Identification of surface composition and chemical states in composites comprised of phases with fluorite and perovskite structures by X-ray photoelectron spectroscopy

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ARTICLE INFO

Article history:

Received 27 July 2012

Received in revised form

16 November 2012

Accepted 13 December 2012

Available online 21 December 2012

Keywords:

X-ray photoelectron spectroscopy (XPS)

Surface composition

Composites with perovskite and fluorite structures

Oxidation state of cerium cations

Binding energy

ABSTRACT

X-ray photoelectron spectroscopy (XPS) has been used to explore the cation rearrangement between the surface and bulk of grains and the surface chemical states of Ce, Mn, Co, Sr, and O ions in the single phase CeO₂-based solid solutions and in the two phase (100 – x)La_{0.6}Sr_{0.4}CoO₃–xCeO₂ (LSCCx) and (100 – x)La_{0.8}Sr_{0.2}MnO₃–xCeO₂ (LSMCx) composites. The well-resolved Ce 3d_{5/2} and Ce 3d_{3/2} spin-orbit components were determined to study the Ce⁴⁺ to Ce³⁺ electronic transition at the surface. The surface of the LSCCx and LSMCx (x = 8–40 mol%) composites is depleted in cerium. Both Ce⁴⁺ and Ce³⁺ cations were revealed. The surface fraction of Ce⁴⁺ cations increases with the rise in CeO₂ content in both systems, but it is higher by about a factor of two in the LSCC composites. A strong enrichment of the surface by Co cations was observed for the composites LSCCx (x = 8–40 mol%), implying that the presence of cerium could facilitate the Co surface segregation. A slight Sr surface enrichment compared to the nominal stoichiometry was found for La_{0.6}Sr_{0.4}CoO₃, CeO₂-based solid solutions, LSCC57, and LSMCx (x = 10–57) composites. In contrast, the surface of the LSCCx (x = 10–37) composites is slightly depleted in strontium cations. The O 1s spectra of the LSCC and LSMC composites contain several contributions associated with the lattice oxygen related to the phases with the perovskite and fluorite structures as well as with different surface states. Their contributions vary with CeO₂ content and a chemical origin of the transition metal cations on the B-site in the perovskite structure. The Ce₂(CO₃)₃-based phase seems to exist at the surface of grains and crystallites in the LSCC57 and LSMC composites.

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1. Introduction

Complex materials containing transition metal and cerium cations have been considered as catalysts, electrodes in fuel cells, and batteries [1–12]. A high activity with respect to a certain catalytic or electrode process could relate to an optimal surface concentration of Ce cations and their involvement in the reversible redox cycle (Ce³⁺ ↔ Ce⁴⁺) [13]. Stoichiometric defects such as oxygen vacancies, which form during reduction of cerium cations, and their mobility on the surface are of great importance for catalytic activity [14–16]. X-ray photoelectron spectroscopy (XPS) is the

method that allows monitoring changes in the local environment of ions and their oxidation states [17]. The surface chemical states of Ce cations have been explored so far preferably for undoped CeO₂ [18–23], CeO₂-based solid solutions [24–26], and composites composed of CeO₂ and transition metals or their oxides [27–34]. It was shown that properties of composite materials (redox properties, formation of surface and bulk oxygen vacancies, oxygen storage and release) can be optimised through the variation of the CeO₂/Me(Me_xO_y) ratios.

In the present work we explore the evolution of the surface composition and chemical states in complex composite systems initially composed of a perovskite phase with transition metal cations on the B-sites (La_{0.6}Sr_{0.4}CoO₃ or La_{0.8}Sr_{0.2}MnO₃) and cerium oxide with fluorite structure. The perovskite–fluorite interface in composite cathodes in fuel cells is responsible for oxygen sorption and reduction, surface mobility of oxygen vacancies, fast oxygen ion exchange between the surface and bulk of grains, and for optimum distribution of catalysts over surface (which depends on wetting characteristics of the interface) [8–12]. A recent computational

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study showed that transition metal cations are responsible for the electrocatalytic activity for oxygen reduction [35], suggesting that a high surface concentration of transition metal cations could facilitate surface processes. XPS and Auger electron spectroscopy studies carried out on perovskites, however, revealed that the surface concentration of the transition metal cations in the cation stoichiometric perovskites is either the same as in the volume of crystallites or lower [36–41]. It is not clear whether the presence of a second phase (cerium oxide) would change the surface concentration of transition metal cations or not. The existence of both $\text{Mn}^{(4+/3+/2+)}$ and $\text{Co}^{(4+/3+/2+)}$ cations in different oxidation states, their ability to be involved in the reversible redox cycle (in particular Co cations) and to be dissolved in the fluorite structure would influence or not the oxidation state of Ce cations at the surface. To address these and other issues we consider our materials in terms of the core-shell model, where the bulk structural parameters of perovskites and cerium oxide were analysed by X-ray powder diffraction (XRD), whereas X-ray photoelectron spectroscopy (XPS) measurements provided summary information on the surface composition and chemical states of cations and oxygen ions at the surface and interfaces.

2. Experimental

The initial perovskites $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) were produced by combustion spray pyrolysis and supplied by PRAXAIR Inc., USA. CeO_2 (99.9%) was delivered by ACROS ORGANICS (New Jersey, USA) and was calcined at 1000 °C for 5 h to remove adsorbed water. Further, compositions in the following series $(100-x)\text{LSC} \cdot x\text{CeO}_2$ (LSCCx) with $x = 8, 10, 25, 37, 57$ mol% and $(100-x)\text{LSM} \cdot x\text{CeO}_2$ (LSMCx) with $x = 2, 10, 25, 36, 57$ mol% were obtained by mechanical mixing of LSC or LSM and CeO_2 in relevant ratios, followed by calcination in air at 1350 °C for 5 h. The initial phases (LSC, LSM, and CeO_2) were also calcined under the same conditions. The $\text{Ce}_{0.905}\text{La}_{0.028}\text{Sr}_{0.019}\text{Co}_{0.048}\text{O}_{2-\delta}$ and $\text{Ce}_{0.808}\text{La}_{0.058}\text{Sr}_{0.038}\text{Co}_{0.096}\text{O}_{2-\delta}$ single phase solid solutions were fabricated through mixing of CeO_2 with 5 and 10.6 mol% $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, respectively, followed by calcination in air at 1350 °C for 5 h.

X-ray photoelectron spectroscopy (XPS) was applied to study the surface composition and the chemical states of ions in the LSCC and LSMC series. The survey spectra and detailed spectra (were recorded on the polished pellets (SiC-paper 2500 grits) with an ESCALAB II spectrometer (V.G., UK) for the LSCC system using nonchromatic Al K_{α} ($h\nu = 1486.4$ eV) radiation and a XPS 5600 spectrometer (Physical Electronic, USA) for the LSMC system using monochromatic Al K_{α} ($h\nu = 1486.4$ eV) radiation. Data were collected at a take-off angle of 45°, allowing the characterisation of the surface and the near surface region. The spectra were analysed with CasaXPS software. The binding energies (BE) are referenced to the C 1s peak at 284.6 eV and given with a precision of 0.1–0.2 eV. The atomic concentrations of elements (relative error: $\pm 15\%$) were calculated from the fitted peak areas using appropriate atomic sensitivity factors. X-ray powder diffraction (XRD) data were recorded in air at room temperature in transmission mode on a Stoe Stadi-P diffractometer with Cu K_{α} radiation (Stoe & Cie GmbH, Germany). The diffraction spectra were registered in the angular range of $15 \leq 2\theta \leq 96^\circ$, with a step size of 0.1° , and a recording time of 70 s for each step. Si powder (Alfa Aesar, Karlsruhe, Germany) was used as the external standard for the calibration of the diffractometer. The diffraction data were refined by the Rietveld method [42], using the program Generalized Structure Analysis System (GSAS) [43], to identify the crystal structure of each constituent phase in the composites investigated.

Fig. 1. XRD patterns of undoped CeO_2 , $\text{Ce}_{0.905}\text{La}_{0.028}\text{Sr}_{0.019}\text{Co}_{0.048}\text{O}_{2-\delta}$, and $\text{Ce}_{0.808}\text{La}_{0.058}\text{Sr}_{0.038}\text{Co}_{0.096}\text{O}_{2-\delta}$ single phase compositions.

3. Results and discussion

3.1. Pure and modified cerium oxides with fluorite structure calcined at 1350 °C in air

The XRD patterns of pure and doped cerium oxide are presented in Fig. 1. Pure CeO_2 , the single phase solid solutions $\text{Ce}_{0.905}\text{La}_{0.028}\text{Sr}_{0.019}\text{Co}_{0.048}\text{O}_{2-\delta}$ and $\text{Ce}_{0.808}\text{La}_{0.058}\text{Sr}_{0.038}\text{Co}_{0.096}\text{O}_{2-\delta}$ have the fluorite structure (space group $Fm\bar{3}m$, no. 225) [44–46]. The lattice parameter of undoped CeO_2 is $5.4103(9)$ Å [46]. On multi-cation doping, the lattice parameter of the modified cerium oxides increases up to $5.4258(1)$ Å and $5.4420(2)$ Å, respectively, for $\text{Ce}_{0.905}\text{La}_{0.028}\text{Sr}_{0.019}\text{Co}_{0.048}\text{O}_{2-\delta}$ and $\text{Ce}_{0.808}\text{La}_{0.058}\text{Sr}_{0.038}\text{Co}_{0.096}\text{O}_{2-\delta}$ [46]. Fig. 2 illustrates the survey spectra of pure and multi-cation doped cerium oxides after calcination in air at 1350 °C. Their surface compositions derived from the XPS measurements are presented in Table 1. The surface composition of pure CeO_2 measured on two different instruments is in a good accord although it differs from the bulk composition (33.3 at.% Ce and 66.7 at.% O). This suggests a strong influence of high-temperature treatment on the surface composition of grains and crystallites within the top several nanometres. In $\text{Ce}_{0.905}\text{La}_{0.028}\text{Sr}_{0.019}\text{Co}_{0.048}\text{O}_{2-\delta}$ and $\text{Ce}_{0.808}\text{La}_{0.058}\text{Sr}_{0.038}\text{Co}_{0.096}\text{O}_{2-\delta}$ single phase solid solutions, only Sr cations were revealed at the surface, indicating that La and Co cations dissolve entirely into the fluorite lattice. Unfortunately, it was impossible to identify the Sr surface states in the single phase solid solutions due to a strong

Fig. 2. Survey spectra of undoped CeO_2 , $\text{Ce}_{0.905}\text{La}_{0.028}\text{Sr}_{0.019}\text{Co}_{0.048}\text{O}_{2-\delta}$, and $\text{Ce}_{0.808}\text{La}_{0.058}\text{Sr}_{0.038}\text{Co}_{0.096}\text{O}_{2-\delta}$ single phase compositions.

Table 1

Surface atomic composition derived from XPS for pure and multi-cation doped cerium oxides with fluorite structure calcined at 1350 °C for 5 h in air.

Composition	Instrument	Atomic concentration, at. % ^a					[Ce ⁴⁺]/[Ce ³⁺] atomic ratio
		Ce	Sr	La	Co	O	
CeO ₂	ESCALAB II	21.7	–	–	–	78.3	4.5
	XPS 5600	18.6	–	–	–	81.4	3.6
Ce _{0.905} La _{0.028} Sr _{0.019} Co _{0.048} O _{2-δ}	ESCALAB II	9.8	1.1	–	–	89.1	4.5
Ce _{0.808} La _{0.058} Sr _{0.038} Co _{0.096} O _{2-δ}	ESCALAB II	24.0	7.5	–	–	68.5	13.2

^a Relative error is ±15%.

differential charging in the detailed Sr 3d (by ~10 eV) and O 1s (by ~8–10 eV) spectra, which were collected after the recording of the Ce 3d detailed spectra. Incorporation of lanthanum into the fluorite structure of CeO₂ should be accompanied by an increase in the lattice parameter or unit cell volume as was observed for the single phase Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-δ} and Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-δ}. The Sr surface segregation may be explained through the largest difference in the ionic radii between the host Ce⁴⁺ cations ($r^{\text{VIII}} = 0.97 \text{ \AA}$) and the doping Sr²⁺ cations ($r^{\text{VIII}} = 1.26 \text{ \AA}$) compared to La³⁺ ($r^{\text{VIII}} = 1.16 \text{ \AA}$) and Co²⁺ ($r^{\text{VIII}} = 0.90 \text{ \AA}$) cations [47]. These results are slightly surprising for Sr as up to 9 mol% SrO can dissolve individually in the fluorite structure of CeO₂ [48]. For other cations it is known that up to 50 mol% La₂O₃ [49,50] and up to 5 mol% Co containing oxides [51,52] can dissolve individually in the fluorite structure of CeO₂ with the formation of solid solutions. Dissolution of a high fraction of Co cations into the fluorite structure of Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-δ} was also slightly unexpected. The results imply that the multi-cation doping approach is more intricate and simultaneous dissolution of different cations within the fluorite structure will not always obey their individual dissolution limits. It seems that at first the dissolution of cations with the lowest difference in the ionic radii between the host and the doping cations takes place. In our case, the difference in the ionic radii between Ce⁴⁺ (as the host cation) and La³⁺, Co²⁺, Sr²⁺ (as dopants) increases in the following way (the numbers in the round brackets are the modulus of the difference in the values of ionic radii): Co²⁺ (0.07 Å) → La³⁺ (0.19 Å) → Sr²⁺ (0.27 Å). Notice that the appearance of Ce³⁺ cations ($r^{\text{VIII}} = 1.14 \text{ \AA}$) within the fluorite structure would change tendency: La³⁺ (0.02 Å) → Sr²⁺ (0.12 Å) → Co²⁺ (0.24 Å).

There are two features in the C 1s spectra of pure CeO₂, the single phase solid solutions Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-δ} and Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-δ}. Apart from the peak at 284.6 eV that corresponds to the adventitious carbon, the peak at 288.4–288.7 eV was observed in the C 1s spectra of CeO₂, Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-δ} and Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-δ}. The feature at 288.4–288.7 eV in pure and doped cerium oxides may be related to several functional groups or compounds containing Ce, C, O and/or Sr (only for Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-δ} and Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-δ}): carbonyl groups (C 1s BE = 288.1–288.3 eV) [53–55], Ce₂(CO₃)₃·8H₂O (C 1s BE = 288.7 eV) [56,57] or SrCO₃·(C 1s BE = 288.8 eV) [56,58]. Because of the strong differential charge observed for Sr 3d (~10 eV) and O 1s spectra (~10 eV), it is difficult to identify more precisely the origin of the features at 288.4–288.7 eV.

The Ce 3d spectra of the pure and multi-cation modified cerium oxides are complex (Fig. 3) resulting from the various initial and final states of Ce³⁺ and Ce⁴⁺ cations (Table 2). In general, the Ce 3d spectra can be individually deconvoluted into five pairs of 3d_{5/2} and 3d_{3/2} spin-orbit components (labelled as ν and u , respectively) describing the Ce⁴⁺ ↔ Ce³⁺ electronic transitions [18–23]. According to the literature [18–23], the four intense components ν (BE ~ 882.2 eV), u (BE ~ 900.8 eV), ν^{III} (BE ~ 898.1 eV), u^{III} (BE ~ 916.2 eV) as well as the two weaker

components ν^{II} (BE ~ 888.8 eV) and u^{II} (BE ~ 906.9 eV) can be attributed to Ce⁴⁺ cations. For Ce³⁺ cations, the ν^{I} (BE ~ 885.6 eV) and u^{I} (BE ~ 903.9 eV) components are more intense, whereas the ν_0 (BE ~ 880.6–881.4 eV) and u_0 (BE ~ 898.9–899.3 eV) components are noticeably weaker and sometimes their contributions in the Ce 3d spectrum can not be clearly distinguished, in particular at a high concentration of Ce⁴⁺ cations [23,26,30]. In pure and multi-cation doped cerium oxides calcinated at 1350 °C, one can distinguish the contribution of the ν^{I} and u^{I} peaks to the spectra, suggesting the presence of both Ce⁴⁺ (major fraction) and Ce³⁺ cations. The concentration of Ce⁴⁺ and Ce³⁺ cations in cerium oxide can be estimated as Eqs. (1)–(3) [23], where the [Ce³⁺] and [Ce⁴⁺] stand for the sums of the integrated peak areas related to their XPS signals respectively:

$$[\text{Ce}^{4+}] = \nu + \nu^{\text{II}} + \nu^{\text{III}} + u + u^{\text{II}} + u^{\text{III}} \quad (1)$$

$$[\text{Ce}^{3+}] = \nu_0 + \nu^{\text{I}} + u_0 + u^{\text{I}} \quad (2)$$

$$[\text{Ce}^{4+}] = [\text{Ce}^{4+}]/([\text{Ce}^{4+}] + [\text{Ce}^{3+}]) \quad (3)$$

The estimated ratio of Ce⁴⁺ and Ce³⁺ cations for pure and doped cerium oxides at the surface is presented in Table 1. Results obtained from the XPS measurement of CeO_{2-δ} on the different instruments show good correlation. In Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-δ} with a relatively low level of multi-cation doping (La, Sr, and Co), the [Ce⁴⁺]/[Ce³⁺] atomic ratio remains the same as in CeO₂, whereas a drastic increase in the surface concentration of Ce⁴⁺ cations is observed in Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-δ} (Table 1). One may assume that the dissolution of Co cations up to a certain level can stabilise Ce⁴⁺ cations due to the close values of the ionic radii and this could explain the increase in the surface concentration of Ce⁴⁺ cations in Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-δ}.

Fig. 3. Curve-fitted Ce 3d core level spectra of pure cerium oxide, Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-δ}, and Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-δ} single phase compositions.

Table 2Initial states and final states of Ce⁴⁺ and Ce³⁺ cations in the Ce 3d core level spectra [18,20].

Cations in Cerium oxides	Initial state	Final state	Peak components	
			Ce 3d _{5/2}	Ce 3d _{3/2}
Ce ⁴⁺ (CeO ₂)	Ce 3d ¹⁰ 4f ⁰ –O 2p ⁶	Ce 3d ⁹ 4f ² –O 2p ⁴	<i>v</i>	<i>u</i>
	Ce 3d ¹⁰ 4f ⁰ –O 2p ⁶	Ce 3d ⁹ 4f ¹ –O 2p ⁵	<i>v</i>	<i>u</i>
	Ce 3d ¹⁰ 4f ⁰ –O 2p ⁶	Ce 3d ⁹ 4f ⁰ –O 2p ⁶	<i>v</i>	<i>u</i>
	Ce 3d ¹⁰ 4f ¹ –O 2p ⁶	Ce 3d ⁹ 4f ¹ –O 2p ⁶	<i>v</i> ^l	<i>u</i> ^l
Ce ³⁺ (Ce ₂ O ₃)	Ce 3d ¹⁰ 4f ¹ –O 2p ⁶	Ce 3d ⁹ 4f ² –O 2p ⁵	<i>v</i> ₀	<i>u</i> ₀

3.2. Surface composition and surface states of Ce cations in the LSCC and LSMC composites consisting of the perovskite phase and modified cerium oxide

Both La_{0.6}Sr_{0.4}CoO₃ (LSC) and La_{0.8}Sr_{0.2}MnO₃ (LSM) perovskites exhibit rhombohedral symmetry, space group *R*3c (no. 167) [39,59,60]. A solubility limit of CeO₂ in the perovskite structure of the LSC and LSM is about 2 mol% [39], although a very weak peak, which is close to the {1 1 1} cubic reflection of CeO₂ (JCPDF 34-0394) [44], was observed in the XRD pattern of the LSMC02 recorded in the reflection mode [39]. The LSMC02 was considered as a nearly single phase composition. According to XRD, the LSCCx (*x* = 8–57 mol%) and LSMCx (*x* = 10–57 mol%) are two-phase compositions (Table 3). They are composed of the perovskite phase with rhombohedral symmetry (space group *R*3c, no. 167) and the modified cerium oxide with fluorite structure (space group *Fm*3m, no. 225). In contrast to the LSMCx (*x* = 10–57 mol%) composites, where the lattice parameter of cerium oxide is much closer to that for undoped CeO₂, a strong increase in the lattice parameter of cerium oxide was revealed in the LSCCx (*x* = 8–57 mol%) composites, suggesting the dissolution of La, Sr, and Co cations within the fluorite structure. The latest was confirmed by scanning electron microscopy in combination with an energy dispersive X-ray analysis (SEM/EDX) [61]. A non-linear change in the lattice parameters of the perovskite constituent in the LSCC series (Table 3) implies the variation in fractions of Ce, La, Sr and Co cations cross-dissolved at the phase interfaces.

Further we studied the surface compositions and chemical states of ions in the LSCC and LSMC composites fabricated at 1350 °C in air. Results obtained from the XPS survey spectra (Fig. 4) were compared with the nominal stoichiometry of the composites that was ascribed further in the text as “nominal stoichiometry” (Tables 4 and 5). According to XPS, the Sr surface concentration in the LSC, LSCC57, and LSMCx (*x* = 2–57) is slightly higher than expected, whereas it is lower in the LSCCx (*x* = 10–37) (Tables 4 and 5). In the single phase LSC and LSMC02, the [Sr]/[La] ratio is slightly higher compared to the nominal stoichiometry (Fig. 5a) that is typical of the perovskites with transition metal cations on the B-sites [36,38–40]. The same trend was observed

for the two-phase compositions in both LSCC and LSMC series. The [Co or Mn]/([La] + [Sr]) ratio is expected to be 1 (Fig. 5b). According to XPS, the [Mn]/([La] + [Sr]) atomic ratio is slightly less than 1 for the LSMC02 and remains the same with further increase in cerium oxide content in the LSMC series (*x* = 10–36). For the LSMC57, the [Mn]/([La] + [Sr]) atomic ratio was slightly higher than 1. In contrast, a complex trend was observed in the LSCC series. The surface concentration of Co cations in LSC is lower by about a factor of 3 than the expected value. On increasing the cerium oxide content (up to 8–37 mol%), the surface of the LSCC composites becomes enriched in Co by about a factor of 3–5 compared to the nominal stoichiometry. However, the surface concentration of Co cations in the LSCC57 drops and it is less by about a factor of two compared to the nominal ratio (Table 4 and Fig. 5b) independent of whether the measurements were carried out on the pellet with 92% rD or on the powders with different fabrication history (*S*_{BET} = 0.18–0.77 m²/g) [61]. This could be interpreted as redistribution of Co cations between the surface and bulk of crystallites.

The [Co or Mn]/[Ce] and ([La] + [Sr] + [Co or Mn])/[Ce] atomic ratios estimated from the nominal stoichiometry of the LSCC and LSMC composites change in a non-linear way with the increase in ceria content (Fig. 6). Similar trends were observed from the XPS measurements, but the surface concentration of Ce in the LSCCx and LSMCx composites (*x* = 8–37) was lower. For the LSCC composites, the difference between the estimated and measured by XPS values was stronger. The modified cerium oxide exists in the LSCCx and LSMCx composites (*x* = 8–37) as a secondary phase and seems to not spread over the surface of the perovskite grains since both [Co or Mn]/[Ce] and ([La] + [Sr] + [Co or Mn])/[Ce] atomic ratios were higher than the expected values. The measured and estimated ([La] + [Sr] + [Co or Mn])/[Ce] ratios are comparable only for nearly equimolar mixtures (LSCC57 and LSMC57).

Analysis of Ce 3d XPS core level spectra [23] showed that both Ce⁴⁺ (high fraction) and Ce³⁺ cations exist at the surface of grains and interfaces in the systems explored (Figs. 7 and 8). Although the measured surface concentration of Ce cations in the LSCC and LSMC series is comparable (Fig. 8a and b), a much higher fraction of Ce⁴⁺ cations seems to exist at the surface of grains in the LSCC series. Due to a low dissolution of Ce cations within the perovskite

Table 3

Lattice parameters of the perovskite phase and cerium oxide in the LSCC and LSMC series.

Composition	Perovskite (<i>R</i> 3c)			Cerium oxide (<i>Fm</i> 3m)	
	Lattice parameters <i>a</i> [Å]	<i>β</i> (°)	Cell volume <i>V</i> [Å] ³	Lattice parameter <i>a</i> [Å]	Cell volume <i>V</i> [Å] ³
LSC	5.4048(1)	60.327(1)	112.467(2)	–	–
LSCC10	5.4063(1)	60.380(1)	112.694(2)	5.4982(2)	166.212(18)
LSCC25	5.4096	60.398(1)	112.943(2)	5.4675(1)	163.441(5)
LSCC37	5.4143(1)	60.383(1)	113.203(3)	5.4640(1)	163.125(5)
LSCC57	5.4110(1)	60.351(1)	112.916(9)	5.4576(1)	162.557(5)
LSMC02	5.4826(9)	60.549(1)	117.962(3)	–	–
LSMC10	5.4820(7)	60.541(1)	117.920(1)	5.413(2)	158.6(2)
LSMC25	5.4801(5)	60.540(6)	117.793(17)	5.4135(6)	158.65(5)
LSMC57	5.4792(5)	60.552(1)	117.764(6)	5.4114(3)	158.47(2)
CeO ₂	–	–	–	5.4103(9)	158.37(5)

Fig. 4. Survey spectra of compositions in the (a) LSCC and (b) LSMC series.

Table 4
Comparison of the surface concentration of elements (at.%) derived from XPS and nominal stoichiometry for the LSC and two-phase compositions in the LSCC system.

Element	LSC		LSCC10		LSCC25		LSCC37		LSCC57	
	XPS ^a	Nominal	XPS ^a	Nominal	XPS ^a	Nominal	XPS ^a	Nominal	XPS ^a	Nominal
La	10.0	12	5.0	11.3	3.5	10	5.7	8.9	5.9	6.7
Sr	11.1	8	5.2	7.5	5.6	6.7	4.7	5.9	5.6	4.5
Co	6.0	20	36.4	18.7	25.8	16.7	31.7	14.8	6.1	11.1
Ce	0	0	1.3	2.1	1.6	5.6	3.1	8.7	8.2	14.8
O	72.9	60	52.1	60.4	63.5	61	54.8	61.7	74.2	62.9

^a Relative error is ±15%.

Table 5
Comparison of the surface concentration of elements (at.%) derived from XPS and nominal stoichiometry for the LSM, LSMC02 and two-phase compositions in the LSMC system.

Element	LSM		LSMC02		LSMC10		LSMC25		LSMC57	
	XPS ^a	Nominal	XPS ^a	Nominal	XPS ^a	Nominal	XPS ^a	Nominal	XPS ^a	Nominal
La	12.1	16	11.6	15.8	11.0	15	10.6	13.3	6.9	9.2
Sr	5.1	4	4.7	3.9	3.9	3.8	4.0	3.3	2.7	2.3
Mn	15.0	20	15.2	19.8	13.1	18.7	13.6	16.7	10.4	11.5
Ce	0	0	0	0.4	0.9	2.1	2.0	5.6	6.9	14.2
O	67.8	60	68.5	60.1	71.1	60.4	69.8	61.1	73.1	62.8

^a Relative error is ±15%.

structure (about 2 mol%), the changes observed in the Ce 3d spectra are thought to be related to the modified cerium oxide with fluorite structure. Stabilisation of Ce⁴⁺ cations in the LSCC series can be explained through the dissolution of Co cations (ionic radius of Co²⁺

is close to that of Ce⁴⁺ cations [47]) within the fluorite structure as it was discussed for the CeO₂-based single phase solid solutions (Section 3.1). The surface concentration of Ce⁴⁺ cations in the two-phase LSMC composites increases with the rise in ceria content,

Fig. 5. Atomic ratios of (a) [Sr]/[La] and (b) [Co or Mn]/([La] + [Sr]) derived from the XPS measurements in comparison with the nominal stoichiometry.

Fig. 6. Comparison of (a) [Co or Mn]/[Ce] atomic ratios and (b) ([La] + [Sr] + [Co or Mn])/[Ce] atomic ratios defined from the XPS spectra with the nominal stoichiometry of the LSCC and LSMC compositions.

but the $[\text{Ce}^{4+}]/[\text{Ce}^{3+}]$ ratio increases only slightly, suggesting the presence of a relatively high fraction of Ce^{3+} cations ($\sim 26\text{--}32\%$) across a wide concentration range. In contrast, Ce^{4+} cations dominate at the surface ($\sim 90\text{--}100\%$) in the composite oxide system $\text{Ce}_{1-x}\text{Mn}_x\text{O}_{2-\delta}$ and $\sim 20\text{--}30\%$ Ce^{3+} cations at the surface can be attained only for $\text{Au-Ce}_{1-x}\text{Mn}_x\text{O}_{2-\delta}$ composites with a high fraction of cerium cations ($x \leq 0.5$) [29]. The surface concentration of Ce^{4+}

cations in the two-phase LSCC composites increases also, but the highest $[\text{Ce}^{4+}]/[\text{Ce}^{3+}]$ ratio was attained for the LSCC37. About 19% Ce^{3+} cations exist at the surface of grains in the LSCC10. This value is lower (8–12%) in the LSCCx ($x = 25\text{--}57$) composites. A low surface fraction of Ce^{3+} cations was reported for $(100 - x)\text{Co}_3\text{O}_4 - x\text{CeO}_2$ composite oxides with a high fraction of cerium oxide ($x \geq 50 \text{ mol}\%$) [30].

Fig. 7. Curve-fitted Ce 3d core level spectra measured for the two phase (a) LSCC and (b) LSMC compositions.

Fig. 8. (a,b) The total Ce surface atomic concentration, atomic concentration of Ce^{4+} and Ce^{3+} cations derived from the XPS survey spectra of the LSCC and LSMC compositions, respectively, in comparison with the stoichiometry; and (c) $[\text{Ce}^{4+}]/[\text{Ce}^{3+}]$ atomic ratios in the LSCC and LSMC series defined from the Ce 3d core level spectra.

Fig. 9. Curve-fitted (a) O 1s, Co 2p_{3/2}, and Sr 3d spectra of the compositions in the LSCC system and (b) O 1s, Mn 2p_{3/2}, and Sr 3d spectra of the compositions in the LSMC system.

3.3. Surface states of Co and Sr cations, carbon, and oxygen ions in the LSCC composites

The Co 2p_{3/2} core level spectrum of the LSC is asymmetric and can be situated at 779.8 eV (Fig. 9a), representing Co³⁺ cations [55,62]. One could extract a small shoulder on the high binding energy side of the Co 2p_{3/2} spectrum. A comparison of the XPS spectra (including shake-up features) reported in the literature for La_{1-x}Sr_xCoO_{3±δ}, SrCo⁴⁺O₃, Co oxides and hydroxides [36,39,62–66] implies that a small peak at 782.6 eV could be related to the presence of Co⁴⁺ cations. This correlates with the result of the thermal gravimetric analysis showing the average oxidation state of Co cations in the LSC as +3.4 [39]. The Co 2p_{3/2} spectra of the LSCC10 and LSCC37 have the same shape as for LSC, but a shift towards low binding energy was observed, indicating the presence of a certain fraction of Co²⁺ cations at the surface. Notice that the Co 2p_{3/2} peak in LaCoO₃ reduced in H₂ at 450 °C is centred at 778.0 eV [66]. The presence of Co²⁺ cations at the surface may be interrelated with the dissolution of Co cations into the fluorite structure of the modified cerium oxide. However, the Co 2p_{3/2} spectra of the LSCC57 are broader compared to the LSC (Fig. 9a), indicating the involvement of Co cations in a local disorder taking place at or near the surface region.

The O 1s spectra recorded for the LSC and LSCCx composites are complex and contain several contributions that vary with an increasing cerium oxide content (Fig. 9a). The O 1s components at a lower binding energy BE ~ 528.2 eV (LSC and LSCC10) and 528.6 eV (LSCC37) can be assigned to the lattice oxygen [36,55,64]. It could be interpreted as similar mobilities of the lattice oxygen in the LSC and LSCC10, indicating an absence of obstructions for oxygen transport in the area directly adjacent to the phase interfaces and across the interface {modified perovskite/modified ceria}. In the LSCC57, the O 1s components at BE ~ 528.2–528.6 eV was not revealed, but the peak at BE ~ 529.4 eV was observed and can be assigned to the lattice oxygen in pure or doped CeO₂ [24,55] and to SrO species on the surface of perovskites [36]. The O 1s component at ~530.6–530.8 eV (LSC, LSCC10, and LSCC37) could be associated with O–Co surface species in perovskites [36] and this component is strong for the LSC, LSCC10, and LSCC37 compositions. The O 1s

components at higher binding energies are slightly different for the LSCCx (x = 10–57) composites and LSC. The O 1s component at 533.2 eV in the LSC could be ascribed to the chemisorbed dioxygen species (BE ~ 532.7–533.5 eV), whereas those at 531.9–532.4 eV in the LSCCx (x = 10–57) could be related to O–Ce surface species.

The Sr 3d spectra recorded for the LSC and LSCCx (x = 10–57) composites contain the two spin–orbit components 3d_{5/2} and 3d_{3/2} (Fig. 9a). The two contributions (at lower and higher binding energies) can be distinguished. The contributions at lower binding energies (130.0–130.7 eV for 3d_{5/2} and 131.8–132.5 eV for 3d_{3/2}) is difficult to assign as it is in general is lower by about 1 eV compared to the values usually reported for the Sr cations in the perovskite lattice (Sr_{latt}) [36]. A peak at a low binding energy of 130.5 eV was reported in [67], but authors were not able to identify the origin of this peak. The features observed at higher binding energy in the LSCC10 (131.8 eV for 3d_{5/2} and 133.6 eV for 3d_{3/2}) could be attributed to the Sr cations in the perovskite lattice (Sr_{latt}) [36]. In the LSC, LSCC37, and LSCC57, the second doublet is located at higher binding energies (132.4–132.8 eV for 3d_{5/2} and 134.2–134.6 eV for 3d_{3/2}) than for the LSCC10 and could be attributed to the Sr surface states (Sr_{surf}). To identify the origin of the Sr_{surf} we compare the BE of Sr 3d, O 1s, and C 1s features. The values of the Sr 3d, O 1s, and C 1s binding energies (in eV) reported in the literature for different Sr, O, and C containing compounds are summarised in Table 6 [36,57,58,68,69]. The feature at 288.5 eV was clearly observed in the C 1s spectra of the LSC perovskite and LSCC57 composite, thereby implying the possibility of carbonate formation. Notice, that Sr 3p spectra (BE ~ 268–269 eV for Sr 3p_{3/2} and BE ~ 278–279 eV Sr 3p_{1/2} [70]) are very close to the C 1s region, making an apparent impression on the existence of several peaks in the C 1s spectra. The Sr_{surf} features revealed for the LSC (BE = 132.8 eV for 3d_{5/2} and 134.6 eV for 3d_{3/2}) could be assigned to Sr(OH)₂ [68], SrCO₃ [58], and SrO₂ [68] (Table 6). The O 1s spectrum of the LSC is complex and the feature at 530.8 eV is strong (Fig. 9a and Table 6), suggesting the coexistence of all three phases: Sr(OH)₂ [68], SrCO₃ [58], and SrO₂ [68]. It seems that SrO surface phase could form in the LSCC37 and LSCC57 composites (BE = 132.4–132.5 eV for 3d_{5/2} and 134.2 eV for 3d_{3/2}). Although the feature at 528.2 eV is not dominant in the O 1s spectra of the LSCC37 and LSCC57 composites (Fig. 9a), one can

Table 6

Comparison of the Sr 3d, O 1s, and C 1s binding energies (in eV) reported in the literature for different Sr and O containing compounds.

Phase	Binding energy, eV				Ref.
	Sr 3d		O 1s	C 1s	
	3d _{5/2}	3d _{3/2}			
Sr(OH) ₂	132.8	134.5	530.5	–	[68]
SrCO ₃	132.7	–	530.9	288.8 eV	[58]
SrCO ₃ (on the surface of perovskites)	134.0	–	532.0	288.5	[36]
SrO (on the surface of perovskites)	133.0	–	529.8	–	[36]
SrO ₂	132.7	134.6	531.1 eV	–	[68]
SrO	132.4	134.0	528.2 eV	–	[69]
Ce ₂ (CO ₃) ₃ ·8H ₂ O	–	–	531	288.7 eV	[57]

distinguish its contribution through the formal fitting procedure. For the LSCC57, in addition, one may assume the existence of SrCO₃ [58] due to the feature at 288.5 eV in the C 1s spectrum although there is some difference in the Sr 3d_{5/2} position ($\Delta = 0.3$ eV). The formation of Ce₂(CO₃)₃-based phase [57] at the surface of grains in the LSCC57 should be also taken into consideration (Table 6).

3.4. Surface states of Mn and Sr cations, carbon, and oxygen ions in the LSMC composites

The Mn 2p_{3/2} and O 1s spectra measured for the LSMC composites are presented on Fig. 9b. The Mn 2p XPS spectra cannot be easily analysed through a simple fitting procedure concerning the contribution of Mn²⁺, Mn³⁺, and Mn⁴⁺ compounds because of the multiple splitting of the Mn 2p spectra of individual Mn²⁺, Mn³⁺, and Mn⁴⁺ cations [71,72]. However, we compared the measured XPS spectra for the LSMC02 and LSMCx ($x = 10$ –57) composites with the XPS spectra for LaMn³⁺O₃ with oxidation state defined from the neutron diffraction and studies of the magnetic properties [62]. The Mn 2p_{3/2} peak of LaMn³⁺O₃ can be centred at 640.4 eV, implying the presence of both Mn³⁺ and Mn⁴⁺ cations in the LSMC02 and LSMCx ($x = 10$ –57) composites. In the LSMCx ($x = 10$ –57), the Mn 2p_{3/2} spectra have the same shape as for the LSMC02 although a very slight shift (~ 0.2 eV) to a lower banding energy was observed in their core level spectra, suggesting a slight decrease in the fraction of Mn⁴⁺ cations on the B-sites within the perovskite structure.

The O 1s spectra measured for the LSMC02 and LSMCx ($x = 10$ –57) composites also have several components. The existence of the feature at 529.4 eV in the O 1s spectra and its increase on the rise in CeO₂ content (Fig. 9b) implies that it could be assigned to both lattice oxygen in Mn containing perovskite phase [73] and lattice oxygen in CeO₂ or mixed oxides [23,55]. A higher value of BE for the lattice oxygen in the LSMC series compared to those in the LSCC series is reasonable as the LSM has lower ionic conductivity than the LSC [74,75]. The O 1s features at 530.5–530.7 eV may be associated with O–Mn surface species in perovskites. Notice that this component is much less for the LSMC composites than for the LSC and LSCCx ($x = 10$ –37) compositions that correlates with a higher value of oxygen surface exchange coefficient in La_{0.5}Sr_{0.5}CoO₃ (by ~ 4 orders of magnitude at $\sim 750^\circ\text{C}$) compared to La_{0.5}Sr_{0.5}MnO₃ [76]. The features at ~ 531.6 –531.8 eV and 533.0–533.3 eV, respectively, could be attributed to the O–Ce surface species and the chemisorbed dioxygen species [36].

The Sr 3d spectra recorded for the LSMC02 and LSMCx ($x = 10$ –57) composites contain the two spin–orbit components 3d_{5/2} and 3d_{3/2} (Fig. 9b). The two contributions (at lower and higher binding energies) can be distinguished. The contributions at lower binding energies (131.6–131.8 eV for 3d_{5/2} and 133.4–133.6 eV for 3d_{3/2}) are close to the Sr 3d features reported for La_{0.8–x}Ce_xSr_{0.2}MnO₃ [77] and could be assigned to the Sr cations in the perovskite lattice (Sr_{latt}). The features observed at higher binding energies (133.2–133.4 eV for 3d_{5/2} and 135.0–135.2 eV for

3d_{3/2}) can be attributed to the Sr surface states (Sr_{surf}). To identify the origin of the Sr_{surf} we also compare the BE of features in the Sr 3d, O 1s, and C 1s spectra obtained in the present study with those reported in the literature for different Sr, O, and C containing compounds (Table 6). The BE values of the Sr_{surf} in the LSMC02 and LSMCx ($x = 10$ –57) composites differ from those reported for SrCO₃ as individual phase [58] and for SrCO₃ states on the surface of perovskites [36] (Table 6). The BE values of the Sr_{surf} in the LSMCx ($x = 2$ –57) are closer to that reported for the SrO states on the surface of perovskites [36]. Their existence could be confirmed by the feature at 529.8 eV in the O 1s spectra [36] of the LSMC compositions. In fact, a strong feature was observed at 529.4 eV in the O 1s spectra of the LSMCx ($x = 2$ –57) (Fig. 9b) and was assigned to both lattice oxygen in perovskite phase [73] and lattice oxygen in CeO₂ or mixed oxides [23,55]. The feature at 529.8 eV is not obvious spectroscopically, but its contribution could be distinguished through the formal curve-fitting solution, suggesting the existence of strontium in the form of the SrO species on the surface of perovskite phase.

The C 1s spectra of the LSMC02 and LSMCx ($x = 10$ –57) composites contain the two components at 284.6 eV and at 288.6–289.0 eV. The least component may be related in general to several carbon containing phases (Table 6): Ce₂(CO₃)₃·8H₂O (C 1s BE = 288.7 eV [57]) and SrCO₃ (C 1s BE = 288.8 eV [58]). Strong features at 132.7 eV or 134 eV in the Sr 3d_{5/2} spectra of the LSMCx ($x = 2$ –57) was not observed. Therefore, one may assume the existence of Ce₂(CO₃)₃-based phase at the surface of grains and crystallites in the LSMC02 and LSMCx ($x = 10$ –57) composites. In this case, the feature at 531.0 eV should be observed in the O 1s spectra of the LSMCx ($x = 2$ –57) compositions [57]. The very strong features at ~ 531.6 –531.8 eV were initially attributed to the O–Ce surface species, but the contributions at 531.0–531.4 eV could be distinguished through the formal fitting procedure and support the above mentioned assumption.

4. Conclusions

The surface composition and chemical states of ions were studied in the single phase CeO₂-based solid solutions, in the La_{0.6}Sr_{0.4}CoO₃–CeO₂ (LSCC) and La_{0.8}Sr_{0.2}MnO₃–CeO₂ (LSMC) composite systems. The composite systems were prepared through reactive sintering at 1350 °C under air. The surface segregation of Sr was revealed for the Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2–δ} and Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2–δ} single phase solid solutions with fluorite structure, La_{0.6}Sr_{0.4}CoO₃ and LSMC02 perovskites, LSCC57 and LSMCx ($x = 10$ –57) composites consisting of the phases with perovskite and fluorite structures. La and Co cations were not found on the surface in the single phase solid solutions, suggesting the complete dissolution of these cations into the fluorite structure. The surface strontium seems to exist in the form of SrO on the surface of the perovskite phase in the LSMCx ($x = 10$ –57) composites. In the LSCC system, the surface state of Sr is more diverse.

$\text{Sr}(\text{OH})_2$, SrCO_3 , and SrO phases could coexist at the surface in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ perovskite. SrO surface phase seems to dominate in the LSCC37 composite. In addition to SrO , SrCO_3 may form at the surface in the LSCC57 composite. The surfaces of grains and interfaces in the LSCC and LSMC systems are depleted in cerium although both Ce^{4+} and Ce^{3+} cations were revealed. The surface fraction of Ce^{4+} cations is higher by about a factor of two in the two phase LSCC compositions that could be explained through the dissolution of Co cations into the fluorite structure. The Mn surface concentration in the LSMCx ($x=2\text{--}37$ mol%) compositions is slightly less compared to the nominal stoichiometry. Both Mn^{4+} and Mn^{3+} cations are present at the surface in the LSMC02 and their ratio remains nearly the same across a wide concentration range ($x=10\text{--}57$ mol%). In the LSCCx ($x=8\text{--}40$ mol%), however, the presence of modified cerium oxide as a secondary phase results in a strong enrichment of the surface by Co cations. The O 1s spectra recorded for the LSCC and LSMC compositions are complex and contain several contributions. In contrast to the LSMC series, much stronger evolution of the O 1s XPS spectra was revealed in the LSCC series, reflecting the variation in origin of the oxygen species involved in the surface processes. The $\text{Ce}_2(\text{CO}_3)_3$ -based phase exists at the surface of grains and crystallites in the LSMC02, LSMCx ($x=10\text{--}57$) and LSCC57 composites.

Acknowledgment

The authors gratefully acknowledge Prof. J.T.S. Irvine for his kind support.

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