Exsolution of Nickel Nanoparticles from Mixed-Valence Metal Oxides: A Quantitative Evaluation by Magnetic Measurements

Tinti, Victor B.; Marani, Debora; Ferlauto, Andre S.; Fonseca, Fabio Coral ; Esposito, Vincenzo; Zanetti De Florio, Daniel

Published in:
Particle & Particle Systems Characterization

Link to article, DOI:
[10.1002/ppsc.201900472](https://doi.org/10.1002/ppsc.201900472)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Tinti, V. B., Marani, D., Ferlauto, A. S., Fonseca, F. C., Esposito, V., & Zanetti De Florio, D. (2020). Exsolution of Nickel Nanoparticles from Mixed-Valence Metal Oxides: A Quantitative Evaluation by Magnetic Measurements. *Particle & Particle Systems Characterization*, 37(2), [1900472]. <https://doi.org/10.1002/ppsc.201900472>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Particle and Particle Systems Characterization

Exsolution of nickel nanoparticles from mixed-valence metal oxides: a quantitative evaluation by magnetic measurements

--Manuscript Draft--

Manuscript Number:	
Article Type:	Full Paper
Corresponding Author:	Daniel Zanetti de Florio Universidade Federal do ABC Santo André, SP BRAZIL
Corresponding Author E-Mail:	daniel.florio@ufabc.edu.br
Order of Authors:	Daniel Zanetti de Florio, PhD Victor Tinti Debora Marani Andre Ferlauto Fabio Fonseca Vincenzo Esposito
Keywords:	exsolution; nanoparticles; magnetic measurements
Section/Category:	
Abstract:	We here demonstrate a fast and accurate experimental method to assess the fraction of exsolved metallic nanoparticles using magnetic measurements. As a benchmark, we use nanometric metallic nickel exsolved from $(\text{La}_{1-x}\text{Sr}_x)(\text{Cr}_{1-y}\text{Ni}_y)\text{O}_{3-\delta}$ for its high relevance as solid oxide fuel cell component. The method is based on the difference in magnetic response of the exsolved metallic nickel (ferromagnetic) and Sr-doped lanthanum chromite ceramic matrix (paramagnetic). The exsolved nickel results in coherent nanoparticles pinned on the surface of the Sr-doped lanthanum chromite ceramic matrix, as evidenced by electron microscopy analyses. The results obtained indicate the procedure as a fast and sensitive method to study the exsolution of ferromagnetic nanoparticles.
Suggested Reviewers:	Ziqi Sun Queensland University of Technology ziqi.sun@qut.edu.au Scott Barnett Northwestern University s-barnett@northwestern.edu
Opposed Reviewers:	
Author Comments:	
Additional Information:	
Question	Response
Please submit a plain text version of your cover letter here.	November the 28th 2019 Dear Professor Mary De Vita, Ph.D. Particle & Particle Systems Characterization Editor-in-Chief Please, find enclosed the manuscript entitled "Exsolution of nickel nanoparticles from mixed-valence metal oxides: a quantitative evaluation by magnetic measurements" to

	<p>be considered for publication as Full Paper on Particle & Particle Systems Characterization.</p> <p>Exsolution has recently emerged as a powerful alternative to produce nanoparticles of catalytic metals. The fact that exsolved nanoparticles are in a chemical equilibrium with their substrates provides great advantages in terms of limited coarsening and lack of morphological or structural deactivation of the catalysis. Moreover, the exsolution concept opens the possibility of catalyst regeneration by solution/exsolution cycles. In particular, exsolution of Ni nanoparticles have attracted great interest for a wide range of applications including catalysis, biomedical devices, magnetic inks, advanced filters, and especially for electrochemical energy devices such as solid oxide electrochemical cells. Despite these compelling advantages, research on nanoparticles exsolution is still in its infancy. Because of intrinsic limitations of the structural and chemical methods generally used on these materials, the quantitative characterization of exsolved metal nanoparticles remains a challenge, especially at low concentrations. These limitations hinder a deeper understanding of exsolving mechanisms and compromises the reproducibility in application studies that require low metal concentrations.</p> <p>In the present work, we demonstrate that magnetic measurements can be used to quantify the fraction of exsolved Ni nanoparticles even at a relatively very low fraction (~0.02 wt%). Our result can provide insights in the exsolving mechanisms which are still not completely understood. We believe that this work entirely fits the scope of Particle & Particle Systems Characterization because it is based on the synthesis-characterization-properties relations of nanoscale materials.</p> <p>On behalf of the co-authors, I declare that the work here described is an original research that has not been published previously, and it is not under consideration for publication elsewhere, in whole or in part.</p> <p>Sincerely</p> <p>Prof. Daniel Zanetti de Florio, Ph.D. UFABC Associate Professor</p>
Do you or any of your co-authors have a conflict of interest to declare?	No. The authors declare no conflict of interest.

**Exsolution of nickel nanoparticles from mixed-valence metal oxides: a quantitative
evaluation by magnetic measurements**

*Victor B. Tinti¹, Debora Marani¹, Andre S. Ferlauto¹, Fabio C. Fonseca², Vincenzo
Esposito³, Daniel Z. de Florio¹*

¹ Federal University of ABC, CECS, Santo André, SP, Brazil

² Nuclear and Energy Research Institute, CCCH, São Paulo, SP, Brazil

³ DTU Energy, Roskilde, Denmark

ABSTRACT

We here demonstrate a fast and accurate experimental method to assess the fraction of exsolved metallic nanoparticles using magnetic measurements. As a benchmark, we use nanometric metallic nickel exsolved from $(\text{La}_{1-x}\text{Sr}_x)(\text{Cr}_{1-y}\text{Ni}_y)\text{O}_{3-\delta}$ for its high relevance as solid oxide fuel cell component. The method is based on the difference in magnetic response of the exsolved metallic nickel (ferromagnetic) and Sr-doped lanthanum chromite ceramic matrix (paramagnetic). The exsolved nickel results in coherent nanoparticles pinned on the surface of the Sr-doped lanthanum chromite ceramic matrix, as evidenced by electron microscopy analyses. The results obtained indicate the procedure as a fast and sensitive method to study the exsolution of ferromagnetic nanoparticles.

INTRODUCTION

Nanomaterials are increasingly applied in a number of key technologies [1,2]. Eminent examples of the strategic use of nanomaterials include biomedical devices [3], inks [4,5], advanced filters [6] and semiconductors [7]. The wide diffusion of the nanomaterials is mainly due to their unique features such as the nano-confinement, high surface-to-volume ratio, and a large specific surface area [1,8]. In catalysis, an extensive reactive surface area allows for a significant increment of the active sites and of their exposure to the reactants [8,9]. Typically, to maximize the exposed surface area and stabilize the nanoparticles against agglomeration, catalysts are dispersed over adequate supports, that can be either inert or can participate in the catalytic process [10–12]. The large majority of supported-nanoparticles are prepared by deposition methods (*e.g.* impregnation) that are very simple, but enable a limited control over critical aspects such as an efficient dispersion of the catalyst [11]. In addition, the prolonged exposure to critical environmental (industrial) conditions (*e.g.* high temperature) and in the presence of contaminants (*e.g.* carbon) leads to the deactivation of the catalysts by either agglomeration or coking [10,11,13].

To mitigate the deactivation phenomena, a post-growth procedure, *i.e.* the redox exsolution, has recently emerged as a reasonable alternative [14–17]. In this route, the catalyst is dissolved as cation into a hosting lattice to produce a solid solution and then exsolved to the surface as socked nanoparticles under reducing atmosphere [10,15,18]. The resulting exsolved nanoparticles have been demonstrated to be more resistant to agglomeration, coarsening, and carbon deposition [10,14,17]. The strategy has been successfully applied to prepare socked metallic nano-catalysts from various doped-perovskites [10,14,16,18,19]. Indeed, the perovskite structure offers an ideal synthetic platform due to its exceptional structural and compositional flexibility [20]. As compared to traditional techniques such as impregnation, the exsolution produces a modest mass fraction of metallic particles [11]. This is mainly associated with the solubility limit of any dopant into a hosting lattice. Yet, high doping ratios might destabilize the matrix and compromise the thermal and chemical stability of the perovskite substrate.

In this context, a precise quantitative analysis of the exsolved nanoparticle is a challenging task. The traditional techniques fail in providing reliable quantitative analysis. For instance, X-ray diffraction, commonly used to determinate and quantifies phases [21,22], is inefficient for small mass fractions ($< 1\%$ in weight) [22,23]. Scanning (SEM) and Transmission Electron Microscopy (TEM) provide detailed information about

the size and distribution of nanoparticles [24] and have been commonly used to characterize exsolved nanoparticles [16,19,25,26]. Yet, microscopy-based techniques are limited to a very small volume of sample, which demands time-consuming procedures to ensure accurate analyses [10].

In this study, we propose an approach based on magnetic properties for quantitative analysis of the mass fraction of exsolved nanoparticles. Magnetic analyses are relatively fast, very precise and the measurement reflects the properties of the whole sample, thus being reproducible and reliable [27]. Such an approach is based on the different magnetic properties of exsolved nanoparticles as compared to the ceramic matrix, making possible the identification of two distinct magnetic contributions. A similar approach was already used in literature to quantify a phase in a steel alloy [27]. Estimation of the mass fraction for the exsolved nanoparticles is then achieved by analyzing the magnitude of the magnetization. However, magnetic data can be complex, with several transitions and intricate behaviors, being necessary a deep knowledge of the magnetic properties of the components under analysis. Also, magnetic measurements are susceptible to unique interferences, like demagnetization factor and anisotropy [28], being a source of errors.

Thus, the materials selected are nickel as the exsolved nanoparticle and strontium-doped lanthanum chromite as the perovskite host. Nickel is selected because of its relevance as a catalyst in many applications [10,29], and Sr-doped lanthanum chromite exhibits thermal stability at high temperatures ($>1600\text{ }^{\circ}\text{C}$) both in oxidizing and reducing atmospheres to allow exsolution heat treatments without significant changes [30,31]. Moreover, nickel is a canonical ferromagnetic, whereas Sr-doped $\text{LaCrO}_{3-\delta}$ is paramagnetic above $\sim 7\text{ }^{\circ}\text{C}$ [32], with a significantly weaker and distinct magnetic behavior.

EXPERIMENTAL

Materials with compositions $(\text{La}_{1-x}\text{Sr}_x)(\text{Cr}_{1-y}\text{Ni}_y)\text{O}_3$, with $x = 0.1$, and 0.2 , and $y = 0$, 0.1 , and 0.2 were prepared via a chemical route based on the Pechini method [33,34].

All starting chemicals were reagent grade ($\geq 99.9\%$) by Sigma-Aldrich: lanthanum nitrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, strontium nitrate $\text{Sr}(\text{NO}_3)_2$, chromium nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, citric acid (CA) and ethylene glycol (EG). CA and EG were used to promote the complexation of the metallic cations and polymerization of the chelates, respectively. The solvent used to dissolve the nitrates was ultrapure water (Milli-Q[®] Type 1). The stoichiometric amount of each salt was dissolved in water with CA, and

1 the solution was kept under stirring at 80 °C for 2 hours. After the addition of EG, the
2 temperature was raised to 180 °C to promote the polymerization. The temperature was
3 kept stable until the formation of a black and brittle polymeric resin [35], which was
4 manually milled to a black fine powder using an agate mortar.
5

6
7 Thermogravimetry (TG) experiments (LABSYS EVO STA, Setaram) were
8 conducted to determine the decomposition temperature of the organic compounds and the
9 crystallization of the desired phase. The samples were heated from room temperature to
10 1600 °C at a rate of 10 °/min in an alumina crucible under synthetic airflow (125 ml/min).
11 According to the TG results, the materials were then calcinated at 1000 °C for 1 hour to
12 ensure the complete removal of the organics and the formation of the desired phase.
13
14

15
16 In order to promote the exsolution of Ni, the as-prepared samples were thermally
17 treated in reducing conditions. Two heat treatments were carried out for the reduction of
18 samples: i) a first one at 750 °C, which is higher than the temperature required to reduce
19 NiO to Ni (usually ~300 °C) [36], but lower than the temperature typically used to
20 promote exsolution; and ii) at 850 °C, which is commonly used for exsolution [10,16,26].
21 Both reducing treatments were carried out for 9 hours in a tubular furnace with a flow of
22 50 ml/min of pure ($\geq 99.999\%$) hydrogen.
23
24

25
26 All samples were characterized by X-ray diffraction (XRD, D8 Focus-Bruker AXS)
27 to determine the structure and phases. The XRD analysis was performed in the 2 θ degree
28 range varying from 20° to 60° with a step length of 0.05° at a rate of 1°/min, using CuK α
29 radiation with the equipment operating at 40 kV and 40 mA.
30
31

32
33 A magnetic properties measurement system (MPMS) by Quantum Design equipped
34 with a vibrating sample magnetometer (VSM) and a superconducting quantum
35 interference device (SQUID) was used for magnetization measurements as a function of
36 the applied magnetic field (MxH) [37]. Magnetic measurements were performed in both
37 as-prepared samples and after thermal treatments in reducing conditions to observe the
38 effect of Ni exsolution on the magnetic properties. The MxH runs were performed at 117
39 °C, which is below the Curie temperature of Ni (~357 °C) and above the Néel transition
40 temperature of LaCrO $_{3-\delta}$ (~7 °C) to maximize the response of exsolved ferromagnetic Ni
41 and to minimize possible influences from the perovskite matrix.
42
43

44
45 The morphology of the samples was studied using TEM (Transmission Electron
46 Microscopy – HRTEM JEM 2011, JEOL) and FESEM (Field Emission Scanning
47 Electron Microscopy – FESEM JMS-6701F, JEOL).
48
49

RESULTS AND DISCUSSION

X-rays diffraction patterns reveal that all samples have the orthorhombic phase of the lanthanum chromite with *Pnma* space group (Figure 1) (ICSD #51191) [18,32,38]. Nickel solubility limit in $\text{LaCrO}_{3-\delta}$ was reported to be close 20 at.%; nevertheless, no diffraction peaks of NiO are detected in the patterns of the investigated samples [31,38]. Within the accuracy of XRD, the experimental data indicate that Ni substituted Cr in the as-prepared chromite lattice rather than segregated as NiO. Moreover, XRD patterns of both as-prepared (Figure S1) and reduced (Figure 1a and 1b) samples are comparable, confirming the stability of the Sr-doped $\text{LaCrO}_{3-\delta}$ at high temperature under both oxidizing and reducing environments [31,38].

It is not possible to detect diffraction peaks related to metallic nickel for the samples subjected to reducing treatments (Figure 1a and 1b). This is expected because the exsolution process results in relatively low weight fraction of metallic nanoparticles (typically under 1 wt.%) [22,23], which is below the detection limit of XRD technique. Indeed, characterizing exsolved nanoparticles is a rather complex task, usually limited to electron microscopy techniques. Imaging techniques are very useful to provide morphological information of the exsolved particles but are statistically limited to the selected observed regions of the samples.

Figure 1: XRD pattern of the samples after reducing treatments at 750 °C (a) and 850 °C (b). The red square (■) identifies the mains peaks of the $\text{LaCrO}_{3-\delta}$ orthorhombic phase.

Rietveld refinement was performed to obtain the variation of the crystal lattice volume for each sample after all treatments (Figure S2). Upon reduction, the volume of all samples decreased. This is explained by the formation of oxygen vacancies. Both reducing treatments produced similar behavior and besides the shrinkage due to the formation of oxygen vacancies, no other effect related to exsolution of particles is observed.

The reducing treatment at 750 °C did not induce significant changes in the morphology and surface of the samples (Figure 2a). This result was expected since $\text{LaCrO}_{3-\delta}$ is highly refractory [39] and 750 °C is lower than the typical temperature used to induce exsolution [10,15,16]. In contrast, after the reduction treatment at 850 °C, the formation of nanoparticles onto the surfaces of larger grains is readily observed (Figure 2b). The nanoparticles have spherical shape and sizes ranging from 20 to 50 nm. The estimated particle sizes are consistent with previously reported data on exsolved

nanoparticles in Sr-doped lanthanum chromite [10,16,38]. It is possible to observe some clustering/agglomeration of exsolved nanoparticles in some regions, possibly due to the long times (9 h) used for the reduction treatment.

Figure 2: SEM images of the $(\text{La}_{0.9}\text{Sr}_{0.1})(\text{Cr}_{0.8}\text{Ni}_{0.2})\text{O}_{3-\delta}$ sample reduced at 750 °C (a) and 850 °C (b); High-Resolution TEM (HRTEM) images (c); TEM EDX maps of Ni (d) and O (e).

The HRTEM image shows an isolated nanoparticle on the ceramic surface (Figure 2c). Its fringes distance corresponds to 1.9 Å, a value that can be associated with the metallic nickel (111) interplane distance. The TEM energy-dispersive X-ray (EDX) maps of Ni and O are shown in Figure 2d-e. Such maps clearly reveal that the surface protuberance is an exsolved Ni nanoparticles with a clear compositional difference from the Sr-doped $\text{LaCrO}_{3-\delta}$. They also indicate that these particles are made by metallic nickel since only a weak oxygen signal is observed on the particle's location, probably due to a thin surface oxide layer.

Figure S3a shows HR-TEM images for the sample $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Cr}_{0.8}\text{Ni}_{0.2})\text{O}_{3-\delta}$ after the reducing treatment at 850 °C. The interface between a nanoparticle and the ceramic

1 substrate is clearly identified. The image shows a well-defined organization of the atoms
2 with fringe spacings of 1.9 Å and 2.6 Å that were indexed to Ni (111) and LaCrO_{3-δ} (201)
3 planes, respectively. The Fast Fourier Transformation (FFT) from the selected area
4 (Figure S3b) confirms the observed interplanar distances and crystal alignment. Both
5 images show characteristic of a coherent orientation between the Ni nanoparticle and the
6 ceramic matrix, as expected from exsolved nanoparticles [25]. In Figure S3b, it is possible
7 to observe that the angle between the particle and the lanthanum chromite crystal planes
8 is 45°, providing similar atomic distances on the interface between metal and perovskite.
9 The crystalline planes of the particle are oriented in a direction that minimizes the misfit
10 between the metallic nickel and the lanthanum chromite lattice. While this is expected for
11 nanoparticles originated via exsolution [10], crystal orientation between Ni metallic
12 nanoparticles and the ceramic support is unlikely to be achieved by
13 impregnated/segregated NiO. This observation is a compelling evidence that Ni
14 nanoparticles have been exsolved from the Sr-doped LaCrO_{3-δ} matrix [10,11].
15
16
17
18
19
20
21
22
23
24
25

26 In Figure 3 magnetization curves (MxH) at 117 °C of both as-prepared samples and
27 the reduced ones at 750 °C evidence a paramagnetic behavior. The substitution of Cr for
28 Ni in the Sr-doped LaCrO_{3-δ} structure induces a slight increase in the specific
29 magnetization of the samples. The magnetic structure of the LaSrCrO_{3-δ} can be altered by
30 doping, a feature previously observed by replacing ions in the chromite structure [32].
31 The doping also explains why a weak ferromagnetic component is observed in all
32 compositions, even after calcination at 1000 °C (Figure 3). It is known that the addition
33 of dopants in the lanthanum chromite, like the Sr and Ni, can create weak ferromagnetic
34 behavior due to distortion of the magnetic arrangement and creation of oxygen vacancies
35 [32,40]. However, the MxH curves of samples reduced at 750 °C (Figure 3) show no
36 significant differences from the as-prepared samples, indicating that the reducing
37 treatment at 750 °C did not provide the necessary driving force for the exsolution process.
38
39
40
41
42
43
44
45
46
47
48

49 Moreover, it is important to note that if segregated NiO was present in the as-
50 prepared samples, it would result in an additional strong ferromagnetic component due to
51 metallic nickel nanoparticles after the reducing treatment at 750 °C (Figure 3). The
52 absence of this contribution further excludes the presence of residual NiO in the as-
53 prepared samples.
54
55
56
57
58
59
60
61
62
63
64
65

Figure 3: $M \times H$ measured at 117 °C of the as-prepared samples (black line), reduced at 750 °C (red line) and reduced at 850 °C (blue line). The results are from the nominal compositions $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (a), $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.8}\text{Ni}_{0.2}\text{O}_3$ (b), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (c) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.8}\text{Ni}_{0.2}\text{O}_3$ (d).

In contrast, the $M \times H$ curves in Figure 3 reveal that the reducing treatment at 850 °C resulted in a strong ferromagnetic behavior for the Ni containing specimens, especially on the 20% Ni-doped compositions. Exsolution is a multistep process that results in the nucleation and growth of nanoparticles on the surface of the hosting material. Both nucleation and growth steps are associated with diffusion of the Ni atoms from within the bulk crystal lattice [10,15] and, thus, are highly dependent on temperature. The increase in the reducing temperature from 750 °C to 850 °C led to a significant enhancement in the diffusion of Ni^{2+} ions in the solid solution, thus enabling efficient exsolution. Nevertheless, it is interesting to note that the temperatures required for exsolution are considerably lower than the ones ($\sim 2/3$ melting point) required for net mass diffusion in ceramics, a feature that deserves further studies [41].

The ferromagnetic contribution observed in Figure 3 in the samples reduced at 850 °C is unequivocally related to the exsolved metallic Ni nanoparticles, in accordance with images shown in Figure 2. On the other hand, the MxH curves collected for the samples reduced at a lower temperature (750 °C), no changes occur for the sample without Ni, demonstrating that there is no significant change of the LaSrCrO₃ ceramic matrix upon reduction (Figure S4).

The magnetization of paramagnetic materials has an almost linear dependence on the applied magnetic field. It follows the equation: $M = \chi H$; where M is the magnetic induction, χ the magnetic susceptibility and H the external magnetic field [28]. By considering that the Sr-doped LaCrO_{3-δ} matrix is paramagnetic at 117 °C it can be easily fitted using a linear function ($y = ax$). Such a contribution can be subtracted from the MxH data of Figure 3 to unveil the ferromagnetic contribution of the Ni exsolved particles. The resulting MxH curves are shown in Figure 4. Using this subtraction, the ferromagnetic response from the exsolved nickel nanoparticles can be isolated.

Since the particles are not embedded inside of the ceramic matrix, but rather dispersed on its surface the demagnetization factor was not considered. Also, the particles are approximately spherical, isolated [10,11] and on the surface of a paramagnetic compound. For this kind of system, the demagnetization can be considered negligible [27,28]. For a polycrystalline powder, the exsolution process produces particles distributed along all the surfaces [14–16], and because of that, the anisotropy effect can also be ignored [28].

Nickel is a canonical ferromagnetic metal and its behavior is well-known. At -273 °C the theoretical saturation magnetization is 57.5 emu/g and with increasing temperature, at 117 °C, this value drops to 51.014 emu/g [28]. Thus, by comparing the experimental saturation magnetization with the nominal value for Ni, the mass fraction of metallic Ni exsolved in the sample can be estimated. The SQUID magnetic measurements enable to quantify extremely low mass fraction with high accuracy, limited by the magnetic measurement's resolution ($\sim 10^{-6}$ emu) and sample mass accuracy (~ 0.1 mg).

Figure 4: $M \times H$ measured at 117 °C of the 10 % (a) and 20 % (b) Sr-doped samples after the subtraction of the paramagnetic contribution.

The estimated values of nickel mass fractions obtained from the $M \times H$ data are listed in Table 1. The higher the Ni concentration in the compound (at.%), the higher is the mass fraction of exsolved nanoparticles. This effect is expected since higher concentrations of nickel ions should facilitate nucleation of particles during the first stage of the exsolution mechanism and later during the growing.

Table 1: Mass fraction values of metallic nickel calculated from magnetic measurements after the reducing treatment at 850 °C.

Samples	Ni mass fraction (%)	Ni ⁰ /Ni ²⁺ (%)
(La _{0,9} Sr _{0,1})(Cr _{0,9} Ni _{0,1})O ₃	0.0216(46)	0,86(18)
(La _{0,9} Sr _{0,1})(Cr _{0,8} Ni _{0,2})O ₃	0.0883(71)	1,77(14)
(La _{0,8} Sr _{0,2})(Cr _{0,9} Ni _{0,1})O ₃	0,0206(74)	0,80(29)
(La _{0,8} Sr _{0,2})(Cr _{0,8} Ni _{0,2})O ₃	0,0704(65)	1,38(13)

It is interesting to note that increasing Sr content in the LaCrO_{3-δ} perovskite inhibits the exsolution of Ni. This is in accordance with previously reported data, which showed that increasing Sr content in the parent compound resulted in smaller size and concentration of exsolved particles [38]. Such a feature was related to the lattice distortion caused by the incorporation of Sr in the host perovskite lattice that induces strain fields that hinder the diffusion of nickel atoms.

After the reduction at 850 °C less than 2 at.% of the nickel in solid solution was exsolved (Table 1). Obviously, since a reducing atmosphere is needed to promote the reduction of nickel in solid solution, the most superficial layers are more susceptible to the exsolution process rather than the bulk. Also, previous studies had shown that the exsolution process only occurs on the surface of the material. It was proposed that this mechanism is strain-driven and only particles close to the surface can nucleate and grow [11,15]. Due to these features, only the Ni²⁺ close to the surface is prone to reduction and formation of Ni⁰. Because of that only in the superficial layers occurs the nucleation and diffusion responsible the formation of the exsolved particle, while the Ni²⁺ in the bulk remains in a stable solid solution (Figure S5). Therefore, only a small Ni⁰/Ni²⁺ ratio (< 2 %) is observed for the samples after the reduction at 850 °C.

It is interesting to note that the Ni⁰/Ni²⁺ ratio varies with nickel concentration. Actually, the Ni⁰/Ni²⁺ ratio of the 10 % Ni-doped samples is approximately half of the 20 % Ni-doped ones. Tae-Sik Oh *et al.* [15] have shown that the nucleation, which is a critical step in the formation of nanoparticles via exsolution, occurs in a limited depth below the matrix surface. A strain field is formed around the seed nuclei that drive the diffusion of the Ni²⁺ ions and promote further growth of the nanoparticles in the subsurface region. Eventually, above a critical particle size, accumulation of stress leads to the expulsion of the particles to the surface. In a simple model, one can assume that the

density of seed nuclei is proportional to Ni^{2+} concentration. Moreover, considering that each nucleus creates a strain field of fixed volume, which is roughly independent of Ni^{2+} concentration, then the total amount of Ni^{2+} that will contribute to nanoparticle growth and be reduced will be proportional to the nuclei density and, consequently, proportional to the square of the original Ni^{2+} concentration. In other words, the $\text{Ni}^0/\text{Ni}^{2+}$ ratio will be proportional to the concentration. (Figure S5). This simple model could explain why the 10 % Ni-doped samples exsolved only approximately half of the $\text{Ni}^0/\text{Ni}^{2+}$ ratio when compared with the 20 % Ni-doped samples.

CONCLUSIONS

The exsolution of Ni nanoparticles from a perovskite matrix lattice was observed and quantitatively analyzed by means of magnetic measurements and electron microscopy analyses. Single-phase lanthanum chromite samples doped with Sr and Ni were successfully synthesized. No segregation of NiO was observed in the as-prepared samples after reduction at 750 °C under hydrogen. The combination of a paramagnetic matrix, resistant to reducing environments at high temperature, and an exsolved ferromagnetic metal allowed for the successful quantification of exsolved nanoparticles by magnetic measurements. The exsolution process was activated at a temperature close to 850 °C. Increasing of nickel doping in $\text{Sr-LaCrO}_{3-\delta}$ resulted in an increased mass fraction of Ni particles exsolved. A higher level of strontium doping was observed to hinder the exsolution of Ni nanoparticles. XRD technique has proven not suitable for the characterization of exsolved systems. However, the characterization of exsolved ferromagnetic nanoparticles by magnetic measurements is a rather quick and extremely sensitive method to gain relevant information about nanostructured exsolved systems.

ACKNOWLEDGEMENTS

The authors acknowledge to CEM (UFABC). VBT acknowledges FAPESP (2015/23899-4) for scholarship. DZF acknowledges to CNPq (309600/2018-9) and FAPESP (2015/24999-2). Authors gratefully acknowledge the support from RCGI Shell (ANP)/FAPESP (grant 2014/50279-4), and CINE Shell (ANP)/FAPESP (grant 2017/11937-4). FCF, DZF, and ASF are CNPq fellows.

REFERENCES

- [1] S.M. Lindsay, Introduction to Nanoscience, Nano Today. 3 (2008) 47.

doi:10.1016/S1748-0132(08)70046-X.

- [2] M.M. Khin, A.S. Nair, V.J. Babu, R. Murugan, S. Ramakrishna, A review on nanomaterials for environmental remediation, *Energy Environ. Sci.* 5 (2012) 8075. doi:10.1039/c2ee21818f.
- [3] D. Bagchi, M. Bagchi, H. Moriyama, F. Shahidi, *Bio-Nanotechnology: A Revolution in Food, Biomedical and Health Sciences*, 2013. doi:10.1002/9781118451915.
- [4] V. Esposito, C. Gadea, J. Hjelm, D. Marani, Q. Hu, K. Agersted, S. Ramousse, S.H. Jensen, Fabrication of thin yttria-stabilized-zirconia dense electrolyte layers by inkjet printing for high performing solid oxide fuel cells, *J. Power Sources*. 273 (2015) 89–95. doi:10.1016/j.jpowsour.2014.09.085.
- [5] D. Marani, C. Gadea, J. Hjelm, P. Hjalmarsson, M. Wandel, R. Kiebach, Influence of hydroxyl content of binders on rheological properties of cerium–gadolinium oxide (CGO) screen printing inks, *J. Eur. Ceram. Soc.* 35 (2015) 1495–1504. doi:10.1016/j.jeurceramsoc.2014.11.025.
- [6] R. Narayan, Use of nanomaterials in water purification, *Mater. Today*. 13 (2010) 44–46. doi:10.1016/S1369-7021(10)70108-5.
- [7] M.K. Nayak, J. Singh, B. Singh, S. Soni, V.S. Pandey, S. Tyagi, Introduction to semiconductor nanomaterial and its optical and electronics properties, in: *Met. Semicond. Core-Shell Nanostructures* *Energy Environ. Appl.*, Elsevier, 2017: pp. 1–33. doi:10.1016/B978-0-323-44922-9.00001-6.
- [8] D. Burnat, R. Kontic, L. Holzer, P. Steiger, D. Ferri, A. Heel, Smart material concept: reversible microstructural self-regeneration for catalytic applications, *J. Mater. Chem. A*. 4 (2016) 11939–11948. doi:10.1039/C6TA03417A.
- [9] D. Marani, R.H. Silva, A. Dankeaw, K. Norrman, R.M.L. Werchmeister, D. Ippolito, M. Gudik-Sørensen, K.K. Hansen, V. Esposito, NO_x selective catalytic reduction (SCR) on self-supported V–W-doped TiO₂ nanofibers, *New J. Chem.* 41 (2017) 3466–3472. doi:10.1039/C6NJ03205B.
- [10] D. Neagu, T.-S. Oh, D.N. Miller, H. Ménard, S.M. Bukhari, S.R. Gamble, R.J. Gorte, J.M. Vohs, J.T.S. Irvine, Nano-socketed nickel particles with enhanced

- coking resistance grown in situ by redox exsolution, *Nat. Commun.* 6 (2015) 8120. doi:10.1038/ncomms9120.
- [11] L. Thommy, O. Joubert, J. Hamon, M.-T. Caldes, Impregnation versus exsolution: Using metal catalysts to improve electrocatalytic properties of LSCM-based anodes operating at 600 °C, *Int. J. Hydrogen Energy*. 41 (2016) 14207–14216. doi:10.1016/j.ijhydene.2016.06.088.
- [12] T.S. Rodrigues, A.B.L. de Moura, F.A. e Silva, E.G. Candido, A.G.M. da Silva, D.C. de Oliveira, J. Quiroz, P.H.C. Camargo, V.S. Bergamaschi, J.C. Ferreira, M. Linardi, F.C. Fonseca, Ni supported Ce_{0.9}Sm_{0.1}O_{2-δ} nanowires: An efficient catalyst for ethanol steam reforming for hydrogen production, *Fuel*. 237 (2019) 1244–1253. doi:10.1016/j.fuel.2018.10.053.
- [13] A.S. Ferlauto, D.Z. de Florio, F.C. Fonseca, V. Esposito, R. Muccillo, E. Traversa, L.O. Ladeira, Chemical vapor deposition of multi-walled carbon nanotubes from nickel/yttria-stabilized zirconia catalysts, *Appl. Phys. A*. 84 (2006) 271–276. doi:10.1007/s00339-006-3617-x.
- [14] Y.-F. Sun, Y.-Q. Zhang, J. Chen, J.-H. Li, Y.-T. Zhu, Y.-M. Zeng, B.S. Amirkhiz, J. Li, B. Hua, J.-L. Luo, New Opportunity for in Situ Exsolution of Metallic Nanoparticles on Perovskite Parent, *Nano Lett.* 16 (2016) 5303–5309. doi:10.1021/acs.nanolett.6b02757.
- [15] T.-S. Oh, E.K. Rahani, D. Neagu, J.T.S. Irvine, V.B. Shenoy, R.J. Gorte, J.M. Vohs, Evidence and Model for Strain-Driven Release of Metal Nanocatalysts from Perovskites during Exsolution, *J. Phys. Chem. Lett.* 6 (2015) 5106–5110. doi:10.1021/acs.jpcllett.5b02292.
- [16] D. Papargyriou, J.T.S. Irvine, Nickel nanocatalyst exsolution from (La,Sr)(Cr,M,Ni)O₃ (M Mn,Fe) perovskites for the fuel oxidation layer of Oxygen Transport Membranes, *Solid State Ionics*. 288 (2016) 120–123. doi:10.1016/j.ssi.2015.11.007.
- [17] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, Self-regeneration of a Pd-perovskite catalyst for automotive emissions control, *Nature*. 418 (2002) 164–167. doi:10.1038/nature00893.

- [18] N.K. Monteiro, F.B. Noronha, L.O.O. da Costa, M. Linardi, F.C. Fonseca, A direct ethanol anode for solid oxide fuel cell based on a chromite-manganite with catalytic ruthenium nanoparticles, *Int. J. Hydrogen Energy*. 37 (2012) 9816–9829. doi:10.1016/j.ijhydene.2012.03.157.
- [19] Y. Zhu, W. Zhou, R. Ran, Y. Chen, Z. Shao, M. Liu, Promotion of Oxygen Reduction by Exsolved Silver Nanoparticles on a Perovskite Scaffold for Low-Temperature Solid Oxide Fuel Cells, *Nano Lett.* 16 (2016) 512–518. doi:10.1021/acs.nanolett.5b04160.
- [20] J. Sunarso, S.S. Hashim, N. Zhu, W. Zhou, Perovskite oxides applications in high temperature oxygen separation, solid oxide fuel cell and membrane reactor: A review, *Prog. Energy Combust. Sci.* 61 (2017) 57–77. doi:10.1016/j.pecs.2017.03.003.
- [21] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Crystallogr.* 2 (1969) 65–71. doi:10.1107/S0021889869006558.
- [22] J. Epp, X-ray diffraction (XRD) techniques for materials characterization, in: *Mater. Charact. Using Nondestruct. Eval. Methods*, Elsevier, 2016: pp. 81–124. doi:10.1016/B978-0-08-100040-3.00004-3.
- [23] B.D. Cullity, *Elements of X-ray diffraction*, 2nd edition, Addison-Wesley Publ. Co. Read. MA. (1978) 100-105,277-279. doi:10.1119/1.1934486.
- [24] R.F. Egerton, *Physical principles of electron microscopy: An introduction to TEM, SEM, and AEM*, second edition, 2016. doi:10.1007/978-3-319-39877-8.
- [25] D. Neagu, G. Tsekouras, D.N. Miller, H. Ménard, J.T.S. Irvine, In situ growth of nanoparticles through control of non-stoichiometry, *Nat. Chem.* 5 (2013) 916–923. doi:10.1038/nchem.1773.
- [26] Y. Sun, J. Li, Y. Zeng, B.S. Amirkhiz, M. Wang, Y. Behnamian, J. Luo, A-site deficient perovskite: the parent for in situ exsolution of highly active, regenerable nano-particles as SOFC anodes, *J. Mater. Chem. A*. 3 (2015) 11048–11056. doi:10.1039/C5TA01733E.
- [27] L. Zhao, N.. van Dijk, E. Brück, J. Sietsma, S. van der Zwaag, Magnetic and X-ray diffraction measurements for the determination of retained austenite in TRIP

- steels, Mater. Sci. Eng. A. 313 (2001) 145–152. doi:10.1016/S0921-5093(01)00965-0.
- [28] B.D. Cullity, C.D. Graham, Introduction to magnetic materials, Mater. Today. 12 (2009) 45. doi:10.1016/S1369-7021(09)70091-4.
- [29] C. Solís, L. Navarrete, M. Balaguer, J.M. Serra, Development and understanding of $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ anodes for $\text{La}_{5.6}\text{WO}_{11.4-\delta}$ -based Proton Conducting Solid Oxide Fuel Cells, J. Power Sources. 258 (2014) 98–107. doi:10.1016/j.jpowsour.2014.02.015.
- [30] L. GROUPP, H.U. ANDERSON, Densification of $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$, J. Am. Ceram. Soc. 59 (1976) 449–450. doi:10.1111/j.1151-2916.1976.tb09517.x.
- [31] G.-Y. Lee, R.-H. Song, J.-H. Kim, D.-H. Peck, T.-H. Lim, Y.-G. Shul, D.-R. Shin, Properties of Cu, Ni, and V doped- LaCrO_3 interconnect materials prepared by pechini, ultrasonic spray pyrolysis and glycine nitrate processes for SOFC, J. Electroceramics. 17 (2006) 723–727. doi:10.1007/s10832-006-0473-1.
- [32] K. Tezuka, Y. Hinatsu, A. Nakamura, T. Inami, Y. Shimojo, Y. Morii, Magnetic and Neutron Diffraction Study on Perovskites $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$, J. Solid State Chem. 141 (1998) 404–410. doi:10.1006/jssc.1998.7961.
- [33] M.P. Pechini, Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor, 1967. <http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Method+of+preparing+lead+and+alkaline+earth+titanates+and+niobates+and+coating+method+using+the+same+to+form+a+capacitor#0>.
- [34] D. Segal, Chemical synthesis of ceramic materials, J. Mater. Chem. 7 (1997) 1297–1305. doi:10.1039/a700881c.
- [35] L.-W. Tai, P.A. Lessing, Modified resin–intermediate processing of perovskite powders: Part I. Optimization of polymeric precursors, J. Mater. Res. 7 (1992) 502–510. doi:10.1557/JMR.1992.0502.
- [36] K. V. Manukyan, A.G. Avetisyan, C.E. Shuck, H.A. Chatilyan, S. Rouvimov, S.L. Kharatyan, A.S. Mukasyan, Nickel Oxide Reduction by Hydrogen: Kinetics and Structural Transformations, J. Phys. Chem. C. 119 (2015) 16131–16138.

doi:10.1021/acs.jpcc.5b04313.

- [37] R.W. Simmonds, Quantum interference heats up, *Nature*. 492 (2012) 358–359. doi:10.1038/492358a.
- [38] V.B. Vert, F. V. Melo, L. Navarrete, J.M. Serra, Redox stability and electrochemical study of nickel doped chromites as anodes for H₂/CH₄-fueled solid oxide fuel cells, *Appl. Catal. B Environ.* 115–116 (2012) 346–356. doi:10.1016/j.apcatb.2011.12.033.
- [39] M. Mori, Sintering behavior of Ca- or Sr-doped LaCrO₃ perovskites including second phase of AECrO₄ (AE=Sr, Ca) in air, *Solid State Ionics*. 135 (2000) 743–748. doi:10.1016/S0167-2738(00)00372-6.
- [40] Z. Wen, Y. Cui, Y. Chen, Y. Zhao, Effect of Ca Doping on the Structure and Magnetic and Electronic Properties of La_{1-x}Ca_xCr_{0.8}Cu_{0.2}O₃ (x = 0~0.3), *J. Supercond. Nov. Magn.* 32 (2019) 2655–2660. doi:10.1007/s10948-019-5003-x.
- [41] V. Esposito, D.W. Ni, D. Marani, F. Teocoli, K.T.S. Thydén, D.Z. De Florio, F.C. Fonseca, Accelerated ceria-zirconia solubilization by cationic diffusion inversion at low oxygen activity, *J. Mater. Chem. A*. 4 (2016). doi:10.1039/c6ta06308j.
- [42] T.J.B. W. M. Haynes, David R. Lide, *CRC Handbook of Chemistry and Physics*, 97th ed., CRC Press, 2016.