Non-stoichiometric $\text{La}_{1-(1-\delta)}\text{NiO}_{3-\delta}$ perovskites produced by combustion synthesis

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La$_{1-(1-\delta)}$NiO$_{(3-\delta)}$ perovskites present high metallic conductivity and Pauli-paramagnetism, and could be used as electrodes in electrochemical devices such as SOFCs, PEMFCs and MCFCs. Additionally, due to its $\sigma^*$ conducting band, this material shows a very high electrocatalytic activity, particularly in oxygen reduction processes, with an efficiency comparable to that of platinum. This work describes the combustion synthesis of La$_{1-(1-\delta)}$NiO$_{(3-\delta)}$ perovskite powders ($x=0$ and 0.1) from mixtures of La(NO$_3$)$_3$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O as cation precursors, and urea as fuel. The as-prepared combustion product, characterized by XRD, DTA/TG, SEM/TEM, BET and dilatometry (after compaction), shows a much higher specific surface area than powders obtained via alternative routes and contains La$_3$NiO$_6$ with a typical K$_2$NiF$_4$-type structure, together with small amounts of NiO. The usual subsequent heat treatments for 1 to 12 h at successively higher temperatures showed that full conversion to La$_{1-(1-\delta)}$NiO$_{(3-\delta)}$ can be readily achieved in air at 750 °C and that the perovskite, after the 12 h heat treatment, remains stable up to 1100 °C. These results show that the combustion technique is a better and much simpler route to the synthesis of perovskite powders.

Introduction

Oxides with the perovskite structure, given the generally high mobility of oxygen ions, are prone to oxygen vacancies and the lanthanum nickel oxide LaNiO$_{3-\delta}$, which displays metallic conduction, finds a possible application as cathodic material in electrochemical devices, such as solid oxide fuel cells (SOFCs), polymer electrolyte membrane fuel cells (PEMFCS) and molten carbonate fuel cells (MCFCs), in which oxygen reduction processes are involved. One of its limitations in this field is instability in the range 750–1100 °C, which includes the device manufacture and/or service temperature, leading to decomposition into La$_2$NiO$_4$ and NiO, or segregation of La$_2$O$_3$. This limitation has so far been partially overcome with the use of lanthanum-deficient oxides, La$_{1-(1-\delta)}$NiO$_{(3-\delta)}$. Such perovskite-type oxides are known to display catalytic activity for a number of chemical reactions, particularly oxidation processes, and the synthesis of oxygenated organic compounds from hydrocarbons, CO$_2$ and H$_2$.1–3 Such perovskite-type oxides can be readily achieved in air at 750 °C. These results show that the combustion technique is a better and much simpler route to the synthesis of perovskite powders.
established irrespective of whether the elements are present in the oxidizer or the fuel components of the mixture. The assumed valences are those presented by the elements in the usual products of the combustion reaction, which are CO2, H2O and N2. The extrapolation of this concept to the combustion synthesis of ceramic oxides means that metals like La and Ni (or any other metals) should also be considered as reducing elements with the valencies they have in the corresponding oxides.

The work that follows describes the powder synthesis of lanthanum nickel perovskites by combustion reaction of redox mixtures of the corresponding metal nitrates with urea.

Experimental

For the combustion synthesis of the LaNiO3−δ perovskites (x = 0 and 0.1), Ni(NO3)2·6H2O (Carlo Erba) and La(NO3)3·6H2O (Merek) were used as cation precursors and urea. CO(NH2)2 (Riedel-de Haën), was used as fuel (batches were calculated on the basis of 5 g of lanthanum nitrate). The reactants were first melted in a wide-mouth vitreous silica basin (300 cm3) by heating up to ca. 300 °C on a hot-plate inside a fume cupboard, under ventilation. Soon after the liquid began frothing, the basin was transferred to a muffle furnace preheated at 500 °C, where ignition took place. The reaction lasted for 2.5 minutes and produced a dry black and very fragile foam, that readily crumbled into powder.

The as-prepared combustion reaction powders were characterized by X-ray diffraction (Cu-Kα/2Ni, Siemens D5000 diffractometer, 40 kV and 20 mA, with a scanning rate of 2°/min), using silicon as an internal standard and Scanning Electron Microscopy (Zeiss DSM-950, 20 kV, after Au coating). Powder density was determined with a Quantachrome He multipienometter and the BET specific surface area with a He–N2 Monosorb MS-13 instrument. The particle size distribution was determined with a Coulter LS-130 instrument. Particle powders were easily deagglomerated into individual crystals by ultrasonication in isopropyl alcohol and crystallite sizes were assessed by determining their electrophoretic mobility and zeta potential in aqueous suspensions (distilled water) as a function of pH with a Malvern ZetaSizer 4 instrument (ZET 5104 cell).

Results and discussion

1 Combustion reactions

To prepare the LaNiO3−δ perovskite by the combustion route, using urea as fuel, crystalline Ni(NO3)2·6H2O can be used as a Ni source (total valencies −10) and La(NO3)3·6H2O as a La source (total valencies −15). From published thermodynamic data such as those listed in Table 1, 21–24 the enthalpy change involved in the various chemical reactions can be calculated. The combustion reaction of urea (total valencies +6), described by the equation R1 in Table 2, is exothermic and would provide the heat needed for the synthesis reaction. The individual decomposition reactions of the precursor nitrates, leading to the corresponding oxides, are also listed in Table 2, as reactions R2 and R3, respectively.

The overall synthesis would then be given by the reaction RT1 = R1 + R2 + R3 (Table 2). For LaNiO3−δ synthesis, reaction RT1, to occur at 25 °C n = 2.11 mol of urea would be needed, solely on the basis of enthalpy change (∆HRT1 = 0).

This amount of urea satisfies the enthalpy requirement for complete decomposition at 25 °C and release of all the corresponding gases, as predicted by reaction RT1 (i.e. 16.23H2O(g) + 4.61NiSO4·2.84O2(g) + 2.11CO2(g)). However, this temperature is not high enough to promote the synthesis of the perovskite and the single oxides (i.e. NiO and 0.5La2O3) would remain as reaction products.

Direct use of the propellant chemistry criterion, with the metal precursors in a 1:1 molar ratio, to determine the urea needed to balance the total oxidizing and reducing valencies in the mixture of oxidizers and fuels, leads to:

\[-10 + (-15) + n(+6) = 0\]

In order to release the maximum energy for the reaction, the stoichiometric composition of the redox mixture would demand that n = 4.17 mol of urea were used. The combustion of the extra 2.06 mol of urea specified by the propellant chemistry calculations will consume all the released oxygen and the heat generated will be absorbed by the resulting gases (i.e. 4.12H2O(g) + 2.06O2(g) + 2.06CO2(g)), the gases already present and the single oxides, raising their temperature. Using the relevant heat capacities listed in Table 1 and the ∆HRT1 value in Table 2, the temperature reached by all the final products would be 857 °C. This temperature should be sufficient to promote perovskite synthesis, although other synthetic methods usually require 12 h exposures at temperatures in excess of 750 °C to produce the LaNiO3−δ phase from a mixture of La2NiO4 and NiO.

Batches were prepared with Ni(NO3)2·6H2O, La(NO3)3·6H2O and CO(NH2)2 in the molar ratio 1:1:4.17. The mixture ignited easily and, after a short reaction time (2–3 min), a dry black foam was produced, accompanied by a large increase in volume when compared to the original volume of liquid. The X-ray diffraction pattern of the as-prepared powder (Fig. 1) showed crystalline LaNiO3 as the major phase present, together with a small amount of NiO.

This result suggests that the overall reaction is more

<table>
<thead>
<tr>
<th>Compound</th>
<th>∆Hf (25 °C)/kcal mol⁻¹</th>
<th>C/°C/cal mol⁻¹</th>
<th>K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(NO3)3·6H2O</td>
<td>−528.6</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>La(NO3)3·6H2O</td>
<td>−732.23</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>La(NO3)3·6H2O</td>
<td>−299.8</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>CO(NH2)2</td>
<td>−79.71</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>La(NO3)3·6H2O</td>
<td>−292.8</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>La(NO3)3·6H2O</td>
<td>−486.7</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>−117.0</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>−57.3</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>La(NO3)3·6H2O</td>
<td>−428.7</td>
<td>26.00</td>
<td></td>
</tr>
<tr>
<td>La(NO3)3·6H2O</td>
<td>−57.976</td>
<td>7.20 + 0.00367 T</td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>−94.051</td>
<td>10.34 + 0.00274 T</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>0</td>
<td>6.50 + 0.00107 T</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
<td>5.92 + 0.00367 T</td>
<td></td>
</tr>
</tbody>
</table>

Note: *c* = crystalline, *g* = gas, *T* = absolute temperature. *C* calculated from discrete values.
accurately described as RT2 = RS2 + mR1 (Table 2). A calculation entirely similar to that described above leads to a theoretical temperature reached by all the final products in reaction RT2 of 796 °C. This temperature, although comparable to the one obtained for reaction RT1, is closer to the experimental value of 750 °C and an indication that the stoichiometric urea content is adequate, if adiabatic conditions prevail. It should be noted, however, that significant heat losses may occur and the actual maximum temperature might well be lower. Also, the short reaction time of 2–3 min is very much shorter than the 12 h exposure usually needed at this temperature.

The lanthanum-deficient perovskite La0.9NiO3−δ was also prepared by combustion reaction from batches prepared with Ni(NO3)2·6H2O, La(NO3)3·6H2O and CO(NH2)2 in the molar ratio 0.9:1:3.92. The mixture also ignited easily and, after an equally short reaction time, a dry black foam was also produced. Again, the X-ray diffraction pattern of the as-prepared powder showed crystalline La2NiO4 as the major phase present, together with a small amount of NiO. At this point, it is worth mentioning that La2NiO4−δ synthesis by the solid state route normally requires exposure to temperatures in the range 900–1200 °C for 24 h and repeated intermediate grinding steps. 23 The combustion synthesis technique will undoubtedly prove to be a much simpler and more reliable route to synthesize this compound as well.

2 Powder characterization

The as-prepared powders were further characterized and the BET specific surface area of the stoichiometric perovskite precursor powder was determined to be 9.5 m² g⁻¹. When observed by TEM, individual crystals could be clearly perceived by alternating bright/dark field. Typically, agglomerates of very fine crystals (ca. 10 nm) could be seen (Fig. 2), producing the electron diffraction rings shown in the inset in Fig. 2. For the La-deficient perovskite precursor powder, which

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**Table 2** Equations describing the various chemical reactions that might be involved in the combustion synthesis

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Descriptive equation</th>
<th>( \Delta H ) (25°C)/kcal²</th>
</tr>
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<tbody>
<tr>
<td>R1</td>
<td>( \text{CO(NH}_2\text{)}_2\quad(\text{g}) + 1.5 \text{O}_2 \quad(\text{g}) \rightarrow \text{CO}_2\quad(\text{g}) + 2\text{H}_2\text{O}\quad(\text{g}) + \text{N}_2\quad(\text{g}) )</td>
<td>-129.9</td>
</tr>
<tr>
<td>R2</td>
<td>( \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) \rightarrow \text{NiO}\quad(\text{g}) + \text{N}_2\quad(\text{g}) + 2.5 \text{O}_2 \quad(\text{g}) + 6\text{H}_2\text{O}\quad(\text{g}) )</td>
<td>124.5</td>
</tr>
<tr>
<td>R3</td>
<td>( \text{La(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) \rightarrow 0.5\text{La}_2\text{O}_3\quad(\text{g}) + 6\text{H}_2\text{O}\quad(\text{g}) + 1.5\text{N}_2\quad(\text{g}) + 3.75\text{O}_2\quad(\text{g}) )</td>
<td>171.1</td>
</tr>
<tr>
<td>R4</td>
<td>( \text{NiO}\quad(\text{g}) + 0.5\text{La}_2\text{O}_3\quad(\text{g}) + 0.25 \text{O}_2 \quad(\text{g}) \rightarrow \text{La}_2\text{NiO}_4\quad(\text{g}) )</td>
<td>-21.2</td>
</tr>
<tr>
<td>R5</td>
<td>( \text{La}_2\text{O}_3\quad(\text{g}) + \text{NiO}\quad(\text{g}) \rightarrow \text{La}_2\text{NiO}_4\quad(\text{g}) )</td>
<td>-0.7</td>
</tr>
<tr>
<td>RS1</td>
<td>( \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) + \text{La(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) \rightarrow \text{La}_2\text{NiO}_4\quad(\text{g}) + 12\text{H}_2\text{O}\quad(\text{g}) + 2.5\text{N}_2\quad(\text{g}) + 6\text{O}_2\quad(\text{g}) )</td>
<td>274.4</td>
</tr>
<tr>
<td>RS2</td>
<td>( \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) + \text{La(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) \rightarrow 0.5\text{La}_2\text{NiO}_4\quad(\text{g}) + 0.5\text{NiO}\quad(\text{g}) + 12\text{H}_2\text{O}\quad(\text{g}) + 2.5\text{N}_2\quad(\text{g}) + 6\text{O}_2\quad(\text{g}) )</td>
<td>295.3</td>
</tr>
<tr>
<td>RT1</td>
<td>( \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) + \text{La(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) + m\text{CO(NH}_2\text{)}_2\quad(\text{g}) + (1.5m - 6)\text{O}_2\quad(\text{g}) \rightarrow \text{La}_2\text{NiO}_4\quad(\text{g}) + (12 + 2m)\text{H}_2\text{O}\quad(\text{g}) + (2.5 + m)\text{N}_2\quad(\text{g}) + m\text{CO}_2\quad(\text{g}) )</td>
<td>274.4 + m(-129.9)</td>
</tr>
<tr>
<td>RT2</td>
<td>( \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) + \text{La(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\quad(\text{g}) + m\text{CO(NH}_2\text{)}_2\quad(\text{g}) + (1.5m - 6.25)\text{O}_2\quad(\text{g}) \rightarrow 0.5\text{La}_2\text{NiO}_4\quad(\text{g}) + 0.5\text{NiO}\quad(\text{g}) + (12 + 2m)\text{H}_2\text{O}\quad(\text{g}) + (2.5 + m)\text{N}_2\quad(\text{g}) + m\text{CO}_2\quad(\text{g}) )</td>
<td>295.3 + m(-129.9)</td>
</tr>
</tbody>
</table>

*Calculated from thermodynamic data listed in Table 1.

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Fig. 1 X-Ray diffractograms of LaNiO3−δ powders, as-prepared and calcined at 750 °C for 1, 2, 4, 8 and 12 h, and at 900 and 1100 °C for 12 h, showing the characteristic peaks of LaNiO3−δ with rhombohedral symmetry.

is also crystalline, a larger crystallite size of 150 nm was found and a BET specific surface area of 8 m$^2$ g$^{-1}$ was obtained.

The powders were then subjected to a temperature of 750 °C for successively longer periods of time (namely, 1, 2, 4, 8 and 12 h), and investigated by X-ray diffraction. The corresponding diffractograms (Fig. 1) show that the LaNiO$_{3-d}$ perovskite is readily produced, with crystallinity increasing with increasing time at the temperature. The perovskites were found to be stable after 12 h exposure to higher temperatures (900 and 1100 °C), as shown by the corresponding X-ray diffractograms also presented in Fig. 1, although the stoichiometric perovskite seems to present a narrower stability range. From the X-ray diffraction patterns of single phase powders calcined at 750 °C for 8 h, $a$ and $c$ lattice parameters (hexagonal structure) were calculated and found to be in good agreement with published values, namely, $a=0.5464(1)$ and $c=0.65799(2)$ nm for the stoichiometric perovskite, and $a=0.5454(1)$ and $c=0.65854(2)$ nm for the La-deficient perovskite.

After 12 h at 750 °C, the powder density was determined to be 7.12 ± 10$^3$ kg m$^{-3}$ for the calcined stoichiometric perovskite and 5.56 ± 10$^3$ kg m$^{-3}$ for the La-deficient perovskite. The typical calcined powder morphology can be observed in the SEM micrograph shown in Fig. 3. The BET specific surface area of the stoichiometric perovskite decreased to 4.5 m$^2$ g$^{-1}$ and the corresponding average particle size was found to be 6.9 μm, within a monomodal grain size distribution [Fig. 4(A)]. As for the La-deficient perovskite, after the same heat treatment the BET specific surface area was determined to be 4.7 m$^2$ g$^{-1}$ and an average particle size of 10 μm was obtained, within a bimodal grain size distribution [Fig. 4(B)]. The narrow particle size distribution of the calcined stoichiometric powder, practically monosized, suggests that it might display low packing densities although its high specific surface area should ensure good sinterability. The submicron features of the as-prepared powders on the other hand, promote densification but associated with unsuitable powder morphology and poor powder packing might cause abnormal grain growth and hinder densification (the driving free energy for mass transport is inversely proportional to particle size, but rapid grain growth by boundary motion and not via surface diffusion only occurs when the body density is greater than 90%).

The thermal analyses (DTA) of the as-prepared combustion powders showed as their salient features an endothermic peak at 750 °C which was attributed to the nucleation of the perovskite phase. The dilatometry study carried out on the as-prepared powders (Fig. 5) showed that the shrinking rate peaks first at 725, then at 980 and finally at 1225 °C. The X-ray

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Fig. 2 TEM micrographs of the as-prepared LaNiO$_{3-d}$ powders, showing: typical particle agglomerates and (inset) electron diffraction pattern of polycrystals.

Fig. 3 Typical calcined powder morphology as seen with SEM (LaNiO$_{3-d}$, 750 °C, 12 h, in air).

Fig. 4 Particle size distribution of the perovskite powders after calcining at 750 °C, 12 h: (A) LaNiO$_{3-d}$ and (B) La$_{0.9}$NiO$_{3-d}$. 

diffractogram of the powder calcined at 725 °C already showed the presence of crystalline perovskite, although with cubic symmetry, and still containing some La$_2$NiO$_4$. Thus, the first maximum in the shrinking rate can be attributed to perovskite phase formation, confirming the DTA results. The second maximum in the shrinking rate could be attributed to a significant oxygen loss as the perovskite changes from cubic to rhombohedral symmetry (the oxygen deficiency was determined as weight gain in oxygen after 3 h at 900 °C, and the values obtained were $\delta = 0.05$ for La$_{1.98}$NiO$_{3.78}$, and $\delta = 0.03$ for LaNiO$_{3.6}$; these figures are below the range of 0.10–0.18 reported in the literature). The last maximum corresponds to the decomposition of the perovskite into La$_2$NiO$_4$ and other La and Ni mixed oxides.

The electrokinetic studies carried out showed that the stoichiometric perovskite has an isoelectric point near pH 2 reaching a stable zeta potential of ca. −50 mV above pH 7 (Fig. 6). According to the DLVO theory, powder suspensions show colloidal instability near the isoelectric pH (e.g. they flocculate) and they are stable away from that pH value. For practical purposes, a repulsive potential greater than ±30–40 mV is needed to guarantee a well-dispersed suspension. The above result shows that aqueous suspensions of the stoichiometric perovskite are fully dispersed and adequate for further processing (e.g. electrode deposition) at neutral pH.

Conclusions

This work shows that the valency based molar proportions of reactants proposed by propellant chemistry can be conveniently used to successfully produce adequate La–Ni perovskite precursors, with good compositional control and homogeneity, which readily transform to crystalline perovskite at low temperatures over short calcination times. In fact, the synthesis of the La$_{1.98}$NiO$_{3.78}$ ($x=0$ and 0.1) perovskites is readily achieved by calcining the as-prepared combustion-produced powder precursors at 750 °C for just 1 h, whereas other synthetic methods require exposures of at least 12 h. This is, no doubt, a consequence of the atomic level homogeneity of the combustion-produced powders. Like various other methods that have been proposed and used to prepare ceramic powders, the combustion synthesis route enables synthesis at low temperatures and the products obtained are in a finely divided state with large surface areas. Unlike other methods, combustion synthesis offers the added advantages of simplicity of the experimental set-up, a surprisingly short time period between the preparation of the reactants and the availability of the final product, savings in external energy consumption and the equally important potential for simplifying the processing prior to forming, providing a simple alternative to other more elaborate techniques.

Even after 12 h at 750 °C, and despite grain growth, the combustion perovskites still presented specific surface areas in the order of 4.5 m$^2$ g$^{-1}$, due to the original very fine particle size, whereas powders produced by the solid state ceramic route typically present values of the order of 0.5 m$^2$ g$^{-1}$. This result suggests that a much higher catalytic activity can be expected from combustion perovskites compared with similar powders produced by alternative routes. The high homogeneity of the as-prepared combustion powders also explains the higher thermal stability observed for these perovskites (i.e. in the 750–1100 °C temperature range used in the manufacture and/or service of SOFCs, PEMFCs and MCFCs) with no signs of segregation of La$_2$O$_3$, a problem commonly displayed by perovskites produced by alternative techniques.

It is also worth mentioning that the major phase present in the as-prepared combustion powders is crystalline La$_2$NiO$_4$, whose synthesis by the solid state route requires exposure to temperatures in the range 900–1200 °C for 24 h and repeated intermediate grinding steps. Again, the combustion synthesis technique will undoubtedly be a much simpler and more reliable route to synthesize this compound.

The pH dispersion range of the perovskites aqueous suspensions was found to be broad and around pH 7, which results in a rather forgiving suspension preparation step prior to further processing.

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References


Fig. 5 Dilatometric curves obtained with the as-prepared powders, highlighting the changes in shrinking rate as a function of temperature ($L_0$ is the length of the test piece, $L_0$ being the initial length).

Fig. 6 Typical zeta potential vs. pH curve for calcined powders suspended in distilled water (LaNiO$_{3.6}$–$\delta$, 750 °C, 12 h, in air)

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