



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

Elena Yu Konysheva<sup>a,b,\*</sup>, Stephen M. Francis<sup>a</sup>

<sup>a</sup> School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK

<sup>b</sup> Ural Federal University, 51 Lenin Av., Ekaterinburg 620083, Russia

## 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 CeO<sub>2</sub>-based solid solutions and in the two phase (100 - x)La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3</sub>-xCeO<sub>2</sub> (LSCCx) and (100 - x)La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub>-xCeO<sub>2</sub> (LSMCx) composites. The well-resolved Ce 3d<sub>5/2</sub> and Ce 3d<sub>3/2</sub> spin-orbit components were determined to study the Ce<sup>4+</sup> to Ce<sup>3+</sup> electronic transition at the surface. The surface of the LSCCx and LSMCx (x = 8–40 mol%) composites is depleted in cerium. Both Ce<sup>4+</sup> and Ce<sup>3+</sup> cations were revealed. The surface fraction of Ce<sup>4+</sup> cations increases with the rise in CeO<sub>2</sub> 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<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3</sub>, CeO<sub>2</sub>-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 CeO<sub>2</sub> content and a chemical origin of the transition metal cations on the B-site in the perovskite structure. The Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>-based phase seems to exist at the surface of grains and crystallites in the LSCC57 and LSMC composites.

© 2012 Elsevier B.V. All rights reserved.

## 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 (Ce<sup>3+</sup> ↔ Ce<sup>4+</sup>) [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 oxidations states [17]. The surface chemical states of Ce cations have been explored so far preferably for undoped CeO<sub>2</sub> [18–23], CeO<sub>2</sub>-based solid solutions [24–26], and composites composed of CeO<sub>2</sub> 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 CeO<sub>2</sub>/Me(Me<sub>x</sub>O<sub>y</sub>) 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<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3</sub> or La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub>) 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

\* Corresponding author. Present address: Department of Chemistry, Xi'an Jiaotong-Liverpool University, Suzhou Dushu Lake Higher Education Town, Suzhou Industrial Park, Suzhou, Jiangsu Province 215123, China. Tel.: +86 512 88161435; fax: +86 512 81880440.

E-mail addresses: [elena.konysheva@gmail.com](mailto:elena.konysheva@gmail.com), [elena.konysheva@xjtlu.edu.cn](mailto:elena.konysheva@xjtlu.edu.cn) (E.Y. Konysheva).

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  $Mn^{(4+/3+/2+)}$  and  $Co^{(4+/3+/2+)}$  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  $La_{0.6}Sr_{0.4}CoO_3$  (LSC) and  $La_{0.8}Sr_{0.2}MnO_3$  (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  $1000^\circ C$  for 5 h to remove adsorbed water. Further, compositions in the following series  $(100-x)LSC \cdot xCeO_2$  (LSCCx) with  $x=8, 10, 25, 37, 57$  mol% and  $(100-x)LSM \cdot xCeO_2$  (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  $1350^\circ C$  for 5 h. The initial phases (LSC, LSM, and  $CeO_2$ ) were also calcined under the same conditions. The  $Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-\delta}$  and  $Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-\delta}$  single phase solid solutions were fabricated through mixing of  $CeO_2$  with 5 and 10.6 mol%  $La_{0.6}Sr_{0.4}CoO_3$ , respectively, followed by calcination in air at  $1350^\circ C$  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  $K_{\alpha}$  ( $h\nu=1486.4$  eV) radiation and a XPS 5600 spectrometer (Physical Electronic, USA) for the LSMC system using monochromatic Al  $K_{\alpha}$  ( $h\nu=1486.4$  eV) radiation. Data were collected at a take-off angle of  $45^\circ$ , 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  $K_{\alpha}$  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  $0.1^\circ$ , 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.

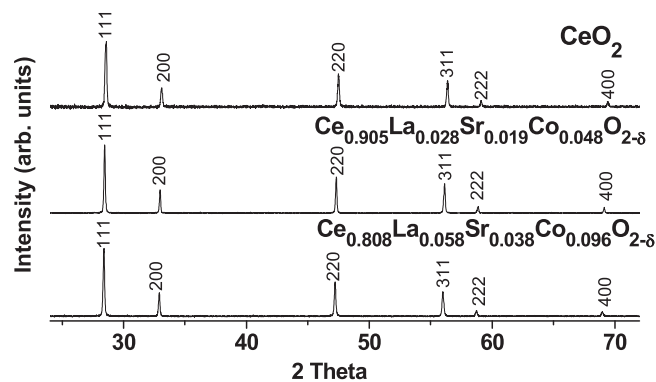


Fig. 1. XRD patterns of undoped  $CeO_2$ ,  $Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-\delta}$ , and  $Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-\delta}$  single phase compositions.

## 3. Results and discussion

### 3.1. Pure and modified cerium oxides with fluorite structure calcined at $1350^\circ C$ in air

The XRD patterns of pure and doped cerium oxide are presented in Fig. 1. Pure  $CeO_2$ , the single phase solid solutions  $Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-\delta}$  and  $Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-\delta}$  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  $Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-\delta}$  and  $Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-\delta}$  [46]. Fig. 2 illustrates the survey spectra of pure and multi-cation doped cerium oxides after calcination in air at  $1350^\circ C$ . 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  $Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-\delta}$  and  $Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-\delta}$  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

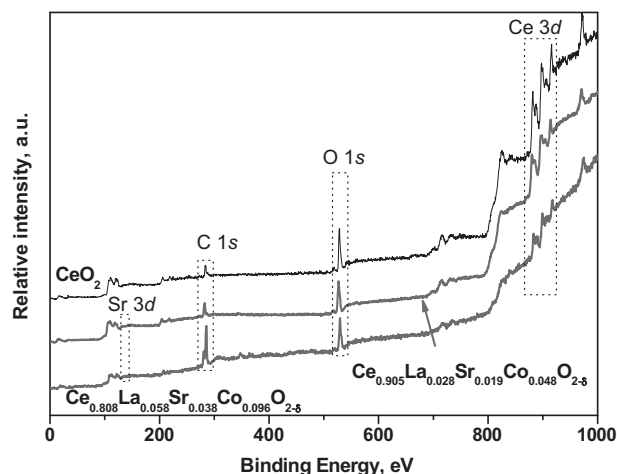


Fig. 2. Survey spectra of undoped  $CeO_2$ ,  $Ce_{0.905}La_{0.028}Sr_{0.019}Co_{0.048}O_{2-\delta}$ , and  $Ce_{0.808}La_{0.058}Sr_{0.038}Co_{0.096}O_{2-\delta}$  single phase compositions.

Download English Version:

<https://daneshyari.com/en/article/5360659>

Download Persian Version:

<https://daneshyari.com/article/5360659>

[Daneshyari.com](https://daneshyari.com)