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Meta-stability and microstructure of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite compound prepared by a modified citrate route

G.C. Mondragón Rodríguez, R. Ochrombel, B. Saruhan *

German Aerospace Center (DLR), Institute of Materials Research,
Cologne, Germany

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Abstract

In this paper we report the synthesis and analysis of lanthanum based perovskites substituted with Pd by employing a modified citrate route. Crystallization and phase sequences of the $LaFe_{0.65}Co_{0.3-x}Pd_xO_3$ ($x = 0$, 0.05) perovskite(s) are analyzed by means of powder XRD and Rietveld refinement. Regarding the crystal phase development at the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite a meta-stable structure can be postulated at temperatures up to 700 °C. Since no PdO species were detected up to the calcination temperature of 700 °C we can conclude that Palladium ions are successfully incorporated into the B-site of the crystal structure of the perovskite. Reduction of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite at 600 °C under 5 vol.% H_2 in N_2 which was precalcined at 700 °C causes segregation of palladium to form metallic particles with sizes between 10 and 15 nm. Reversible Pd ions reincorporation into the crystal lattice of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700 °C perovskite can be concluded since no PdO was detected after re-oxidation at 600 °C.

Keywords: Citrate route; Perovskite structure; Palladium segregation; La (Fe,Co,Pd)O_3

1. Introduction

The increasing prices of noble metals such as Pt, Rh, and Pd driven partly by the large demand of the automotive industry motivates the investigation for material concepts to reduce the precious metal content in automotive catalysts. Since the precious metals cannot be completely removed away from NO_x after treatment catalysts, from H_2 storage catalysts in fuel cells or from catalysts to produce synthesis gas, increasing demand for precious metals at all these applications areas can be foreseen in the near future. In the practice, it may often occur that the classically supported catalysts are exposed to extreme corrosive environments e.g. redox conditions, and/or high temperatures. Under these conditions deposition of Zn, Pb, P, and Ca atoms, sintering and alloying are common deactivation mechanisms as reported by Granados[1] and references therein. As a future trend, improved catalysts with better catalytic properties and high durability in service under extreme environments are needed. Catalysts with better durability would inherently result in lower precious metal consume.

Palladium substituted in perovskite structures is believed to respond in a reversible manner under cyclic redox conditions, which can be found in the new gasoline engines. Local reduction conditions may cause the segregation of palladium as metallic nanocrystals; the presence of oxygen may suppress agglomeration and crystal growth of palladium. Consequently the Pd substituted perovskite applied as a catalyst will show eventually better catalytic performance and longer durability.[2,3,4] Under redox conditions structural modifications can be present in La-based perovskites. Orlovskaya et al.[5] documented the presence of twins, antiphase domains, stacking faults, and dislocations present in $LaCoO_3$ perovskites after and during exposition to different temperatures in reducing atmospheres. In the same report annealing of the $La_{0.8}Ca_{0.2}CoO_3$ system at 800 °C for 1.5 h led to the surface formation of Co oxide precipitations. Recent results[6,7] describe the structural instability and surface modifications of Pd-$LaCoO_3$ after reduction in H_2 at 773 K and during the reaction under $0.15\%NO + 0.5\%H_2 + 3\%O_2$ with increasing temperatures up to 1173 K. The initial rhombohedral structure of the perovskite was transformed into Co^0 particles

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[*] Corresponding author. Tel.: +49 2203 601 3228; fax: +49 2203 69 64 80.
E-mail address: Bilge.Saruhan@dlr.de (B. Saruhan).

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and La_2O_3 under these conditions. However, high degree of Pd dispersion in the Pd-$LaCoO_3$ catalyst was anticipated, since bulk palladium species were not observed. It is suggested that the $LaCoO_3$ perovskite may help to preserve the metallic character of palladium. The substitution of Fe at the B-site in $LaCoO_3$ confers structural stability to the perovskite even under extreme reducing conditions.[4] Under reduction conditions 30% of all the elements at the B-site in the $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ perovskite were reduced into metallic state. After exposure to oxidant atmospheres the metallic species were fully reincorporated into the frame lattice of the $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ perovskite.

The $LaFe_xCo_{(1-x)}O_3$ perovskite with ABO_3 type structure is formed with La-atoms at the A-site coordinated with 12 oxygen and with (Fe,Co) at the B-site coordinated with six oxygen atoms. The $LaFeO_3$ is orthorhombic and the $LaCoO_3$ is rhombohedral.[8] The tolerance factor $(t) = (r_A + r_O)/\sqrt{2} \times (r_B + r_O)$ is one requirement to form a perovskite structure and must lie between $0.8 < t < 1.0$.[2] Due to this tolerance wide variety of elements can be combined without change in the original structure. Precious metals Pd, Pt, Rh, can also be incorporated into the crystal lattice. The expected advantages by substitution of precious metals in perovskite structures are to improve the catalytic activity and thermal induced phase stability. Precious metals strongly bonded with the perovskite bulk structure may segregate slowly to form oxides or other alloys at high temperatures. Moreover, such structures may have self-healing properties under redox conditions.[3] On the other hand higher metal dispersion would provide major active surface area which is very important in most applications.

In this paper we describe a synthesis method based on the citrate route and modified for incorporation of Pd in La-based perovskites. Since Pd overtakes the catalytic reduction task and its durability under extreme application conditions is of importance, we analyze the state of Pd in the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite by employing XRD and Rietveld refinement. For comparison purposes, a Pd impregnated $LaFe_{0.65}Co_{0.35}O_3$ is also synthesized by the same method and analyzed in analogy to the Pd substituted perovskite $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$. Particular attention is taken to the phase stability of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ structure after exposure to temperatures up to 900 °C under static air. The reduction under 5 vol.% H_2 in N_2 at 600 °C and re-oxidation of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite at 600 °C have been carried out to illustrate the diffusion of Pd ions in and out of the frame lattice. This work is an attempt to study the thermal meta-stability of main and immediate phase(s) formed in $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ based compound prepared by a modified citrate route.

2. Experimental

2.1. Perovskite synthesis method

The palladium integrated perovskite was prepared employing the citrate route.[9] First, an aqueous solution of lanthanum acetate was prepared (A-site). Separately, Co-acetylacetonate and Fe-nitrate were dissolved in distilled water (B-site of the perovskite). Concentrated nitric acid was used for sol formation of the Co-acetylacetonate. Then a Pd di-nitrate aqueous solution was slowly added to this mixture. The Fe-, Co-solution was mixed with stoichiometric amount of citric acid with respect to the B-site of the perovskite. The resulting solution was mixed with the La acetate aqueous solution under constant stirring. At this point ethylene glycol was added at a mass ratio of 40:60 with respect to the citric acid. The solvent was then eliminated with rota-vapour at 80 °C. The temperature was maintained constant up to almost the complete elimination of the solvent and resin formation. Partial combustion and elimination of hydrocarbons was made over a heated plate. Finally, the sample powders were slightly grounded with agate mortar, kept in an oven at 80 °C for 24 h and calcined for 3 h at various temperatures, ranging from 500 to 900 °C. For comparison the $LaFe_{0.65}Co_{0.35}O_3$ perovskite without palladium was prepared using the same synthesis method. Fig. 1 displays a schematic diagram of the synthesis method applied at this study. Additionally, synthesis of the Pd supported perovskite was carried out by direct impregnation of the $LaFe_{0.65}Co_{0.35}O_3$ powder. For this purpose, the $LaFe_{0.65}Co_{0.35}O_3$ powder was first thermal treated at 900 °C/3 h to obtain a well-defined perovskite structure and the so obtained sample was then impregnated with palladium nitrate aqueous solution, dried and calcined at 700 °C/3 h for further analysis (see Table 1 for sample designation).

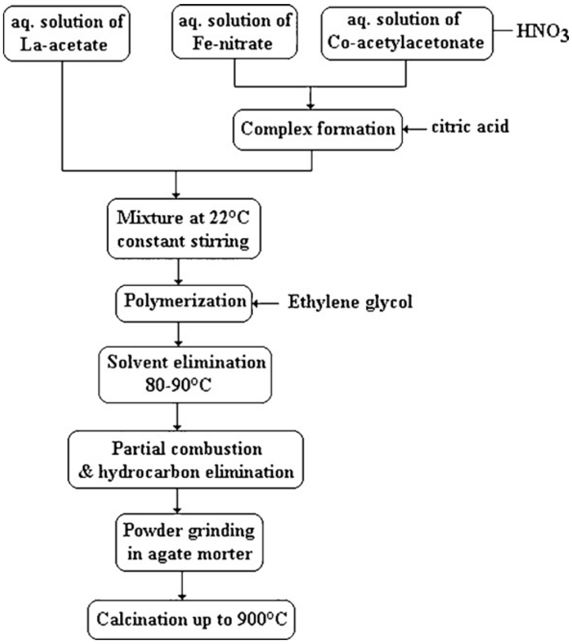

Fig. 1. Synthesis route for $LaFe_xCo_{0.95-x}Pd_{0.05}O_3$ perovskites.

2.2. Characterization methods

The X-ray diffraction (XRD) powder method was employed to determine and analyze the phase(s) of synthesized samples. XRD diffraction patterns presented in this work were obtained by using a diffractometer of type SIEMENS D5000 in Bragg Brentano geometry using Cu $K\alpha_{1+2}$ radiation. Samples were slightly grounded in an agate mortar and mounted on SiO_2 single crystal sample holders by steric adhesion using 2-propanol for

Table 1
Synthesized and analyzed La-based perovskite samples

Sample	Treatment	Sample code
$LaFe_{0.65}Co_{0.35}O_3$	700 °C/3 h under static air	LFC-700
$Pd/LaFe_{0.65}Co_{0.35}O_3$	700 °C/3 h under static air	P-LFC-700
$LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$	500–900 °C 3 h each temperature under static air	LFCP-500, LFCP-600[a], LFCP-640[a], LFCP-700, LFCP-750, LFCP-900
$LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700 °C	Reduced under 5% H_2 in N_2 at 600 °C/1 h	LFCP-$H_2$600
$LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700 °C-after reduction treatment	Re-oxidized under static air at 600 °C/1 h	LFCP-Reox600

[a] After DSC experiment.

dispersion. Rietveld refinement of the XRD patterns yielding lattice parameters calculation and quantitative determination of phase composition was done with the program Wyriet 3.[10]

Differential scanning calorimetry (DSC) analysis was made with a NETZSCH 404 analyzer. Tablets of 4.65 mm diameter of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-500 °C/3 h were prepared. The temperature was raised up to 900 °C at a constant heating rate of 10 °C/min under static air. DSC experiments under the same conditions were carried out up to the detected transition temperatures and immediately cooled down to room temperature; after that the powder samples were analyzed with XRD.

Reduction treatment of the synthesized $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700 °C perovskite was carried out in 5 vol.% $H_2 + N_2$ at 600 °C/1 h. During cooling of the sample constant flow of 5 vol.% H_2 in N_2 was maintained until the oven reached approximately 250 °C. Further cooling of the sample to room temperature was achieved under constant flow of nitrogen to avoid further oxidation processes. The reduced Pd substituted perovskite was re-oxidized at 600 °C for 3 h in oven under static air (Table 1). Finally, the samples were analyzed with XRD and with SEM microscope LEO Gemini GSM 982 equipped with an energy dispersive X-ray spectrometer (EDS) from Oxford Instruments.

3. Results and discussion

3.1. Crystal phase characterization

Fig. 2 shows the results obtained by DSC measurement of the palladium substituted La-based perovskite which was heat-treated at 500 °C/3 h prior to the DSC measurements. The DSC spectrum show two exothermic signals; one at 600 °C with a weight loss of 3.2% and the second at 640 °C with a weight loss of 5.1%. Both are related to the crystal phase evolution of the La-based perovskite (Fig. 3). The XRD spectrum of the powder calcined at 500 °C shows the typical characteristics of highly amorphous material which begins to crystallize at around 560 °C as seen with the DSC measurement given in Fig. 2. The early well-defined signals of the perovskite are observed at the XRD spectra of the palladium substituted perovskite calcined at 600 °C due to the start of its crystallization (Fig. 3). It is important to note that this spectrum still shows some characteristics of an amorphous phase as can be seen particularly at lower 2θ values. Fully crystallized perovskite is obtained at around 660 °C. The diffractogram taken after DSC-measurement at 640 °C also shows well-defined reflections corresponding to a single orthorhombic phase with the composition $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$. At this temperature no other single or mixed oxides were detected and no reflections related to the presence of palladium oxide were found, suggesting the substitution of the B-site with Pd ions in the perovskite (ABO_3) structure.

Rietveld refinement of the diffraction pattern from LFCP-700 with two phases the cubic and orthorhombic structures shown in Fig. 4, confirmed the presence of only the orthorhombic

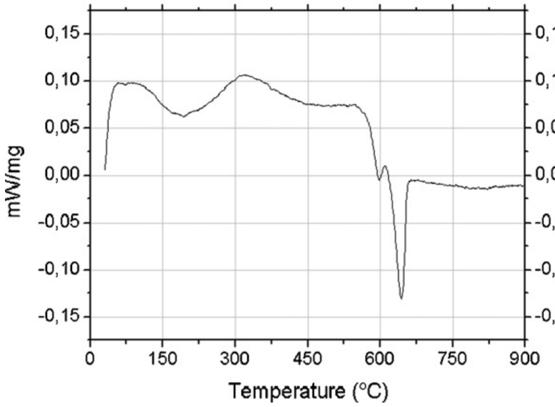

Fig. 2. DSC analysis of $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite.

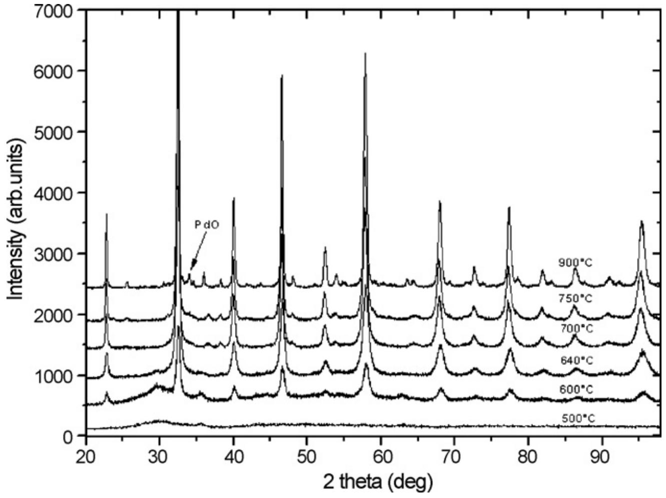

Fig. 3. Phase evolution of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite with temperature (data taken from $2\theta = 10°$ to $90°$, at a step size of $0.05°$, counting time of 5 s/step and 0.6 mm slit).

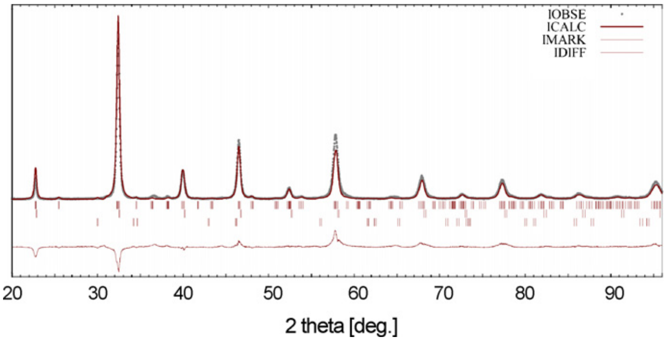

Fig. 4. Rietveld refinement of the diffraction pattern from LFCP-700 including orthorhombic (space group *Pnma*) and cubic perovskite (space group *Pm*3-*m*). The lowest positions correspond to PdO. Data collected from $2\theta = 20°$ to $98°$, step size = 0.02°, counting time = 20 s/step, and 0.2 mm slit.

perovskite structure. The weak reflection at $2\theta = 30.9°$ of the perovskites calcined at 700 °C is related to the presence of very small amount of cobalt oxide according to data JCPDS 80-1543. The substitution with Pd at expense of Co at the B-site in the $LaFe_{0.65}Co_{0.35-x}Pd_xO_3$ perovskite lead to lower cobalt content and less cobalt oxide segregation (see spectra (a) and (b), Fig. 5). At 750 °C no significant changes were observed in the main perovskite structure, but PdO segregates out of the crystal lattice. At 900 °C the crystallinity of the sample increases showing the reflections of the orthorhombic perovskite structure and tetragonal PdO. In this work, the increase of cobalt at the expense of iron at the B-site of the $LaFe_xCo_{0.95-x}Pd_{0.05}O_3$ ($x = 0.65, 0.475, 0.4$) perovskite causes a shift to higher 2θ values (results not provided here), thus providing the stability of the orthorhombic structure and the incorporation of cobalt into the main perovskite lattice. The cobalt increase in our $LaFe_xCo_{0.95-x}Pd_{0.05}O_3$ perovskites lead to major cobalt oxide content in the samples. In contrast to our study, McCready and Kingsley[7] obtained only the orthorhombic perovskite at 850 °C with composition $LaFe_{0.6}Co_{0.4}O_3$ synthesized using the glycine-nitrate combustion process. In our work, the reflections between $2\theta = 33.5°$ and $34.5°$ (see JCPDS 75-0584 data) observed at the spectra of the powder calcined at 750 °C correspond to PdO, suggesting meta-stability of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ structure at temperatures up to 700 °C. The literature data suggests stability of palladium ions in the perovskite composition $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ prepared by precipitation method and calcined up to 800 °C.[2,3] More recently Singh et al.[11] prepared a perovskite based catalyst $BaCe_{(1-x)}Pd_xO_{3-\delta}$ ($x = 0.00, 0.05, 0.1$) which seems to be stable up to 1000 °C. After reduction in 5%H_2 at 1000 °C/1 h they found the presence of fcc-Pd^0 with estimated size of 80 nm. Reoxidation of this perovskite $BaCe_{(1-x)}Pd_xO_{3-\delta}$ resulted in the reincorporation of Pd ions into the frame lattice. Although the authors did not mention any possibility of meta-stable compound we estimate that the meta-stability of Pd substituted perovskite structures is very sensitive to calcination temperature and reaction conditions depending on the host perovskite composition, the ratio of the element(s) sharing the B-site and the synthesis method.

Fig. 5 compares the diffraction patterns of the perovskite without palladium $LaFe_{0.65}Co_{0.35}O_3$ (LFC-700), the palladium substituted perovskite $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ (LFCP-700) and the perovskite impregnated with Pd (P-LFC-700), all powder samples and calcined at 700 °C/3 h under static air. The perovskite sample P-LFC-700 (curve c, Fig. 5) clearly shows the reflections that correspond to PdO. The diffraction spectrum of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite indicates the integration of palladium in the crystal lattice at this temperature (see curve b, Fig. 5). The $LaFe_{0.65}Co_{0.35}O_3$ perovskite calcined at 900 °C/3 h (LFC-900) presented no signals between $2\theta = 33.5°$ and $34.5°$ thus confirming the phase purity of the perovskite synthesized with modified citrate route (not shown here). The reflections between $2\theta = 33.5°$ and $34.5°$ are related to the presence of other oxides such as $LaFeO_3$ and not to the presence of PdO in a cobalt free perovskite.[12] Based on the chemical shift observed from the XANES spectra of substituted $LaFe_{(1-x)}Pd_xO_3$ perovskite treated at 800 °C, Uenishi et al.[12] demonstrated the higher oxidation state of palladium in the perovskite, implying its substitution in the crystal lattice. Our results suggest that the perovskite composition $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ appears to be meta-stable between 700 and 750 °C. Under oxidation con-

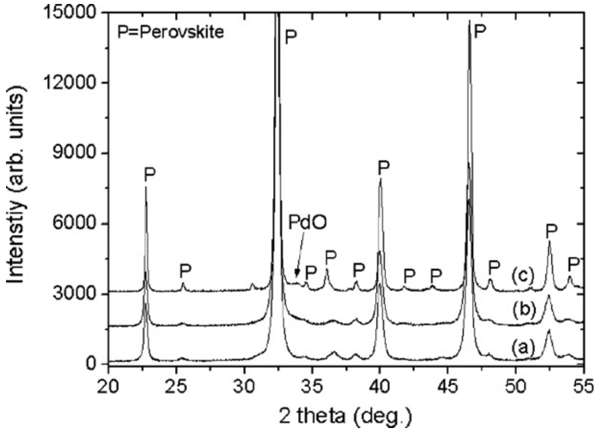

Fig. 5. Diffractogram of (a) $LaFe_{0.65}Co_{0.35}O_3$-700 °C/3 h, (b) $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700 °C/3 h, (c) (Pd/$LaFe_{0.65}Co_{0.35}O_3$-900 °C)-700 °C, data collection from $2\theta = 20°$ to $98°$, step size = 0.02°, counting time = 20 s/step and 0.2 mm slit.

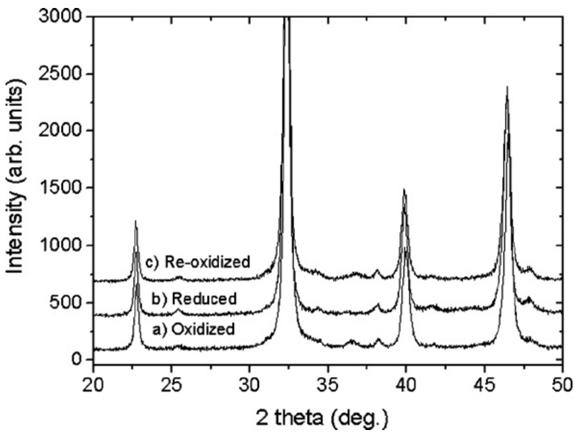

Fig. 6. Powder XRD of $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$; (a) as prepared 700 °C/3 h, (b) after reduction in 5 vol.%$H_2 + N_2$ 600 °C/1 h, (c) after re-oxidation 600 °C/3 h in static air. Data collection from $2\theta = 20°$ to $98°$, step size = 0.02°, counting time = 20 s/step and 0.2 mm slit.

Table 2
Lattice constants of the $LaFe_{0.65}Co_{1-0.65-x}Pd_xO_3$ ($x = 0, 0.05$) perovskites calculated after Rietveld refinement

Sample	Treatment	a_1	a_2	a_3	Phase (s)
$LaFe_{0.65}Co_{0.35}O_3$-700 °C	As prepared	5.4998	7.7926	5.5339	Perovskite
$LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700 °C	As prepared	5.5024	7.7972	5.5358	Perovskite
$LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700 °C	5%H_2 in N_2 600 °C	5.5262	7.8093	5.5520	Perovskite
$LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700 °C	Re-oxidized 600 °C static air	5.5214	7.8052	5.5488	Perovskite

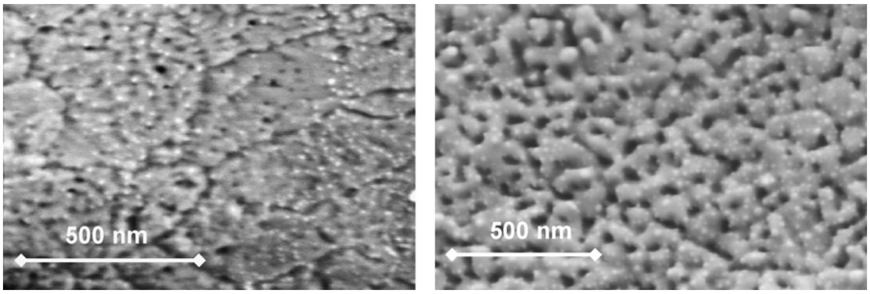

Fig. 7. Microstructure of $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ (left) and Pd/$LaFe_{0.65}Co_{0.35}O_3$ (right) after 5 vol.%$H_2 + N_2$ at 600 °C/1 h.

ditions above 750 °C palladium ions may migrate to form PdO as mentioned above. Mixed oxides containing Pd and lanthanide elements such as Er, Gd, Dy, among others, are believed to be meta-stable in air. Lanthanum mixed oxides with palladium may decompose into the single oxide and metallic palladium at temperatures starting from 800 °C depending on the La/Pd ratio.[13] In our case the meta-stability of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ system may explain the phase(s) split and PdO formation at temperatures higher than 700 °C.

3.2. The reversible redox behaviour of $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite

Fig. 6 compares the phase changes occurred by reduction and re-oxidation of the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite. Slight structural changes can be observed after reduction of the perovskite as shown in the measured and calculated crystal lattice data given in Table 2. The diffusion of Pd ions out of the crystal structure is possibly related to these modifications. The lattice constants after reduction and re-oxidation treatments lie near, and thus, imply a non-reversible behaviour in the La-perovskite structure. It must be noted that the reduction of the sample was carried out under very strongly reducing conditions with flowing gas and the re-oxidation of the perovskite was made in oven with static air. It is likely that oxygen vacancies and structure defects in the perovskites synthesized in this study maintain the charge neutrality of the whole structure.

Besides the reversible diffusion of Pd ions out of the perovskite structure, the nano-scale alloy formation during reduction between Pd and Fe and/or Co, or even with La, are phenomena that cannot be completely ruled out. This aspect was discussed by Nishihata et al.[3,4] they reported the diffusion of Pd-ions and alloy formation with Co in the $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ perovskite after reduction in 10%$H_2 + N_2$ at 800 °C/1 h. About half of the Co and around 10% of the Fe were reported to be reduced to Fe^0, which implies the possibility of alloying with palladium. Similarly, Pd_3La-alloy formation on Pd/Al_2O_3-La_2O_3 supported catalyst after the exposure to NO + H_2 gas mixture at 700 °C was proposed by Barrera et al.[14,15]

The SEM micrographs in Fig. 7 compare the microstructures of $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite (left) and Pd/$LaFe_{0.65}Co_{0.35}O_3$ (right), after reduction treatment, both reduced with 5%H_2 in N_2 at 600 °C/1 h. Palladium particles higher than 50 nm can be found in the Pd impregnated $LaFe_{0.65}Co_{0.35}O_3$ catalyst whilst the $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ substituted perovskite contains fine Pd-particles with sizes below 10 nm. Since the microstructure of the substituted perovskite contains no more Pd-particles, it can be postulated that the re-oxidation treatment of the reduced $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ causes the reversible incorporation of Pd ions into the crystal structure of the perovskite.

4. Conclusions

A citrate synthesis method modified to produce Pd substituted La-based perovskites was successfully employed. The single phase $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite which forms above 640 °C seems to be meta-stable up to 700 °C. At temperatures higher than 700 °C, the perovskite system tends to decompose by segregation of Pd-ions to form PdO. On exposure to reducing atmosphere at about 600 °C, the Pd ions appear to diffuse out of the perovskite structure as metallic particles. In comparison to the Pd impregnated $LaFe_{0.65}Co_{0.35}O_3$ perovskite where particles with larger sizes are detected, the particles in substituted perovskite are below 10 nm and disappear on further re-oxidation process.

In our case reversible reincorporation of Pd ions into the crystal structure of the perovskite appears to be plausible at temperatures below 700 °C, since the substituted perovskite demonstrate meta-stability up to temperatures around 700 °C. The degree of reversibility of the Pd integrated perovskite may depend on the compositional variations and ratios at the

B-site. Although the Rietveld refinement results imply the occurrence of slight irreversible changes at the lattice constants of perovskite on reduction and re-oxidation, these are probably caused by the accommodation of oxygen vacancies generated to keep the charge neutrality of the perovskite after reduction. Considering the unusual oxidation state of the substituted Pd ions, it is plausible to find structural defects such as vacancies or other distortions in order to equilibrate the electronic charge of the system. SEM investigation shows that metallic Pd which segregates out of the perovskite lattice on reduction as 10 nm and finer particles disappear in a reversible manner to be incorporated into the crystal lattice, confirming the reversible redox behaviour of the Pd-substituted $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ perovskite.

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