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Pr₄Ni₃O_{10+δ}: a new promising oxygen electrode material for Solid Oxide Fuel Cells

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Abstract

The present work is focused on the study of Pr₄Ni₃O_{10+δ} as a new cathode material for Solid Oxide Fuel Cells (SOFCs). The structural study leads to an indexation in orthorhombic structure with Fmmm space group, this structure being thermally stable throughout the temperature range up to 1000 °C under air and oxygen. The variation of oxygen content (10+δ) as a function of temperature under different atmospheres show that Pr₄Ni₃O_{10+δ} is always oxygen over-stoichiometric, which further suggests its MIEC properties. The polarization resistance (R_p) of Pr₄Ni₃O_{10+δ} electrode is measured for GDC/co-sintered and two-step sintered half cells. The R_p for co-sintered sample is found to be 0.16 Ω·cm² at 600 °C under air, which is as low as the one of highest performing Pr₂NiO_{4+δ} nickelate (R_p = 0.15 Ω·cm² at 600 °C). Moreover, an anode supported (Ni-YSZ//YSZ) single cell including GDC//Pr₄Ni₃O_{10+δ} co-sintered electrode shows a maximum power density of 1.60 W·cm⁻² at 800 °C and 0.68 W·cm⁻² at 700 °C. Here, the work is emphasized on the very close electrochemical performance of Pr₄Ni₃O_{10+δ} compared to the one of Pr₂NiO_{4+δ} with higher chemical stability, which gives great interests to consider this material as a very interesting oxygen-electrode for SOFCs.

Keywords: SOFC, Nickelates, Chemical stability, Oxygen over-stoichiometry, OER

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1. Introduction

The decrease of the operating temperature of the SOFCs is a critical challenge for their commercialization. Currently, the main objective is to decrease it down to around 600 – 700°C, in an effort to decrease the device cost (for example, using stainless steel instead of ceramics as interconnects) and to improve the cell durability. However, since the electrode reactions as well as ion transport through the electrolyte are temperature-driven, the electrochemical performance drastically decreases with temperature. Hence, it is mandatory to improve the materials and architecture of the cell in order to reach reasonable performances at intermediate temperatures (600–700 °C). It is well known that promising materials for cathodes are Mixed Ionic and Electronic Conducting (MIEC) oxides [1-7]. Several attempts were made to find the best MIEC material for SOFCs in last few decades.

Recently Ruddlesden-Popper (RP) phases $\text{Ln}_{n+1}\text{NiO}_{3n+1}$ ($\text{Ln} = \text{La}, \text{Pr}$ or Nd) have shown excellent transport and electrochemical properties [6, 8-9]. The crystal structure of these phases can be described by the stacking of a finite number ($n = 1, 2, 3$ mainly) of perovskite-type LnNiO_3 layers and one rock salt LnO layer along the crystallographic c -direction $((\text{LnO}).(\text{LnNiO}_3)_n)$ [10-11]. The first member of the RP family of nickelates, $n = 1$, is $\text{Ln}_2\text{NiO}_{4+\delta}$, which adopts the K_2NiF_4 -type structure with one layer of corner-sharing NiO_6 octahedra along the c -direction.

In the second member of RP nickelates, $n = 2$ ($\text{Ln}_3\text{Ni}_2\text{O}_{7\pm\delta}$), two infinite NiO_6 sheets are connected in c -direction between the rock salt layers. For $n = 2$, the electrical conductivity is significantly enhanced compared to $\text{Ln}_2\text{NiO}_{4+\delta}$ as the nickel oxidation state and electronic correlation along c -direction increases.

Similarly, the structure of $\text{Ln}_4\text{Ni}_3\text{O}_{10+\delta}$ ($n = 3$) is built with three infinite NiO_6 sheets connected in c -direction between the rock salt layers. Greenblatt reported that the smallest rare earth ion able to still stabilize $\text{Ln}_4\text{Ni}_3\text{O}_{10+\delta}$ is Nd [11]. A metallic conductivity is observed for all the $\text{Ln}_4\text{Ni}_3\text{O}_{10+\delta}$ phases and a metal-to-metal transition is observed for the $\text{Ln} = \text{Pr}$ and Nd at 145 and 165K, respectively [11, 12]. The $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ has higher conductivity value in the 25–300 K temperature range than $\text{Nd}_4\text{Ni}_3\text{O}_{10+\delta}$, but lower than $\text{La}_4\text{Ni}_3\text{O}_{10+\delta}$. Regarding $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$, Bassat *et al.* have previously shown that the material is metallic [12], the transport properties being highly dependent on the δ -value. Depending on the synthesis technique the δ varies from -0.1 to $+0.1$.

The first member of RP family, $\text{Ln}_2\text{NiO}_{4+\delta}$ ($\text{Ln} = \text{La}, \text{Pr}$ and Nd) compounds have already evidenced promising results when used as cathode materials for SOFCs due to their MIEC properties [13-15]. $\text{Pr}_2\text{NiO}_{4+\delta}$ has the best electrochemical properties among three nickelates, especially at intermediate temperature (600–700°C) [16]. We have recently reported the decomposition of $\text{Pr}_2\text{NiO}_{4+\delta}$ into $\text{PrNiO}_{3-\delta}$, $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ and Pr_6O_{11} at the operating temperature range (600 to 800 °C) during long term [17]. A very interesting point is that even after complete dissociation the electrochemical performance, at least under $i_{\text{dc}} = 0$ condition, do not show significant change (*i.e.* the same polarization resistance (R_p) values are obtained before and after ageing). Therefore, it is our goal to study the behaviour of these new forming materials, and in this study we especially focused on $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$.

According to author's knowledge, the literature on $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ remains scarce and limited to non-stoichiometry, transport and magnetic properties [10, 12], whereas its use as oxygen electrode in the field of SOFCs has never been reported. An effort was then made to investigate the properties of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$, mainly the non-stoichiometry, chemical stability under different $p\text{O}_2$ and electrochemical activity under air for use as an oxygen electrode material of SOFCs.

2. Experimental

2.1. Powder preparation

The $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ phase was synthesised using the Glycine Nitrate Process (GNP) [18]. The corresponding precursors were $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich , 99.99%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros Organics, 99%) and glycine (Sigma Aldrich , 99.9%). The final annealing was performed at 1000 °C for 48 h under oxygen leading to well crystallized phases. Intermediate grinding and annealing steps were performed 3 times.

2.2. X-ray diffraction analysis

The powders were first investigated by X-Ray diffraction (XRD) at room temperature using a PANanalytical X'pert MPD diffractometer with Cu-K_α incident radiation to check the purity of phase. The XRD vs T (*i.e. in situ* XRD) were performed to check the stability of phase with temperature under air. The data were recorded for both heating and cooling, from room temperature up to 1000°C, by steps of 100°C. The heating and cooling rate was fixed to 2 °C.min⁻¹, the powder being thermally equilibrated for 2 h at each particular temperature prior to the XRD data recording. The X-ray diffractogram recorded on the powder during cooling is preferentially reported here thanks to a thermal equilibrium which is expected to be more easily reached in this case.

The ageing test of powder was performed under air. Green pellets were first prepared and then left into a furnace for 1 month at 600, 700 and 800 °C, before the XRD characterization. Each X-ray diffractogram was fitted by profile matching using the Fullprof software.

2.3. SEM analysis

The microstructures of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ powder and the electrodes morphology were observed by field emission Scanning Electron Microscopy (JEOL JSM 6330 A) equipped with an EDS detector.

2.4. Thermo Gravimetric analysis (TGA)

TGA experiments were carried out using a TA Instrument TGA-Q50 device, with the aim *i)* to determine the delta value, δ , at room temperature under air, *ii)* to investigate the thermal stability vs. $p\text{O}_2$ and *iii)* to study the δ variation vs. T under air and oxygen atmospheres. In the first case the powders were beforehand heated under air up to 1000 °C, then cooled down to room temperature with a slow rate (2 °C.min⁻¹), this cycle being reproduced twice to ensure a stable state of the material, *i.e.* a reproducible oxygen content. Then, a second cycle was performed under Ar - 5% H₂ flux with a very slow heating rate of (0.5 °C.min⁻¹), the decomposition of the material leading to the determination of the oxygen stoichiometry after cycling the sample down to room temperature (Pr₂O₃ and metallic Ni being formed as checked by XRD after the thermal cycle). Secondly, the thermal stability of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ was investigated as a function of $p\text{O}_2$, the variation of the oxygen stoichiometry of the materials being successively studied under air ($p\text{O}_2 = 0.21$ atm) and oxygen ($p\text{O}_2 = 1$ atm), using heating and cooling rates of 2 °C.min⁻¹. For this purpose, the powders were first thermodynamically equilibrated under air in the TGA device as described above (*i.e.* two cycles were performed under air). The gas was changed at room temperature and again two cycles were performed under oxygen. During cycling, the powder was left for 1 h at 1000 °C and room temperature.

2.5. Conductivity measurements

It was first expected to prepare dense pellets by sintering the green pellets at 1000 °C for 24 h under oxygen, which are mandatory conditions to ensure keeping the pure $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ phase. However, it is worth mentioning that we could not succeed probably because of such limitation of temperature, 70 % being the highest density value obtained. The electrical conductivity was then determined under air using the four-probe technique, in the temperature range 20 – 800 °C with the heating and cooling rate of 1 °C.min⁻¹.

2.6. Preparation of symmetrical half cells

For the electrochemical studies, symmetrical half cells (electrode//GDC//8YSZ//GDC//electrode) were prepared. Dense pellets of 8YSZ (8 mol.% yttria stabilized zirconia) with diameter $\approx$ 18 mm and thickness $\approx$ 1.2 mm (preliminarily sintered at $T = 1400$ °C) were used. The symmetrical half-cells were prepared by screen printing using two ways, *i.e.* two-step or co-sintering of the GDC/electrode layers. Terpeneol-based slurries were prepared from as prepared $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ powder and commercial GDC powder (Rhodia-Solvay). In order to increase the electrochemical performances of the half-cells [16], a 2-3 μm GDC bi-layer was initially screen printed on both sides of the 8YSZ electrolyte pellet. The main role of GDC is, a) to obtain good interface and b) to stop the reactivity, between electrode and electrolyte.

Regarding the two steps sintering way, the GDC layer was first sintered at 1375 °C for 1 h under air. The electrode layer was then screen printed on each side of the GDC//8YSZ//GDC. The sintering study of the electrodes will be detailed in the Results and Discussion part.

The symmetrical half cells were also prepared by co-sintering the GDC and electrode layers. For this purpose, in a first step a single GDC layer was deposited on both sides of 8YSZ pellet.

After drying ($T \sim 80\text{ }^{\circ}\text{C}$), the electrode layer was deposited on both sides by screen printing technique and co-sintered with GDC layer at $950\text{ }^{\circ}\text{C}$ for 2 h under air.

A single cell was fabricated starting from a commercial anode supported half cell (Elcogen ASC-10C type) made of a $500\text{ }\mu\text{m}$ thick Ni-8YSZ anode and a $3\text{ }\mu\text{m}$ thick 8YSZ electrolyte membrane ($\varnothing = 50\text{ mm}$). A GDC layer ($\varnothing = 25\text{ mm}$) was first deposited on Ni-8YSZ//8YSZ support and then dried at $80\text{ }^{\circ}\text{C}$. After the deposition and sintering of the cathode layer ($\varnothing = 16\text{ mm}$, see Single Cell measurements part), a $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LNF) layer ($\varnothing = 16\text{ mm}$) was deposited to improve the current collection [19].

2.7. Electrochemical measurements

The electrochemical properties of the symmetrical half-cells were characterized by Electrochemical Impedance Spectroscopy (EIS). The initial EIS measurements were carried out under air, in the temperature range $500 - 800\text{ }^{\circ}\text{C}$ under zero dc conditions. Gold grids (1.024 cm^{-2} meshes) were used as current collectors. The impedance diagrams were recorded at steady state under potentiostatic control with 50 mV ac amplitude, from 10^6 Hz down to 10^{-1} Hz , using a frequency response analyser module Autolab FRA2, coupled with a potentiostat/galvanostat PGSTAT 302N. The polarization resistance (R_p) values were obtained by taking the difference between the low frequency (LF) and the high frequency (HF) intercepts with the real Z' -axis of the Nyquist representation. The complex impedance diagrams were fitted using an equivalent circuit by means of the Zview® (Scribner Associates) to measure the R_p of different processes.

Prior to single cell measurements, the anode was reduced using the following procedure: after heating in N_2 up to $800\text{ }^{\circ}\text{C}$, the anode side was flushed with hydrogen gas with a flow rate of $250\text{ ml}\cdot\text{min}^{-1}$. On the cathode side, synthetic flowing air was supplied as oxidant with flow rate

of 500 ml.min⁻¹. The impedance diagrams were recorded at OCV, 0.9, 0.8 and 0.7 V, at the operating temperatures, namely 800 and 700 °C. The ageing of a single cell at 700 °C was performed at a current density of 0.3 A·cm⁻², using a Frequency Response Analyzer module Autolab FRA2, coupled with a potentiostat/galvanostat PGSTAT 302N.

3. Results and discussion

3.1. XRD analysis

The XRD characterization of as-prepared Pr₄Ni₃O_{10+δ} phase shows that the material crystallizes in an orthorhombic structure with Fmmm space group. The full pattern profile matching refinement leads to determine the following lattice parameters: a = 5.3714(2) Å, b = 5.4611(2) Å and c = 27.5271(3) Å (Fig. 1a), these values are in good agreement with the previously reported results [10, 12].

3.1.1. Thermal behaviour of the material with temperature under air (XRD vs. T)

The thermal variation of the X-ray diffractogram under air shows that the Pr₄Ni₃O_{10+δ} phase remains stable up to 1000 °C; with increasing temperature, the structure keeps always the orthorhombic symmetry and is indexed with the *Fmmm* space group. An example is given in Fig. 1a; at 1000 °C the refinement of the data leads to the following lattice parameters: a = 5.4300(4) Å, b = 5.4858(3) Å and c = 27.8910(3) Å. The absence of additional peaks with regard to the room temperature diagram confirms the stability of the material up to 1000 °C under air.

3.1.2. Variation of lattice parameters with temperature: determination of TEC

In Fig. 1b, the variations of a , b and c lattice parameters as a function of temperature are plotted. All of them show linear increase throughout the temperature range. The thermal expansion coefficient of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ was calculated from the thermal variation of the lattice parameters *i.e.* the slope of $(\lambda - \lambda_0/\lambda_0)$ vs T (Fig. 1c), where λ and λ_0 are cubic root of volume at particular temperature and room temperature respectively. The value of TEC is close to $\sim 10 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ which is in the same order of those of the other components of SOFCs [20]. Following dilatometry measurements, a TEC value of $12 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ was also determined; the observed discrepancy could be assigned to the fact that the pellet was not sufficiently dense.

3.2. TG analyses

Because the electrochemical behaviour of the material will be studied under air, we aim first to determine the over-stoichiometry value δ after thermal equilibration under air, following the synthesis which is performed under oxygen. Later on, the evolution of δ vs. T under air and oxygen will be recorded. Another part of this TGA study will aim to determine the thermal stability range of the material either under air or oxygen.

3.2.1. Determination of δ of material equilibrated under air

The δ -value for $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ was calculated using TGA experiments performed under reducing conditions (5% H_2/Ar atmosphere, Fig. 2a). Two major weight losses occur: the first one at around $400 \text{ }^\circ\text{C}$, which corresponds to the reduction of Ni^{3+} into Ni^{2+} (corresponding plateau $\text{Pr}_4\text{Ni}_3\text{O}_9$ is formed [21]), while the second weight loss corresponds to the complete reduction of Ni^{2+} into metallic Ni^0 . Finally the total reduction of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ into Pr_2O_3 and Ni (within the appropriate ratio) is then evidenced, leading to the determination of δ . The

calculated value corresponding to the first plateau and after total reduction results in the almost same value, $\delta = 0.10 \pm 0.01$ at room temperature.

3.2.2. Behavior under air and oxygen

TGA experiments were carried out under air and oxygen with the aim to investigate the chemical stability and to find the most appropriate temperature and atmosphere for the sintering of electrodes made of this material (refer to experimental part). Fig. 2b and 2c show the variation of the weight loss with temperature for $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ in air and in oxygen atmosphere, respectively; the results largely depend upon $p\text{O}_2$. Under air, $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ exhibits thermal stability up to $\sim 1050^\circ\text{C}$. Above this temperature it starts decomposing and around $T = 1140^\circ\text{C}$, it is completely decomposed into $\text{Pr}_2\text{NiO}_{4+\delta}$ and NiO (Fig. 2b). This decomposition was checked by XRD, both on the powder at the end of this TGA cycle (*cf.* Fig. S1a) or after quenching another set of powder from 1200°C to RT in a separate furnace (not reported). This decomposition is completely irreversible under air, $\text{Pr}_2\text{NiO}_{4+\delta}$ phase being stable under air as confirmed by a second TGA cycle (not reported).

Under oxygen, $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ shows higher stability than in air, up to 1120°C (Fig. 2c) and above this temperature, it decomposes again into $\text{Pr}_2\text{NiO}_{4+\delta}$ and NiO (as checked by XRD again). However, the behaviour when cooling under oxygen is completely different than what was previously observed under air. Indeed, $\text{Pr}_2\text{NiO}_{4+\delta}$ starts again changing into $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ and PrO_x (around 950°C). The XRD analysis at the end of cooling process shows the presence of mixture of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$, $\text{Pr}_2\text{NiO}_{4+\delta}$, PrO_x and NiO (*cf.* Fig. S1b), which is in agreement with the previously reported results for $\text{PrNiO}_{3-\delta}$ [22].

3.2.3. Variation of the oxygen content (δ value) under air and oxygen

In the following, the thermal variation of the oxygen content was investigated over the stability domain of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$, *i.e.* from room temperature up to 1000 °C (*cf.* Fig. 2b, c). Before starting the experiment, the powder was first equilibrated under air, ensuring the starting value of $\delta \sim 0.10$. For both atmospheres, two cycles were performed to reach the reversibility while the powder was kept for 1 hour at the 1000 °C before cooling. The thermal variation of the oxygen content, $10+\delta$, under air and oxygen is plotted in Fig. 2d. In air, a reversible behaviour is observed during both cycles.

Under oxygen, the material is up taking oxygen during first cycling, then, a reversible behavior is observed (2nd cycle is reported). One should point out that the material is always oxygen over-stoichiometric within the whole stability temperature range.

The cycling was also performed under argon up to 800 °C (*cf.* Fig. S2 and S3), and as expected a small decrease in oxygen content is observed during first cycle while during second cycle a reversible behavior is observed. The calculated δ values at room temperature after thermal equilibration under the considered atmospheres are 0.14 ($\text{Ni}^{3+} \sim 76\%$), 0.10 ($\text{Ni}^{3+} \sim 73\%$) and 0.07 ($\text{Ni}^{3+} \sim 71\%$) under oxygen, air and argon, respectively. Furthermore it can be concluded that the material is “breathing” oxygen quite easily *i.e.* it is easy to include more interstitial oxygen under oxygen after equilibration under air, and it is also quite easy to remove the same amount of oxygen under argon (~ 0.03 in both cases).

As an intermediate conclusion, the above TGA study indicates that the thermal stability limit is 1120 °C and 1050 °C under oxygen and air, respectively, but we are aware that these observations are governed by kinetics. Moreover we checked that the long term thermal stability of the material is ensured at 1000 °C under oxygen, indeed this is the synthesis condition of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$. It was also investigated that the material is stable under air at 950 °C. Such observations were further used as guidelines for the sintering of electrodes.

3.2.4. Long term chemical stability at operating temperatures

Following previous studies performed till high temperature, it's also mandatory to check the thermal stability of the material at the operating temperatures of SOFCs. Then the ageing of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ powder was performed under air during one month at 600, 700 and 800 °C.

The corresponding XRD diffractograms along with as prepared powder are shown in Fig. 3. The material is chemically very stable at these SOFCs operating conditions, indeed, only a very small peak of PrO_x is observed (however existing in the as-prepared powder as well). This long term stability indicates that this material is suitable to be used as oxygen electrode, which will be checked in the final part regarding electrochemical measurements.

3.3. Electrical Conductivity

The variation of the total electrical conductivity σ vs. $1000/T$ for $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ is reported in Fig. 4, and compared with the corresponding data for $\text{PrNiO}_{3-\delta}$ and $\text{Pr}_2\text{NiO}_{4+\delta}$. $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ shows metal-like behaviour over the temperature range up to 20–800 °C under air, as $\text{PrNiO}_{3-\delta}$ but unlike $\text{Pr}_2\text{NiO}_{4+\delta}$ which shows semiconducting behaviour. The maximum conductivity value observed for $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ is close to 200 S.cm^{-1} (at room temperature) which is the highest value among $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$, $\text{PrNiO}_{3-\delta}$ and $\text{Pr}_2\text{NiO}_{4+\delta}$ phases and is in agreement with the one earlier reported result [12]. The conductivity varies from ~85–200 S.cm^{-1} from 800 °C to room temperature. At a typical operating temperature of 600 °C, $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ shows electrical conductivity, $\sigma = 90 \text{ S.cm}^{-1}$, similar to those of other Pr-based nickelates for ex. $\text{PrNiO}_{3-\delta}$ ($\sigma \sim 106 \text{ S.cm}^{-1}$) and $\text{Pr}_2\text{NiO}_{4+\delta}$ ($\sigma \sim 112 \text{ S.cm}^{-1}$) (Fig. 4), meeting the requirement for a SOFC cathode material.

In general, in a material showing metallic behavior the decrease in conductivity observed with increasing temperature can be understood in terms of decrease of the charge carrier mobility while the charge carrier amount remains almost constant. Here, because the material is exchanging oxygen with the surrounding atmosphere upon heating (*cf.* Fig. 2d), one can wonder if the corresponding decrease of the holes amount (Ni^{3+}) is large or not. As the Ni^{3+} percentage is not showing significant change with increasing temperature (73 to 70 % from room temperature to 800 °C), it can be concluded that the decrease in the conductivity is due to a decrease of the charge carrier mobility as expected.

Considering the expected MIEC properties of the $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ phase, as in all atmospheres, the material remains always oxygen over-stoichiometric (see TGA part), the behavior should be MIEC whatever the $p\text{O}_2$ throughout the temperature range of stability, however it would be to confirm experimentally measuring the ionic (oxygen) conductivity.

3.4. Electrochemical studies

In the second part of the work, we aimed first at the preparation of electrode ink using $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ powder prior to its shaping by screen-printing on 8YSZ//GDC supports. The sintering was performed using two different ways. The EIS *vs.* T measurements were performed and the results discussed comparing both sets of data obtained with the two kinds of half cells. Finally, single cells measurements (*i-V* curves recording at the operating temperatures 800 and 700°C) were performed using the sintering way optimized in the previous step (at $i_{\text{dc}}=0$).

3.4.1. Morphology of as-prepared powder

Before the preparation of ink, the morphology of the as prepared powder was investigated by SEM (*cf.* Fig. S4). It evidences grains which are highly connected with each other. The high

flame temperature which characterized the auto-combustion GNP process may explain this result. Therefore this powder was attrited with zirconia balls in ethanol medium for 1 h with the aim to obtain very fine powder, indeed a mean particle size of about 0.6 μm (as checked using laser granulometry measurements) was finally obtained.

3.4.2. EIS characterization: symmetrical cell

EIS measurements were carried out on $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ //GDC//8YSZ symmetrical half cells. These ones were prepared using two routes, either by a two-step process or co-sintering GDC and the electrode (detailed in experimental part). Then it will be possible to compare the polarization resistances, R_p , and the shape of impedance curves obtained in both cases.

3.4.3. Optimization of the two-step sintering process

The two-step sintering condition was first optimized using several sintering temperatures under oxygen. The sintering was first performed at the temperature corresponding to the phase stability limit, i.e. 1000 $^{\circ}\text{C}$ as discussed above. However one hour sintering is not sufficient from the mechanical point of view (confirmed by "tape test"); therefore 2 h of sintering is minimal. When the sintering was performed during 2 h at 1000 $^{\circ}\text{C}$, the R_p value is very high ($R_p = 2.7 \Omega\cdot\text{cm}^2$ at 600 $^{\circ}\text{C}$, *cf.* Fig. S5). Hence for better electrochemical performances it is mandatory to sinter the electrode at higher temperature.

The sintering at $T > 1050$ $^{\circ}\text{C}/1\text{h}$ leads to partial decomposition into $\text{Pr}_2\text{NiO}_{4+\delta}$ and NiO , however, a slow cooling under O_2 leads to the re-formation of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ (*cf.* Fig. 2c) [22]. The lowest the cooling rate is, the lowest the amount of $\text{Pr}_2\text{NiO}_{4+\delta}$ is expected. Then for preparing the electrodes, the half cells were cooled at 1 $^{\circ}\text{C}/\text{min}$ from the sintering temperature ($T = 1050, 1150$ and 1200 $^{\circ}\text{C}$) and also kept at 950 $^{\circ}\text{C}$ for 6 h under O_2 , to make sure of the

recovery of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ phase. The corresponding X-ray diffractogram of the half cell sintered at 1150°C shows $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ as major phase and no peak for $\text{Pr}_2\text{NiO}_{4+\delta}$ is observed (cf. Fig. S6).

Progressive increase of sintering temperature up to 1050 and 1150°C leads to further decrease in the R_p values down to 1.05 and $0.25\ \Omega\cdot\text{cm}^2$ respectively at 600°C . Further increase of the sintering temperature leads to small increase of R_p , up to $0.40\ \Omega\cdot\text{cm}^2$ when the sintering temperature is 1200°C . Hence the sintering at 1150°C for 1 h is obtained as an optimized condition, however it leads to the appearance of some additional phases (PrO_x and NiO) (cf. Fig. S6). To avoid such additional phases, it's important to perform the sintering up to 1000°C (thermal stability domain of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$). For this purpose, co-sintering of GDC and electrode was applied.

3.4.4 Co-sintering of GDC and $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ half cell

Aiming at favoring pure $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ phase, the symmetrical half cells were prepared by co-sintering GDC with the electrode at 950°C for 2 h . The sintering condition was already optimized in our group. Air was chosen instead of oxygen for sake of simplicity. *In-situ* (in the electrochemical cell) and *ex-situ* (in the furnace) co-sintering experiments lead to similar R_p values of $\approx 0.16\ \Omega\cdot\text{cm}^2$ at 600°C . Moreover after the co-sintering thermal cycle, no change is observed in the X-ray diffractogram of the electrode with respect to the starting $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ powder (cf. Fig. S7).

3.4.5. Discussion

The EIS data were recorded between 500 and 800 °C. In Fig. 5 (a, b) and Fig. 5 (c, d) the Nyquist impedance diagrams are compared at 600 °C and 700 °C for two-step sintered and co-sintered half-cells, respectively. In both cases, three processes for $T < 700$ °C (P_1 , P_2 and P_3) instead of two (P_2 and P_3) for $T \geq 700$ °C are distinguished. At higher temperature, $T \geq 700$ °C, as all processes are shifted toward higher frequencies, the process P_1 is hidden by the inductance of the wires and hence could not be distinguished anymore. The processes P_1 (appearing at high frequency ($10^4 - 10^3$ Hz)) and P_2 (appearing at middle frequencies ($10^3 - 1$ Hz)) were fitted using two parallel R//CPE elements for the sake of simplicity, at 600 °C. The origin of process P_1 is likely due to O^{2-} solid state diffusion in the interphase formed at the interface of GDC//electrode layer, as reported for $Pr_2NiO_{4+\delta}$ [23]. Indeed, at the electrode//GDC interface Pr-cations partly diffuse into the GDC layer forming Pr-doped ceria interphase, and the O^{2-} diffusion should occur on this new phase formed thanks to its MIEC properties [24, 25]. The process P_2 is assigned to the oxygen electrode reaction (OER) at the $Pr_4Ni_3O_{10+\delta}$ electrode (R//C shape), it is due to the relaxation of oxygen exchange reaction at the interface gas//electrode similar as $Pr_2NiO_{4+\delta}$ [23]. The process P_3 is due to gas diffusion impedance as already reported [26, 27], and usually fitted using one Warburg element W_s . The fit of the impedance data was carried out in order to extract only the R_p values. The total R_p , calculated for all temperatures (500–800 °C range) for the two-step sintered and co-sintered half cells under air, are plotted in Fig. 6a.

The R_p values obtained by co-sintering are slightly lower than those corresponding to the two-step sintering way, for ex. at 600 °C, the R_p for co-sintered and two-step sintered half cells are 0.16 and 0.25 $\Omega \cdot cm^2$, respectively. However, these R_p values remain close to that of $Pr_2NiO_{4+\delta}$ ($R_p = 0.15 \Omega \cdot cm^2$ at 600 °C), which is currently the lowest value exhibited by nickelates [28].

In order to identify the origin of the difference in R_p values, the thermal variations of R_p related to the three processes namely P_1 , P_2 and P_3 , are plotted in Fig. 6b. Interestingly, the R_p values of the P_1 and P_3 processes for co-sintered and two-step sintered half cells are almost the same, however the differences are only observed for P_2 process, depending on the sintering way. For the co-sintered half-cell, the R_p values are lower than that for the two-step sintered half cells. So it can be concluded that in both ways of sintering, the main difference is coming from the OER due to $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ electrode (process P_2). The slightly higher value of R_p for P_2 of two-step sintered half cells can either be related to the presence of additional phases (PrO_x and NiO (cf. Fig. S6)) or to the electrode microstructure. In general, at high sintering temperature, the particles coarsening should result in the decrease in active surface area that could affect the OER.

The frequency of relaxation of different processes involved in both fabrication processes are compared in Fig. 6c. Only the P_1 process shows some differences, which is likely related to the morphology of the interface (cf. Fig. 7). Indeed, for the two-step sintered half cell, the GDC layer (sintered separately at 1375 °C for 1h) is much denser than the one of the co-sintered half cell, which leads to a higher relaxation frequency. It is worth noting that the frequencies of processes P_2 (OER on $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ electrode) and P_3 , (gas diffusion process), are logically almost identical for both processes.

3.4.6. Morphology of half cells after EIS measurements

SEM observations of the $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ electrode were carried out after EIS measurements (Fig. 7). The thicknesses of the electrodes are estimated to be $\sim 10 \mu\text{m}$. It can be noticed that all the layers are well adhered with each other. From the SEM micrographs it seems that the GDC layers are different in both two-step and co-sintered half cells. The thickness of GDC is $\sim 2 \mu\text{m}$

and 3 μm respectively for two-step sintered and co-sintered half cells. A careful observation of the microstructure also suggests the morphology of the electrode is denser in case of two-step sintering. This can be linked to particles coarsening at high sintering temperature.

3.4.7. Single cell measurements

The cathode sintering was performed using the previous optimized conditions determined for half cells, which is co-sintering together with the GDC layer at 950 °C for 2 h under air. The single cell was mounted into the measurement setup, with flows of air and N_2 on the cathode and anode sides, respectively. The cell was heated at 800 °C and N_2 at the anode side was progressively replaced by dry hydrogen (H_2) to reduce NiO into metallic Ni . The open circuit voltage (OCV) was around 1.1 V as expected. The i-V characteristic was measured from OCV down to 0.4 V, and the impedance diagrams were recorded at OCV, 0.9, 0.8, and 0.7 V (not reported). Then the temperature was decreased at 700 °C to measure again the i-V characteristic and impedance diagrams.

Fig. 8a shows the cell voltage as a function of the current density, as well as the resulting power density at 800 °C and 700 °C. The cell performance is high, reaching maximum power densities of $1.6 \text{ W}\cdot\text{cm}^{-2}$ at 800 °C and $0.68 \text{ W}\cdot\text{cm}^{-2}$ at 700 °C. For a potential of 0.7 V, the current density is $1.6 \text{ A}\cdot\text{cm}^{-2}$ at 800 °C and reaches $0.64 \text{ A}\cdot\text{cm}^{-2}$ at 700 °C.

Following the measurements at 800 and 700 °C, the cell was aged at 700 °C for 500 h at a current density of $0.3 \text{ A}\cdot\text{cm}^{-2}$. Fig. 8b shows the cell voltage as a function of time; the potential started at around 0.80 V, then a slight decrease is observed and after 500 h the potential is around 0.76 V.

4. Conclusion

This work reports the structural, stability and electrochemical studies of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ as a new promising cathode material for SOFCs. $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ was successfully synthesized via glycine-nitrate route under normal oxygen flow ($p\text{O}_2 \sim 1 \text{ atm}$). It crystallizes in orthorhombic structure with $Fmmm$ space group. The XRD vs. temperature experiment under air shows a stable phase throughout the temperature range up to 1000°C .

An over-stoichiometry, delta value $\delta = 0.10$ is obtained under air. The measurement of oxygen content vs. T shows that the material is always over-stoichiometric whatever the $p\text{O}_2$ is, which should indicate that this material is MIEC-type under oxygen and air up to 1000°C . $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ phase is stable maximum for 2 h under air and fully stable under oxygen at 1000°C . Further increase of temperature leads to decomposition into $\text{Pr}_2\text{NiO}_{4+\delta}$ and NiO , under air and oxygen.

The half cell prepared by co-sintering process shows lower R_p value ($R_p = 0.16 \Omega\cdot\text{cm}^2$ at 600°C) than the one made by two-step sintering ($R_p = 0.25 \Omega\cdot\text{cm}^2$ at the same temperature), which is almost same as $\text{Pr}_2\text{NiO}_{4+\delta}$. A single cell with $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ electrode produced high power density of $1.60 \text{ W}\cdot\text{cm}^{-2}$ at 800°C and $0.68 \text{ W}\cdot\text{cm}^{-2}$ at 700°C .

Endly, the $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ phase is highly stable during long term up to 1 month under air at different SOFC operating temperatures: 600 , 700 and 800°C , contrarily to $\text{Pr}_2\text{NiO}_{4+\delta}$ which forms $\text{PrNiO}_{3-\delta}$, $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ and Pr_6O_{11} in the same conditions [17]. It can be then concluded that the electrochemical behavior of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ is similar to that of $\text{Pr}_2\text{NiO}_{4+\delta}$, but with a quite higher stability, which gives great interests to consider this material as a very promising oxygen electrode.

Supplementary information

S1: X-ray diffractograms after TGA performed on $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ powder under (a) air and (b) oxygen. **S2:** Thermal variation of weight loss for $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ under argon atmosphere. **S3:** Thermal variation of the oxygen content ($10+\delta$) under argon ($30\text{ }^\circ\text{C} \leq T \leq 800\text{ }^\circ\text{C}$). **S4:** Morphology of as-prepared powder after synthesis by GNP. **S5:** R_p measured at $600\text{ }^\circ\text{C}$ under air on the half cells prepared by two-step sintering process at $1000^\circ\text{C}/2\text{h}/\text{O}_2$, $1050^\circ\text{C}/2\text{h}/\text{O}_2$ (+ $950\text{ }^\circ\text{C}/6\text{h}/\text{O}_2$), $1150^\circ\text{C}/1\text{h}/\text{O}_2$ (+ $950\text{ }^\circ\text{C}/6\text{h}/\text{O}_2$) and $1200^\circ\text{C}/1\text{h}/\text{O}_2$ (+ $950\text{ }^\circ\text{C}/6\text{h}/\text{O}_2$) and slowly cooled. **S6:** X-ray diffractogram of half cells after sintering at $1150\text{ }^\circ\text{C}$ for 1 h under O_2 (+ $950\text{ }^\circ\text{C}/6\text{h}/\text{O}_2$). **S7:** X-ray diffractograms after EIS measurements performed by co-sintering technique (comparison with powder).

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Figures

Fig. 1. (a) Fullprof refinement of the XRD patterns at 25 and 1000 °C using *Fmmm* space group, (b) variation of lattice parameters and (c) variation of $(\lambda - \lambda_0)/\lambda_0$ under air as a function of temperature up to 1000 °C.

Fig. 2. (a) TGA plot under 5% Ar-H₂ for the determination of delta value, thermal variation of weight loss under (b) air, (c) oxygen atmospheres and (d) thermal variation of the oxygen content ($10+\delta$) under air and oxygen at $30\text{ }^{\circ}\text{C} \leq T \leq 1000\text{ }^{\circ}\text{C}$.

Fig. 3. X-ray diffractograms of $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ powder after 1 month ageing at 600, 700 and 800 °C under air.

Fig. 4. Thermal variation of the electrical conductivity of Pr₄Ni₃O_{10+δ} compared with PrNiO_{3-δ} and Pr₂NiO_{4+δ}, under air up to 800 °C.

Fig. 5. Nyquist plots recorded for $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ electrode at 600 °C and 700 °C for both two-step sintered (1150 °C/1h) and co-sintered (950 °C/2h) half cells and fitted using R_s (series resistance), R /CPE and Warburg element (W_s).

Fig. 6. (a) Variation of total R_p , (b) R_p of different processes and (c) frequency of relaxation of different processes, as a function of temperature for both two-step and co-sintered half cells under air for $Pr_4Ni_3O_{10+\delta}$ electrode.

Fig. 7. SEM morphology of half cells after EIS measurements (a) two-step sintering and (b) co-sintering.

Fig. 8. (a) i - V curves and resulting power densities of a single cell made of a commercial half-cell and $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ as cathode and (b) ageing of the single cell at $700\text{ }^{\circ}\text{C}$, with a current density of $0.3\text{ A}\cdot\text{cm}^{-2}$, for 500 h.

Graphical Abstract

Supplementary Materials

$\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$: a new promising oxygen electrode material for Solid Oxide Fuel Cells

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Fig. S1. X-ray diffractograms after TGA performed on $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$ powder under (a) air and (b) oxygen.

Fig. S2. Thermal variation of weight loss under argon atmosphere.

Fig. S3. Thermal variation of the oxygen content ($10+\delta$) under argon ($30\text{ }^{\circ}\text{C} \leq T \leq 800\text{ }^{\circ}\text{C}$).

Fig. S4. Morphology of as-prepared powder after synthesis by GNP.

Fig. S5. Polarization resistances, R_p , measured at 600 °C under air on the half cells prepared by two-step sintering process at 1000°C/2h/O₂, 1050°C/2h/O₂ (+ 950 °C/6h/O₂), 1150°C/1h/O₂ (+ 950 °C/6h/O₂) and 1200°C/1h/O₂ (+ 950 °C/6h/O₂) and slowly cooled.

Fig. S6. X-ray diffractogram of half cells after sintering at 1150 °C for 1 h under O_2 (+ 950 °C/6h/ O_2).

Fig. S7. X-ray diffractograms after EIS measurements performed by co-sintering technique (comparison with powder).