ref. 11), its energy is sensitive to statistical entropy contribution.

9. Hydrogen production from water

9.1. Polycrystalline $\text{Ce}_{1-y}\text{Fe}_y\text{O}_2$

Fig. 18 presents hydrogen production on CeO_2 , $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ and $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ from water, these were prior reduced with hydrogen 973 K (700 °C). The use of hydrogen allows reduction at temperature low enough where phase segregation is minimal. Moreover, while the TCWS technology relies on direct energy input from the sun using solar concentrators, with its considerable challenges,⁸⁵ at the laboratory scale heat is provided by electrical furnaces instead in order to maintain a controlled and stable energy source. The objective here is to relate H_2 production (performance) to the observed reduced states (spectroscopy) of the oxides. Because, as indicated by XRD, the two mixed oxides are not segregated when heated to this temperature, a link to spectroscopic measurements is possible. CeO_2 alone shows negligible activity, while the Fe-substituted cerium oxides are active. The activity of the $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ is almost twice that of the $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_{2-\delta}$ catalyst. This suggests that the activity is more linked to Ce^{3+} than to Fe^0 (based on the XPS Ce 3d and XPS Ce 5p/O 2s spectra).

9.2. Polycrystalline $\text{Ce}_{1-y}\text{U}_y\text{O}_2$

The water splitting to hydrogen at 973 K for the series polycrystalline $\text{Ce}_{1-x}\text{U}_x\text{O}_{2\pm\delta}$ (where $0.05 \leq x \leq 0.75$, including pure CeO_2 and UO_2) was further studied to see the effect of substituting Ce^{4+} by U^{4+} cations on the reaction. Fig. 19A presents H_2 production from water (vapor pressure 23 torr) as

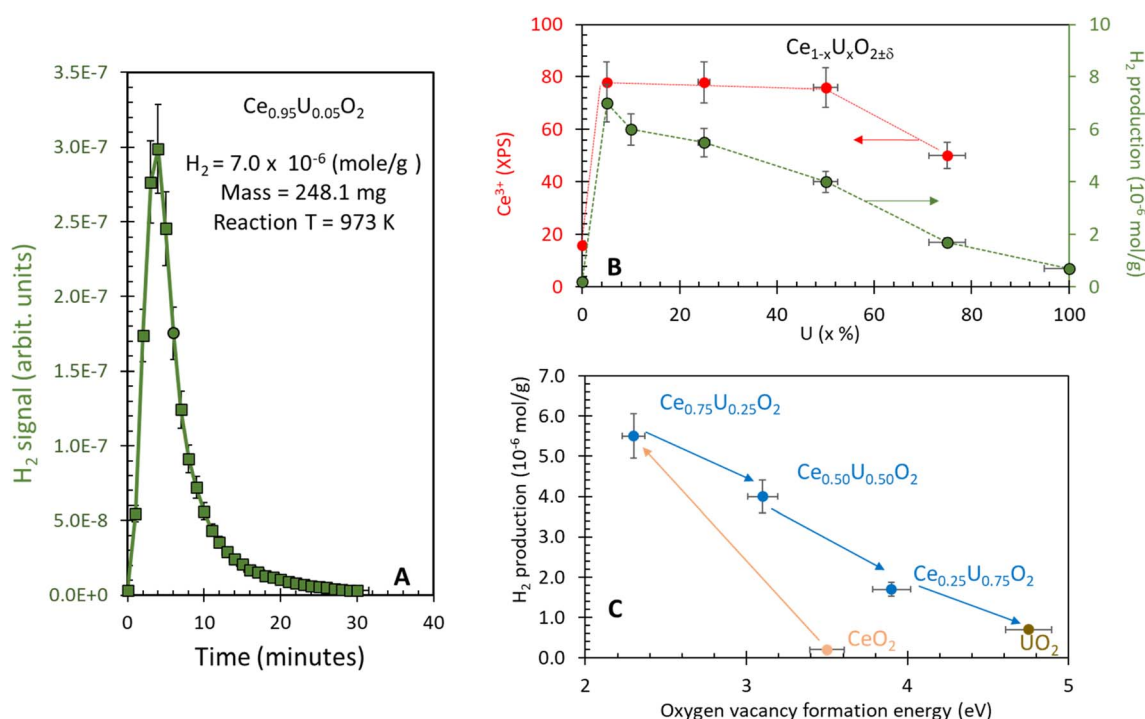


Fig. 19 (A) H_2 production from water at 973 K on pre-reduced $\text{Ce}_{0.95}\text{U}_{0.05}\text{O}_2$. (B) H_2 production on a series of $\text{Ce}_{1-x}\text{U}_x\text{O}_{2\pm\delta}$ mixed oxide as a function of U content (right y-axis). The percentage of Ce^{3+} (XPS Ce 3d lines from ref. 20) cations obtained upon reduction with Ar-ions prior to XPS collection is shown in the left y-axis. (C) H_2 production on a selected samples from the series presented in (B) as a function of V_{O} formation energy computed using DFT+U, from ref. 12. From ref. 22 (no permission is needed: Creative Commons Attribution 4.0 License).



a function of time over a prior reduced $\text{Ce}_{0.95}\text{U}_{0.05}\text{O}_2$. The calculated total H_2 production per weight over these oxides is presented in Fig. 19B. The binary oxides (CeO_2 and UO_2) show a small activity at both ends of the plot. The presence of U in small amounts resulted in an enhancement of H_2 production by *ca.* 30 times when compared to CeO_2 . Increasing the amounts of U, while still showed enhancement compared to CeO_2 , was less pronounced. Also presented are the percentage of Ce^{3+} states (as obtained from XPS Ce 3d lines²⁰) that were produced upon Ar-ions sputtering of the same polycrystalline mixed oxide series. The trend is similar to H_2 production: substituting Ce by U cations increased the reduction of Ce^{3+} considerably. Fig. 19C presents some of the data of the H_2 production shown in Fig. 19B as a function of bulk V_{O} formation energy (E_{VO}), computed using DFT+ U ($U_{\text{eff}} = 4$ eV for U and 5 eV for Ce) taken from ref. 13. E_{VO} represents the energy required to remove an oxygen atom from the oxide lattice and is defined as the energy difference between a reduced slab and the sum of the energies of the corresponding stoichiometric slab and the removed oxygen atoms. If oxygen vacancies were isolated and non-interacting, one expects a linear relationship between E_{VO} and the extent of reduction δ , taking in consideration that H_2 production is proportional to $\delta/2$ (as per eqn (2)).

The introduction of U considerably decreased the energy needed to remove bulk oxygen atoms. The effect is offset by increasing U content, because it is harder to reduce U^{4+} cations.

10. Thermal water splitting ($\text{Ce}_{1-y}\text{Fe}_y\text{O}_2$)

Fig. 20 presents the activity of reduced CeO_2 and reduced $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ for thermal water splitting at 1200 °C while Fig. 21 presents the STEM, EDX and EELS results of the $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ oxide after the reaction. The reduction was conducted upon heating to 1550 °C for two hours in the absence of H_2 (under N_2). The incorporation of Fe ($\text{Fe}/\text{Ce} = 0.05$) into CeO_2 has resulted in two main effects. It increased the kinetic of H_2 production (Fig. 20C) and the yield; total amount has almost doubled (per unit weight of oxide) (Fig. 20B and C). This is in line with spectroscopic results where there is an increased reduction of CeO_2 due to the presence of Fe cations (up to a threshold level). The FWHM of the production peak decreased from *ca.* 35 min to about 10 min which gives a simple observation on the kinetic effect. To further see the effect of Fe on the reduction kinetics, the decay part of the peaks was fitted with an exponential function. Attempts with a single exponential decay fit were not successful, a double exponential fit was found to be adequate with R^2 of 0.999. Table 7 presents the different parameters of the decay for both oxides. The addition of Fe has increased the time constant for water splitting by a factor of 2 when compared to CeO_2 alone. However, increasing the number of reduced sites, should not change the decay time but mostly affect the amplitude (pre-factors A_1 and A_2) if these sites were all of similar nature and do not interact with each other. The

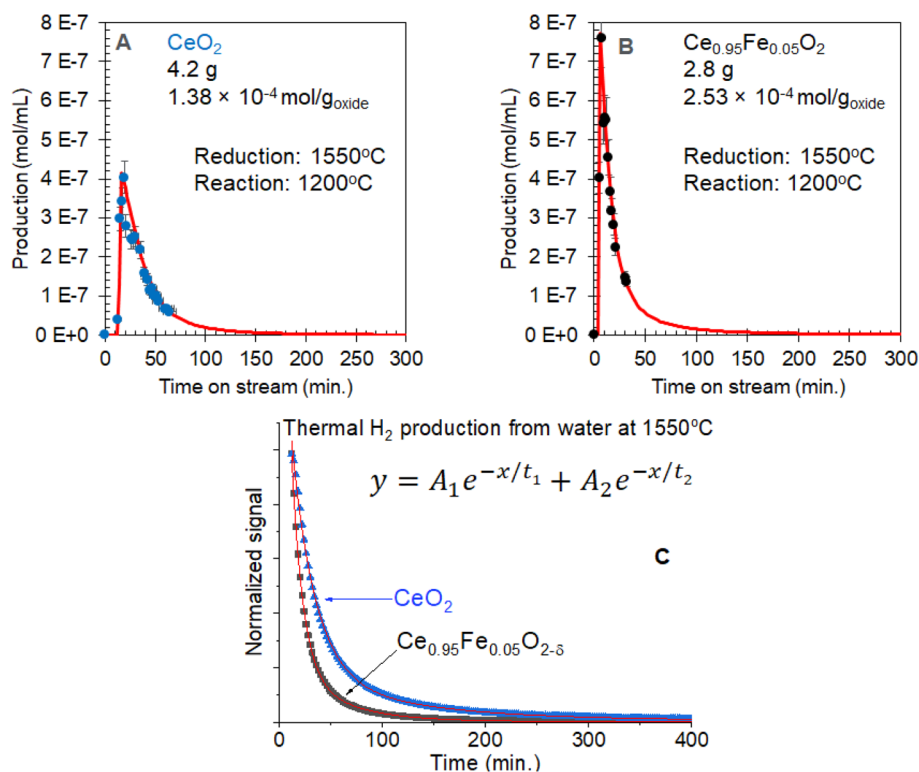


Fig. 20 Thermo-chemical water splitting over CeO_2 (A) and $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ (B) at 1200 °C (1473 K), the oxides were reduced under N_2 at 1550 °C (1823 K) for two hours prior to use. The total amount of H_2 from water per g of oxide is indicated. (C) Normalized fitting of the decay part of H_2 production using a bi-exponential function for both oxides. From ref. 50, permission license number 6133081449846.



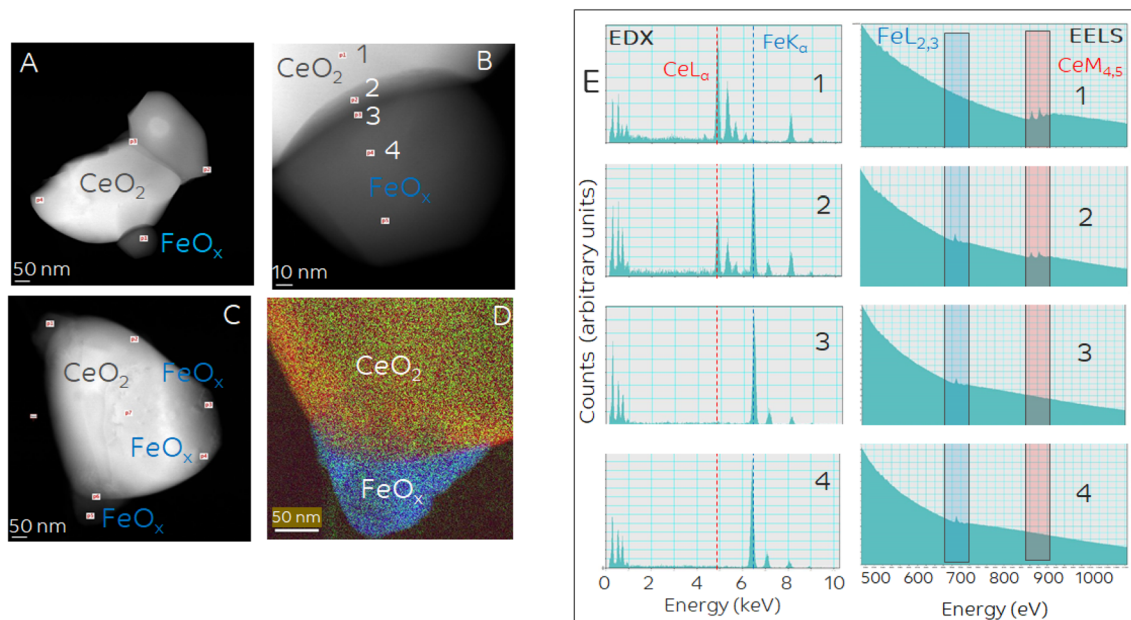


Fig. 21 STEM, EDX, EELS of $\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\delta}$ after the reaction presented in Fig. 20. (A) and (B) are for one particle and (C) and (D) are for another particle. (D) An elemental EELS map of the particle in (C). The numbers 1 to 4 in (E) are labeled in (B). While segregation of iron to the edges of CeO_2 is seen some iron is still present within the crystallite (also note the presence of FeO_x on the large CeO_2 crystallite in (C)). The crystallite size (TEM) is close to $1\ \mu\text{m}$ (an increase of about 200 times when compared to that calcined at $500\ ^\circ\text{C}$). Yellow for cerium, blue of iron and red for oxygen atoms. From ref. 50, permission license number 6133081449846.

Table 7 Fitting parameters for the decay part of the H_2 production profile (at $1473\ \text{K}$) from water as a function of time of the pre-reduced oxides at $1823\ \text{K}$. The time constant $\tau = 1/t$. A double exponential decay equation was used $y = A_1 e^{-x/t_1} + A_2 e^{-x/t_2}$

Oxide	A_1 (mol mL^{-1})	t_1 (min)	τ (min) $^{-1}$	A_2 (mol mL^{-1})	t_2 (min)	τ (min) $^{-1}$	t_1/t_2
CeO_2	7.3×10^{-7}	22.5 ± 0.2	0.044	9.7×10^{-8}	108.8 ± 2.9	0.009	0.21
$\text{Ce}_{0.95}\text{Fe}_{0.05}\text{O}_2$	1.2×10^{-6}	10.7 ± 0.06	0.093	1.3×10^{-7}	47.3 ± 0.6	0.021	0.23

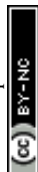
^a From ref. 50, permission license number 6133081449846.

increase of the time constant by a factor of two indicates that the reduced sites are more reactive than those of reduced CeO_2 alone. It is not simple to attribute a separate physical meaning to both decay constants. It is possible that the (t_2) decay describes events requiring more (or additional) energy than the first one; such as defects diffusion from the bulk to the surface. Initially defects are statistically distributed in the bulk and on the surface, then with the reaction progress more available defects are healed (and the process would more dependent on diffusion of O^{2-} (or V_O) within the oxide), and this decreases the reaction rate. In other words, the first decay might be largely independent from defects distribution and migration while the second is affected.

The activation energy for oxygen diffusion in CeO_2 is typically a small fraction from that needed to reduce it (10–20% or so).⁸⁶ In the process of oxidation of the reduced CeO_2 with water vapor two chemical steps occur. (i) Water dissociative adsorption and (ii) oxygen anions diffusion from the surface to the bulk (or V_O diffusion from the bulk to the surface). (i) The first one is different on a stoichiometric surface when compared to defected ones and therefore their kinetic effect on the reaction

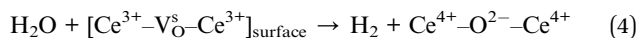
is expected to be different (water dissociative adsorption over reduced CeO_2 has a stronger energy than that on stoichiometric surface⁸⁷). (ii) The particles have considerably sintered (Fig. 21) due to heat, so intra particle pore diffusion of water molecules may be neglected. While the increase of the volume to surface ratio upon sintering makes the process mostly bulk driven (since the majority of the oxygen defects would be located in the bulk) the reaction would still be surface driven first if the adsorption of water is a limiting step. While a fraction of Fe oxides has segregated out there is still some Fe inside as seen by EDX and EELS (Fig. 21). It is therefore possible that, in some locations, the interface has the needed gradient concentration of Fe cations to affect the reaction rate when compared to pure CeO_2 .

The three following equations summarize the main reactions that occur during water oxidation. Large crystallites of CeO_2 are (111) O-terminated in the fluorite structure and these terminated oxygen anions are bonded to three Ce cations in the second layer, yet for the sake of simplicity it is easier to write them as (Ce–O–Ce) bearing in mind that they are not in the same plane.



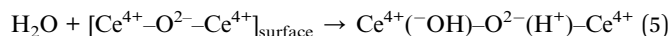
10.1. Reaction steps

Electron transfer reaction: water dissociative adsorption on surface oxygen defect followed by oxidation and hydrogen generation.

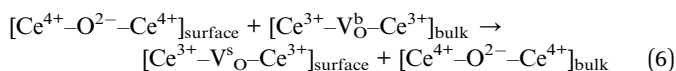


$\text{V}_\text{O}^{\text{s}}$ is for a surface oxygen defect and Ce^{3+} is for a reduced cation in the second layer of the (111) terminated surface.

Acid–base interaction: water dissociative adsorption over stoichiometric sites (no charge transfer).



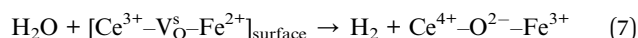
Diffusion: surface oxygen diffusion into the bulk (or V_O diffusion to the surface) driven by heat and water dissociative adsorption (eqn (4) and (5)).



$\text{V}_\text{O}^{\text{b}}$ is bulk oxygen defect.

The two protons in eqn (5) (of the two surface hydroxyls) become one molecule of hydrogen upon the reaction with two electrons from eqn (6).

The substitution of a fraction of Ce cations by Fe cations on the surface and in the bulk affect eqn (4) and (6). Eqn (5) is an acid–base exchange reaction that is largely not affected by the change in the nature of a metal cation. Although it can be affected by the degree of coordination⁸⁸ (such as in different surface structures) this may be neglected here because of the small energy difference. The concentration of V_O has increased in the presence of Fe cations and this affects primarily eqn (4). However, the faster kinetics indicate that the dissociative adsorption of water on oxygen vacancy sites is also accelerated when Fe cations are present. Therefore, in the presence of Fe cations in the CeO_2 lattice, eqn (7) below, is expected to be faster than eqn (4) if the dissociative adsorption energy is higher on $\text{Fe-V}_\text{O}^{\text{s}}\text{-Ce}$ when compared to $\text{Ce-V}_\text{O}^{\text{s}}\text{-Ce}$ centers.



11. Conclusions

The chemical states of Ce^{3+} cations in $\text{Ce}_{1-y}\text{Fe}_y\text{O}_2$ are analyzed by their deep (XPS Ce 3d) and shallow (XPS Ce 5p) core levels in addition to their valence level (XPS Ce 4f) spectroscopy at different Fe^{3+} concentrations. Moreover, the states of U^{x+} in $\text{Ce}_{1-y}\text{U}_y\text{O}_2$ were further analyzed by their core levels and DFT+ U methods. HR-STEM and EELS for the as prepared mixed oxides showed, in line with XRD results, that the cations (Fe^{3+} or U^{4+}) are homogeneously distributed inside CeO_2 . While the addition of Fe^{3+} cations doubled the reaction yield and considerably increased the cycle kinetics, phase segregation occurred upon thermochemical water splitting reaction when the mixed oxide was reduced by heating in an inert environment at 1550 °C. A

three-step mechanism for the water splitting reaction is presented in which the dissociative adsorption, the bulk diffusion of oxygen anions and the hydrogen re-combinative desorption are discussed. Results point to the role of Ce-O-Fe sites in improving the reaction kinetics, yet the considerable sintering indicates that maintaining oxide homogeneity is needed for long-term stability. In the case of $\text{Ce}_{1-y}\text{U}_y\text{O}_2$, the TCWSR to H_2 is sensitive to the content of U, where low percentages of U cations considerably enhanced the production. This enhancement is attributed to the increase in Ce^{4+} cations reduction to Ce^{3+} cations. The trend of this $\text{Ce}^{4+}/\text{Ce}^{3+}$ conversion studied by *in situ* XPS of single crystalline mixed oxides showed evidence of charge transfer ($\text{Ce}^{4+} + \text{U}^{4+} \rightarrow \text{Ce}^{3+} + \text{U}^{5+}$) at low U content. Evidence of charge transfer was further obtained computationally using the DFT+ U method, giving more support to the experimental $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{U}^{4+}/\text{U}^{5+}/\text{U}^{6+}$ results. This charge-transfer effect is sensitive to the local distribution of U^{4+} cations in the ceria lattice. One of the key conclusions is the need to lower the reduction temperature of the mixed oxide phase considerably to prevent phase separation. There is also a need to further study the entropical effect of the mixed oxides on the reduction of the host material, as it appears to be an important factor for the charge transfer reaction. Several strategies are discussed to mitigate phase segregation in ceria-based redox materials, including maintaining low dopant concentrations to preserve solid solutions, selecting dopants with compatible ionic radii and crystal structures, and employing synthesis methods that promote homogeneous cation distribution.

Conflicts of interest

The author declares no conflicts of interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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