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Densification study of Pr₆O₁₁ as a limiting step for the determination of its oxygen transport properties

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Abstract

This study describes the successful sintering of Pr₆O₁₁, which is recently developed as a promising oxygen electrode for Solid Oxide Cells (SOCs). Using dense pellets or thin films is mandatory prior to an accurate measurement of the ionic transport properties *via* the isotopic oxygen exchange method here involved. Dilatometry experiments performed under different atmospheres (argon, air, oxygen) and sintering tests with different thermal cycles allowed overcoming the detrimental phase changes of Pr₆O₁₁ and densifying this oxide with a sintered relative density of 95%. Dense pellets of large sizes were prepared. In a second part, the ionic transport properties of Pr₆O₁₁ have been determined in the range 400 < T°C < 800 thanks to Isotopic Exchange Depth Profiling (IEDP) measurements.

Key words: SOC oxygen electrode, sintering, Pr₆O₁₁, ionic conductivity

1. Introduction

For the commercialization of SOCs (Solid Oxide Cells), the ceramic cells should have an improved lifetime and chemical stability, as well as a lower cost. An efficient way to achieve these objectives is to decrease their operating temperature, down to approximately 600°C [1]. However, at this reduced temperature, the electro-catalytic activity of air and fuel electrodes has to be improved. To optimize the performance of the cell when it operates in such a range of temperatures, the thickness of the electrolyte has to be reduced, and the surface can be modified *via* catalytic activation. It is also beneficial to increase the active surface area. One of the ways is to elaborate a composite electrode (containing both ionic and electronic conductors). In this case, the active reaction zones are only located at the junction between electronic and electrolyte conductors, which is especially detrimental regarding the efficiency of the oxygen electrode. The next step was then, in this latter case, to increase further the oxygen surface exchange kinetics by using a MIEC (mixed ion-electron conductor) electrode, then to delocalize the reaction(s) on the entire surface of the MIEC in the oxygen electrode [2-4].

Research breakthroughs have been achieved to improve the performance of cells, either by developing new materials or improving the microstructure of the electrodes. Regarding the second way, infiltration of a catalyst into a porous anionic conducting skeleton (for instance gadolinium-doped ceria, GDC) is a very interesting method to shape the SOCs oxygen electrodes and to improve their electrochemical performances. Infiltration has been widely used to fabricate novel architected oxygen electrode structures based on LSM [5, 6], LSCF [7, 8], LSBT [9, 10] and Ruddlesden-Popper materials such as $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ ($n = 1, 2, 3$)-YSZ [11, 12] or $\text{Nd}_2\text{NiO}_{4+\delta}$ [13, 14]. These studies showed that the infiltrated electrodes provided superior performance compared to the conventionally sintered electrodes. It not only improves the catalytic activity (through the presence of dispersed nano-particles), but it also increases the ionic and electronic conductivity (through an interconnected network of nano-particles), which overall leads to an increase of TPB length and reduction of the cell resistance. A new composite oxide was developed at ICMCB in Bordeaux, a few years ago: the praseodymium oxide, Pr_6O_{11} , infiltrated in a Gd- doped ceria (GDC) backbone. This composite electrode allowed obtaining a very low polarization resistance ($R_p = 0,03 \Omega \cdot \text{cm}^2$ at 600°C) [15]. Actually, thanks to the Pr+III/Pr+IV mixed valence, PrO_x exhibits a good activity to reduce oxygen [16]. Following this result, several works aimed to prepare efficient electrodes where Pr_6O_{11} was infiltrated as part of a composite oxygen electrode [see for instance refs 17 - 20].

Therefore, the characterization of the ionic conductivity of Pr_6O_{11} , which is currently not well-known, is of first importance for a better understanding of its efficient behavior as oxygen electrode. However, since this oxide is a mixed conductor, it is not possible to carry out conventional impedance measurements without the use of blocking electrodes. An alternative route is to perform Isotopic Exchange Depth Profiling (IEDP) measurements, or Electronic Conductivity Relaxation measurements (ECR) to determine the oxygen diffusion and surface exchange coefficients. In both cases it is absolutely mandatory to use dense pellets. However, upon heating, Pr_6O_{11} easily changes to Pr_9O_{16} , Pr_7O_{12} and/or Pr_2O_3 , also depending on the surrounding pO_2 [21]. It is then highly challenging to obtain near fully dense materials without cracking with the right oxygen stoichiometry. To the best of our knowledge, no work about the optimization of an adapted thermal cycle for the full densification of Pr_6O_{11} pellets has been already reported in the literature. This is the objective of the study reported in this article. In a first section, the optimization of the sintering process of Pr_6O_{11} is described with regard to its behavior during thermal treatment under different atmospheres and for different thermal cycles (heating/cooling rates, dwells duration). In a second part, the ionic transport properties (D^* and k^* coefficients) of Pr_6O_{11} sintered pellets have been determined by IEDP.

2. Experimental

The Pr_6O_{11} powder under study was a commercial powder provided by Solvay company. The mean particle size of the initial powder was $d_{50} = 5 \mu\text{m}$ because of agglomerates. Then, this powder was attrition milled in ethanol medium with zirconia balls (diameter of 2 mm) at 700 rpm during one hour. The final powder was poly-dispersed, with three mean particle sizes, located around $d_{50} = 200 \text{ nm}$, 600 nm and 2 μm , as determined by laser granulometry measurements in water.

To study Pr_6O_{11} sintering, the powders were uniaxially pressed at 100 MPa or 200 MPa to prepare green pellets with a diameter of 6 mm: for the highest sintering temperature (1450°C) the applied pressure was 100 MPa while it was increased up to 200 MPa for lower sintering temperatures (see Table 1). Green relative densities were about 48 % d_{th} (theoretical density) when pressed at 100 MPa and about 52 % d_{th} for 200 MPa. According to our own XRD measurements the crystallographic structure of Pr_6O_{11} was refined in the fluorite-type structure and then the corresponding theoretical density is $6.91 \text{ g}\cdot\text{cm}^{-3}$. These pellets were then sintered using different sintering cycles, as described in the Results and Discussion part (Table 1), the goal being to densify the pellets to more than 95 % of relative density. Final densities were determined from the average value issued from geometrical measurements and from the Archimedes' method.

A second type of samples was prepared for the IEDP measurements (part 2.3). For this purpose, our goal was to sinter a unique pellet with a diameter of 25 mm, in order to polish it, then to cut it with a diamond saw to get small identical pieces to perform the different isotopic exchanges. The green pellets were prepared by uniaxial pressing at 200 MPa and sintered with the best sintering cycle.

2.1 Dilatometry measurements

Dilatometry measurements were performed using a horizontal dilatometer (Netzsch DIL 402 C) on cylindrical pellets with initial thickness of about 5 mm (l_0) (heating and cooling rates = 5°C/min, dwell time = 10 min). The temperature ranged from room temperature up to 1450°C. Different atmospheres were used for the dilatometry measurements: Ar, air or O₂ and the gas flow was fixed to 75 ml/min.

2.2 Sintering cycles

Following the dilatometry measurements, two different thermal cycles were used, while maintaining the same heating and cooling rates at 5°C/min. In the first cycle, called “one-step sintering” the sintering temperature, surrounding atmosphere and dwell time were the adjustable parameters. The second cycle was the so-called “two step sintering”. This process is based on a first heating step performed at high temperature in order to induce the densification process, followed by a fast cooling, down to an intermediate temperature to continue the densification without grain growth. This procedure, described elsewhere, should lead to fine and dense microstructures [22-23].

2.3 IEDP measurements

The oxygen diffusion coefficient D^* and surface exchange coefficient k^* were determined by the so-called isotopic exchange depth profile (IEDP) technique combining isotopic exchange of ¹⁸O (used as an oxygen tracer) and determination of the ¹⁸O penetration profiles by TOF-SIMS (Time-Of-Flight Secondary Ion Mass Spectrometry) analyses. The procedure is described in detail elsewhere [24-26]. The ceramics were first abraded with silicon carbide papers of successive grades, and then polished with an alumina paste down to a roughness close to 0.3 μm. Prior to each exchange, a pre-annealing step was performed, which consisted of equilibrating the sample at the temperature of interest (same temperature as the subsequent exchange) in dry natural ¹⁶O oxygen (99.9 % purity

with natural abundances for (all) the oxygen isotopes) at 210 mbar. The time used for the pre-anneal step in natural oxygen was always much longer (at least ten times) than the exchange time. In a second step the samples were annealed at a pressure of 210 mbar in an ^{18}O enriched atmosphere (97%, Eurisotop) for $400 < T \text{ } ^\circ\text{C} < 800$. In order to limit the oxygen stoichiometry change during the heating and cooling ramps, a tubular furnace was rapidly withdrawn to set the samples to the annealing temperature and later rolled off to rapidly cool it down. The ^{18}O penetration profiles, *i.e.* normalized ^{18}O isotopic fraction ($^{18}\text{O} / (^{16}\text{O} + ^{18}\text{O})$), were recorded as a function of the analyzed depth using a TOF-SIMS 5 Ion-Tof SIMS apparatus with a Cs^+ ions source. From the $^{16}\text{O}^-$ and $^{18}\text{O}^-$ SIMS intensity data acquired, the normalized ^{18}O isotopic fraction was calculated. Due to the sintering issues related to this material (possible presence of cracks), several trials have been performed at a given temperature. The oxygen profiles were then fitted with an appropriate solution of the gas diffusion equation in solids, according to Fick's second law and given by Crank [27], *i.e.* relation (1):

$$C'(x) = \operatorname{erfc}\left(\frac{x\sqrt{D^*t}}{2}\right) - \exp\left(\frac{k}{D^*}x + \frac{k^2}{D^*}t\right) \operatorname{erfc}\left\{\left(\frac{x\sqrt{D^*t}}{2}\right) + \left(\frac{k}{D^*}\sqrt{D^*t}\right)\right\} \quad (1)$$

$$\operatorname{erfc}(x) = \int_0^x \exp(-x^2) dx \quad \text{with} \quad \text{and} \quad C'(x,t) = \frac{C(x,t) - C_0}{C_s - C_0}$$

$C(x,t)$ is the $^{18}\text{O}_2$ isotopic concentration in the solid obtained by SIMS at the depth x , $C'(x,t)$ is the isotopic fraction corrected for the natural isotopic background level (referred to as $C_0 = 0.2 \%$) and for the isotope enrichment of the gas (referred to as $C_s = 97\%$), t (s) is the duration of the isotope anneal; D^* is the oxygen tracer diffusion coefficient and $h = k^* / D^*$, as previously defined.

3. Results and discussion

3.1 Sintering studies

The sintering behavior under air (dilatometric measurements) of a green Pr_6O_{11} pellet, pressed at 100 MPa ($d_{\text{green}} = 48 \%$ d_{th}) is presented in Fig. 1-a as a function of temperature. The derivative with respect to time of this curve, *i.e.* the shrinkage rate is given in Fig. 1-b (heating) and 1-c (cooling). A first small shrinkage is observed between 200 and 400°C, probably related to the departure of some volatile species (water, carbonates,...) and grain rearrangement [28]. The real densification begins above 700°C and an overall large shrinkage is observed, *i.e.* more than 20%, which seems

high according to the initial relative density of the green sample. Actually, many accidents are observed on the shrinkage curve. They are more clearly identified on the derivated curve. During heating (Fig. 1-b), a sharp discontinuity is observed between 1180 and 1220°C that will be referred in the following as $T_{\text{discontinuity}}$. This could be related to changes in the oxygen stoichiometry of Pr_6O_{11} and therefore to crystallographic structure changes, as described in the literature [21, 29]. Previously reported TGA measurements showed that during heating under air, Pr_6O_{11} is transformed into Pr_9O_{16} , Pr_7O_{12} and/or Pr_2O_3 with an oxygen loss [21, 30]. A particular point concerns the cooling stage. A significant increase in linear shrinkage is also noticed below 1100°C: it corresponds to a large increase in the volume of the sample that is already densified and leading to macroscopic cracking of the ceramic. Correspondingly, a swelling of the sample is observed a few hours after the end of the cycle, resulting in a complete cracking of the pellet.

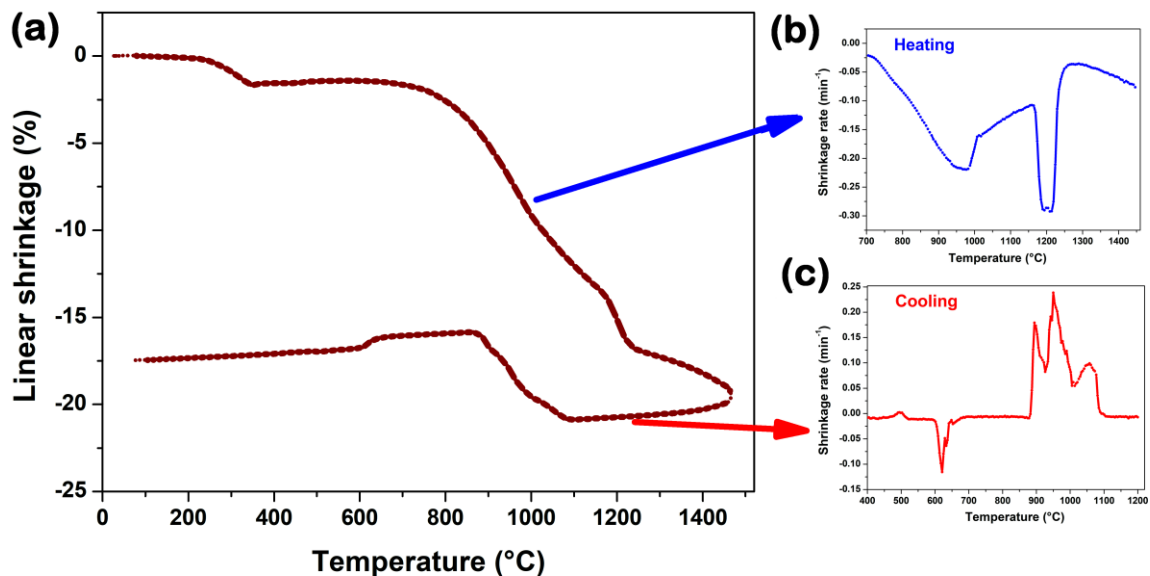


Figure 1. Dilatometric behavior in air of a Pr_6O_{11} green pellet ($d_{\text{rel}} = 59\% d_{\text{th}}$) (a) linear shrinkage and (b) shrinkage rate (derivation of the curve 1-a with respect to the time) during (b) heating and (c) cooling as a function of temperature

In order to avoid, or at least to limit these detrimental phenomena for getting high density and keeping the integrity of the material, likely correlated to the oxygen stoichiometry evolution of Pr_6O_{11} , densification experiments were carried out under different atmospheres (Fig 2). For the three selected oxygen partial pressures (*i.e.* 1, 0.2 and around 1 Pa for oxygen, air and argon, respectively), the initial behaviour remains the same, with a small initial shrinkage, while the densification only begins above 700°C. Then, the thermal behaviour of Pr_6O_{11} samples strongly

depends on the sintering atmosphere. One can first notice the evolution of $T_{\text{discontinuity}}$ as a function of Po_2 . It increases from Ar, to air and oxygen: $T_{\text{discontinuity}} \sim 1000^\circ\text{C}$, 1200°C and 1400°C respectively (see arrows in Fig. 2). This is in agreement with the transition temperature evolution of Pr_6O_{11} towards PrO_x compounds with higher oxygen content [21]. An opposite variation of dimension is observed during cooling. It occurs at the highest temperature under pure oxygen while no volume increase is observed under argon. For the latter case, after the dilatometric measurement, the pellet remains dense. However, one day later after staying at room temperature, it is swelled and turns partly yellow without keeping any mechanical cohesion. XRD analysis evidences a large amount of praseodymium hydroxide. Then, despite the absence of volume increase during cooling, the densification performed under argon atmosphere did not deserve our attention.

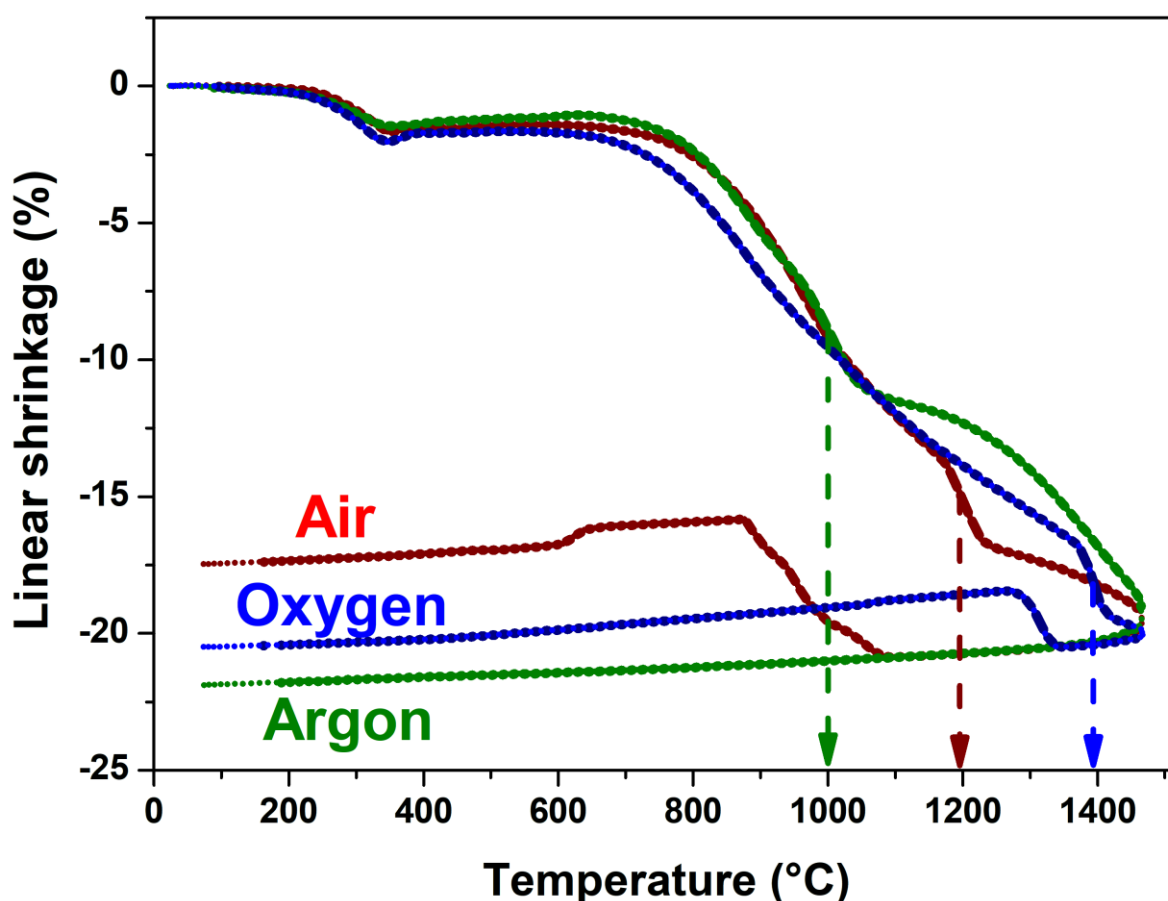


Figure 2. Linear shrinkage of Pr_6O_{11} green pellets heat-treated under argon, air or oxygen as a function of temperature ($5^\circ\text{C}/\text{min}$ heating and cooling rates).

In the following, a more accurate study is then performed either under oxygen or under air, while keeping in mind that a thermal treatment performed under oxygen preferentially leads to the formation of PrO_2 , which is a more oxidized phase than Pr_6O_{11} .

Regarding sintering under air, the large volume expansion observed below 1100°C should be avoided and then, two thermal cycles were considered. First, a long dwell time (30 h) was performed under air at 1100°C, in order to activate the sintering process before the phase transition (Table 1, cycle 1). Secondly, two-step sintering cycles were carried out: i) heating up to 1450°C, followed by a rapid cooling down to 1100°C (*i.e.* below the phase transition) with a plateau of 1 h (cycle 2); ii) heating up to 1150°C, followed by rapid cooling down to 1000°C, with a long dwell performed at this temperature (30 h, cycle 3). The objectives of the two-step sintering were to avoid the phase changes maintaining a high densification. Whatever the case, the relative density of the sintered pellets remained too low (81 % in the best case, cycle 2). Moreover, only one pellet did not break after thermal cycling, the one for which the transition temperature (1150°C) was not exceeded. Note that under argon no expansion is observed, giving strength to the hypothesis that the volume increase resulting in the crack of the pellet is directly related to an oxygen up-take.

Under oxygen, Fig. 2 shows that the pellet volume still increases during cooling, but to a lesser extent than under air. The final relative density in that case (1450°C with a dwell time of 10 min) is about 87 % (Table 1, cycle 4) and the ceramic appeared uncracked. An XRD analysis shows that PrO₂ is dominant, at least on the surface. A second thermal treatment was then performed at 700°C during 7 h under air to adjust the oxygen stoichiometry, which allowed recovering Pr₆O₁₁. Increasing the dwell time at 1450°C to 1 h (cycle 5) does not improve the relative density but increases the brittleness of the final ceramic. Actually, a simple sintering under oxygen did not allow obtaining dense and pure Pr₆O₁₁ ceramics.

Table 1 – Thermal cycles used for the sintering of Pr₆O₁₁ pellets (the diameter and thickness of the green pellets were 5 and 3 mm, respectively). The cold uniaxial pressure applied to prepare the green pellets was 100 MPa for the cycles 1 to 5, and 200 MPa for the cycles 6 to 10 (marked with a *). The lab co-precipitated powders were attrited (1h), and the resulting granulometry measurements evidences three populations, which are centered around 0.2, 0.6 and 1µm, respectively.

Thermal cycle	Dwell (T°/duration)	Visual observation	Sintered density (g/cm ³)	Relative density (%)
Air atmosphere – commercial powder				
1	1100°C/30 h	Good	5.4	78
2	Two steps: 1450°C + 1100°C/1 h	Cracked pellet	5.6	81
3	Two steps: 1150°C + 1000°C/30 h	Cracked pellet after 1 week	5.2	75

Oxygen atmosphere – commercial powder				
4	1450°C/0.16 h	Good	6.0	87
5	1450°C/1 h	Some cracks	6.0	87
6*	1350°C/10 h	Good	6.3	91
7*	1370°C/15 h	Some cracks	6.2	90
8*	1355°C/40 h	Few cracks	6.3	92
Oxygen atmosphere – lab co-precipitated powder				
9*	1355°C/40 h	Very few cracks	6.4	93
10*	1370°C/15 h + 700°C/7h under air	Good	6,5	95

The analysis of the shrinkage curve under O₂ (Fig. 2) indicates that T_{discontinuity} is around 1400°C, beginning at 1370°C, *i.e.* about 200°C higher than under air, which could be a favourable feature for improving the densification without crystallographic changes. So, the first attempts were made just below the phase transition temperature, *i.e.* 1370°C, by adjusting the sintering temperature and the dwell duration. It corresponded to cycles 6 to 9, reported in Table 1. Moreover, the uniaxial pressure applied to prepare the green pellets was increased from 100 to 200 MPa in order to improve the green relative density (from 48 to 52,5 % d_{th}) and therefore the final densities. These samples are marked with a star in Table 1. As a result, the sintered relative densities of sample 6 to 8 were increased up-to 92 %. However, some cracks remained after the thermal treatment performed at the highest temperature (1370°C) that should be too close to the phase transition temperature. A rather good result (92% of relative density) was obtained for T = 1355°C combined with a long duration dwell (40 h).

The last attempts were performed using a home-made powder that was prepared using a classical co-precipitation route, followed by an attrition step. Using that powder, a significant improvement in green density was obtained (d_o = 57 % d_{th}), resulting in a final density (d_f = 93 % d_{th}) slightly higher than the previous one, for the same sintering cycle at T = 1355°C during 40 h (cycle 9). Finally, a two stage sintering process was used involving two different atmospheres (cycle 10): 1) sintering at 1370°C during 15 h under oxygen; 2) cooling down to 700°C under air; 3) 7 h stage at 700°C in air (to fully recover the Pr₆O₁₁ phase), and then cooling under air down to room temperature (cycle 10). This last experiment gave the best sintered density, 95 % d_{th}, without any macroscopic cracks.

SEM observations of fractured sintered pellets obtained from cycles 5 and 10 are presented in Fig. 3. The respective relative densities are 87 % (Fig. 3-a) and 95 % (Fig.3-b). Fig. 3-a clearly evidences a quite high remaining porosity, with both closed and open porosity. Conversely, Fig. 3-b mostly shows spherical pores, characteristic of closed porosity. Image analysis (ImageJ software) of this

SEM micrograph gave a porosity of about 3 %, which is quite in agreement with the measured density. One could also notice the absence of visible cracks on this fractured sample.

As a conclusion, the cycle 10 allows obtaining dense and uncracked Pr_6O_{11} ceramics. Therefore, this sintering treatment is selected to prepare large samples for the IEDP measurements as described in the following.

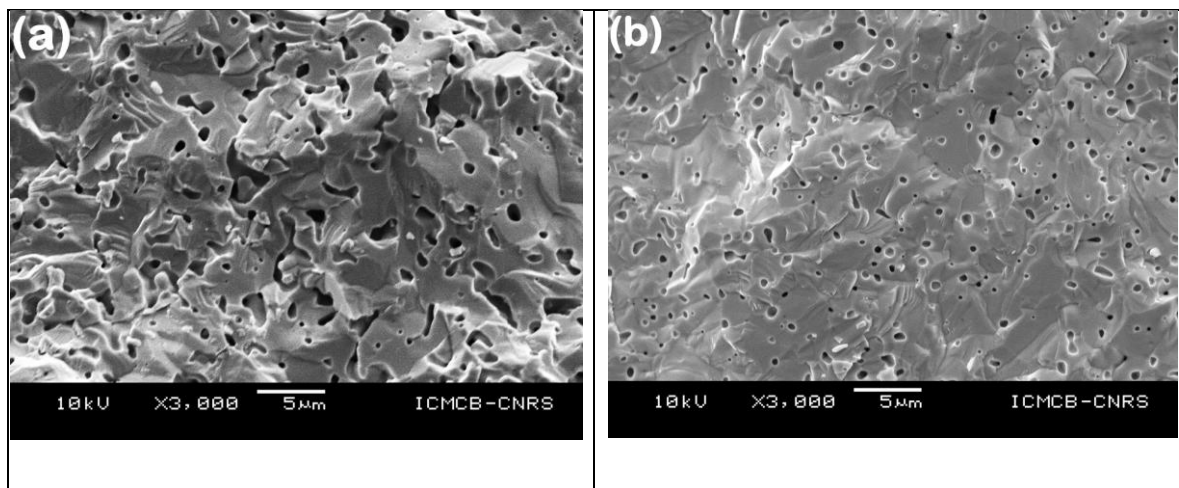


Figure 3. SEM cross section micrographs of Pr_6O_{11} pellets sintered (a) at $1450^\circ\text{C}/1\text{h}$ under O_2 (cycle 5, $d_f = 87\% d_{th}$), (b) at $1370^\circ\text{C}/15\text{ h}$ under O_2 followed by a rapid cooling to 700°C under air with a 7 h stage (cycle 10, $d_f = 95\% d_{th}$).

3.2 Isotopic Exchange Depth Profiling (IEDP) measurements

A drawback encountered when using the previously sintered Pr_6O_{11} pellets could be the presence of micro-cracks. It can be of course a major issue if the oxygen mapping is performed in such a kind of area, because the oxygen diffusion is accelerated in the crack compared to the bulk diffusion; it is well illustrated in Fig. 4a where an horizontal micro-crack is well visible causing an increase of the ^{18}O concentration (abnormally enhanced yellow part). This increase is larger and larger closer to the crack as oxygen can diffuse preferentially inside the crack. Such a feature would lead to an artificial increase of the isotopic oxygen concentration and then to an over-estimation of the D^* and k^* coefficients. On the contrary, Fig.4b which was obtained in a dense area without crack; a clear ^{18}O gradient (from yellow to red color, from the edge to the center of the pellet) was evidenced and used to determine the D^* and k^* coefficients.

Then, the mapping was carefully carried out in selected zones where the gradient remains constant along a significant thickness.

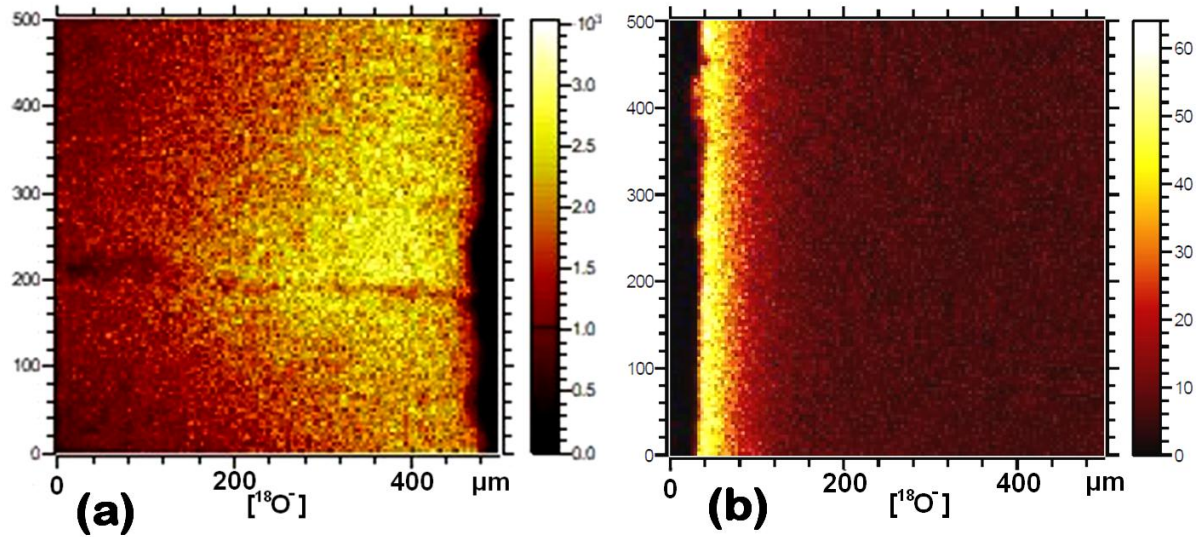


Figure 4. a) Mapping of the ^{18}O concentration around a micro-crack area, observed after an oxygen isotopic exchange performed at $T = 600^\circ\text{C}$ during 4920s;

b) Mapping of the ^{18}O concentration in a dense area, without crack, observed after an oxygen isotopic exchange performed at $T = 400^\circ\text{C}$ during 15420s.

IEDP measurements were performed in the range $400 - 800^\circ\text{C}$. An example of profile, *i.e.* the evolution of the normalized ^{18}O concentrations ($[\text{O}^{18}] / [\text{O}^{18}] + [\text{O}^{16}]$) vs. pellet thickness is shown in Fig. 5 ($T = 400^\circ\text{C}$, exchange duration time: 15420s).

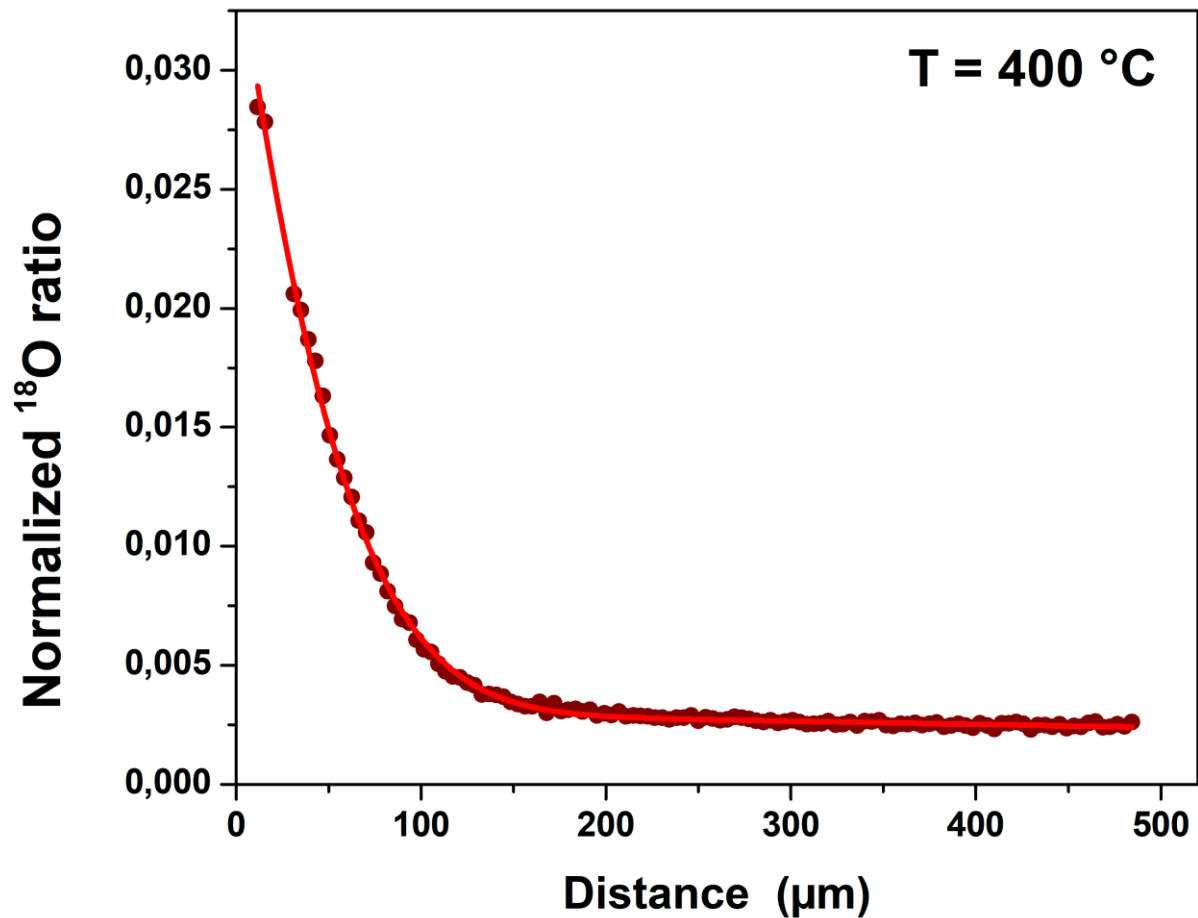


Figure 5. ¹⁸O diffusion profile recorded by TOF-SIMS analysis on a Pr₆O₁₁ pellet after oxygen isotopic exchange performed at T = 400°C during 15420s.

The initial (distance = 0 µm) normalized ¹⁸O ratio (¹⁸O / ¹⁸O + ¹⁶O) is un-expectedly quite low (it was the case for each of the performed exchanges). However, the most important point is that the ratio in the “queue” of the profile, *i.e.* when no diffusion occurs, is very close to the natural abundance of the ¹⁸O isotope, *i.e.* 0.2%. The analysis of the fit allows to accurately determine the D* and k* coefficients according to relation (1): $D^* = 1.73 \times 10^{-9} \pm 2.46 \times 10^{-11} \text{cm}^2 \cdot \text{s}^{-1}$, $k^* = 1.02 \times 10^{-8} \pm 6.59 \times 10^{-11} \text{cm} \cdot \text{s}^{-1}$ at T = 400°C.

The temperature dependences of the D* and k* coefficients are plotted in Figs 6 and 7, respectively.

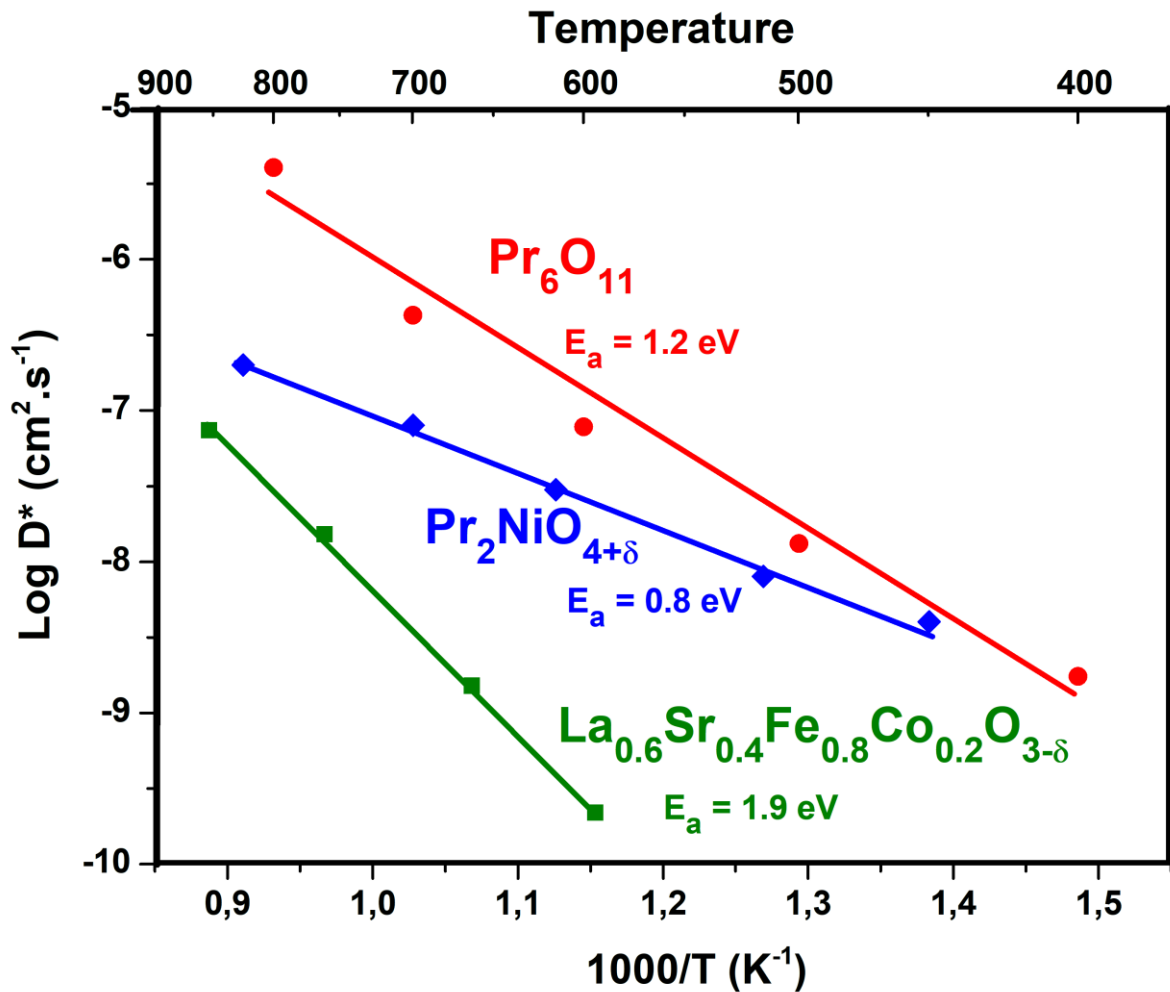


Figure 6. Arrhenius plot of the D^* coefficient vs. $1000/T$ determined for Pr_6O_{11} . Comparison with the corresponding values determined for $\text{Pr}_2\text{NiO}_{4+\delta}$ [31], and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ [32].

Fig. 6 clearly evidences that the oxygen diffusion coefficient of Pr_6O_{11} is significantly higher than those of other usual oxygen electrode materials used for SOC applications, such as $\text{Pr}_2\text{NiO}_{4+\delta}$, and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$. Especially, the very high mobility of oxide ions in Pr_6O_{11} observed at low temperature is likely one of the main reasons of the exceptional catalytic properties and electrochemical performances as oxygen electrode material at 600-400°C. Besides, the activation energy associated to oxygen transport mechanism for Pr_6O_{11} is close to 1.2 eV (determined in the $450 < T^\circ\text{C} < 800$ temperature range), *i.e.* similar to the value observed for yttrium doped zirconia (1.1eV-0.97eV) [33].

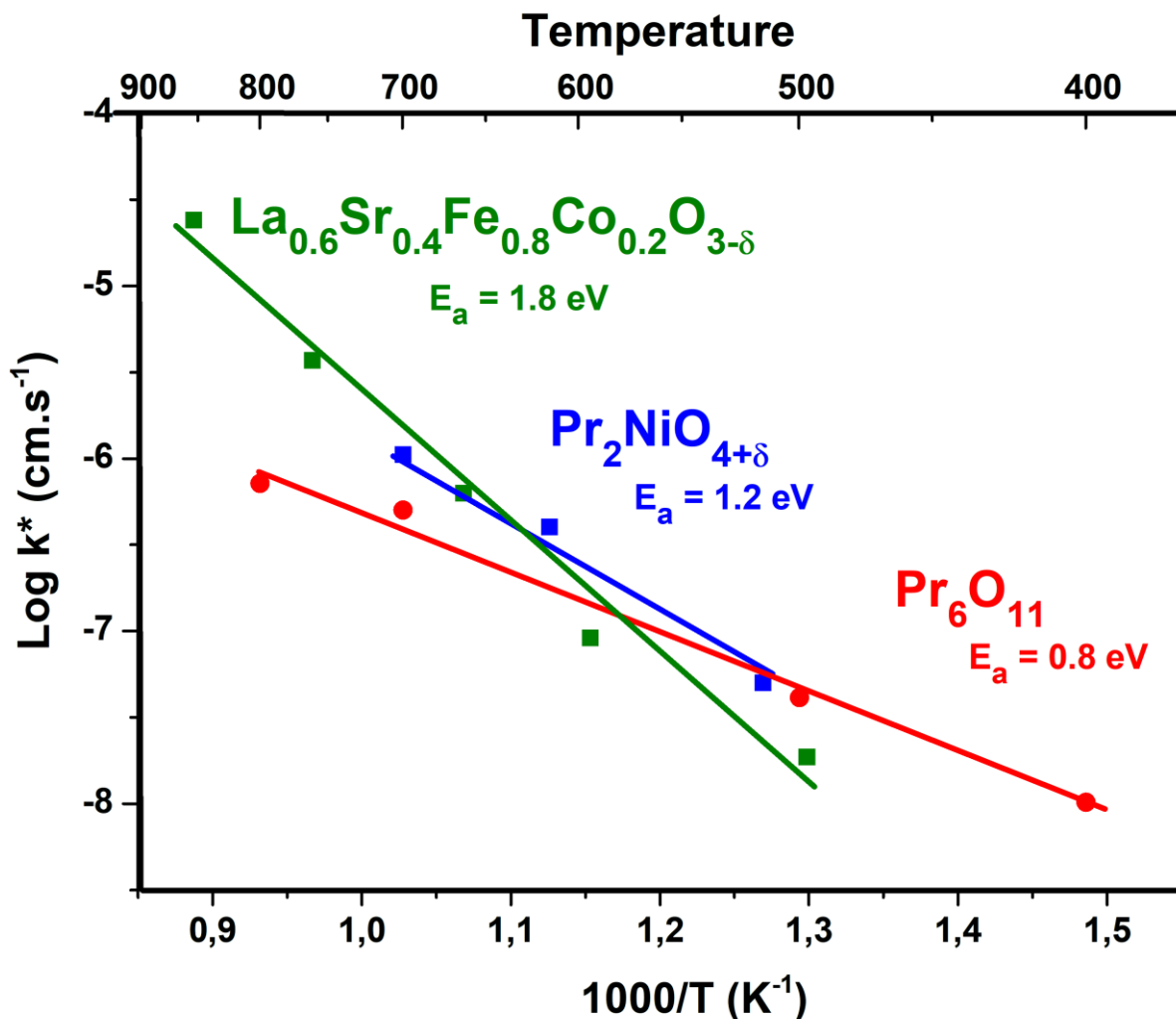


Figure 7. Arrhenius plot of the k^* coefficient vs. $1000/T$ determined for Pr_6O_{11} . Comparison with the corresponding values determined for $\text{Pr}_2\text{NiO}_{4+\delta}$ [31], and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ [32].

Fig. 7 evidences that the oxygen surface exchange coefficient for Pr_6O_{11} is somewhat higher or at least comparable to those of other usual materials (*i.e.* $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$) at low temperature ($< 550^\circ\text{C}$). Besides, the activation energy associated to the oxygen surface exchange mechanism at the surface of Pr_6O_{11} is exceptionally low (0.8eV, determined in the $400 < T^\circ\text{C} < 800$ temperature range), in comparison with those of $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$, 1.2 eV and 1.8 eV, respectively.

De Souza evidenced a strong correlation between the D^* and k^* coefficients for numerous mixed ionic and electronic conductors (MIEC) [34]. For instance, MIEC materials with the highest oxygen diffusion coefficients (D^*) also exhibit the highest oxygen exchange coefficient (k^*). Then, the exceptional electrochemical performances of Pr_6O_{11} , in particular the high oxygen exchange

coefficient (k^*), could be mainly linked to the high oxygen mobility (or D^*) in Pr_6O_{11} structure at low temperature (600-400°C).

The ionic conductivity (σ_{ion}) evolution vs. $1000/T$ was evaluated using the Nernst-Einstein relation (2),

$$\sigma_{\text{ion}} = -\frac{4F^2C_0D_0}{RT} \quad (2)$$

where the oxygen diffusion coefficient D_0 is assumed to be close to D^* , the oxygen molar concentration (C_0) is equal to $0.073 \text{ mol.cm}^{-3}$ for Pr_6O_{11} (the lattice parameter of Pr_6O_{11} being $a = 5.494 \text{ \AA}$); R is the universal gas constant, F , the Faraday's constant and T , the temperature (K).

Fig. 8 shows the temperature dependence of the calculated ionic and measured total conductivities, and ionic transport vs. temperature for Pr_6O_{11} . The ionic transport number was determined using the following relation (3):

$$t_i = \frac{\sigma_{\text{ion}}}{\sigma_{\text{Total}}} \quad (3)$$

As expected, in the temperature range 400-800°C, Pr_6O_{11} is a mixed ionic and electronic conductor with predominant electronic conductivity at low temperature (which was measured in ref. [35]). For instance the calculated ionic transport number of Pr_6O_{11} is close to 0.064 at 700°C and close to 0.022 at 600°C; it is particularly high in comparison with other MIEC materials; as a comparison the ionic transport number of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ is smaller than 10^{-4} at 700°C, a value which was determined from the ionic and electronic conductivity values available in the literature [36].

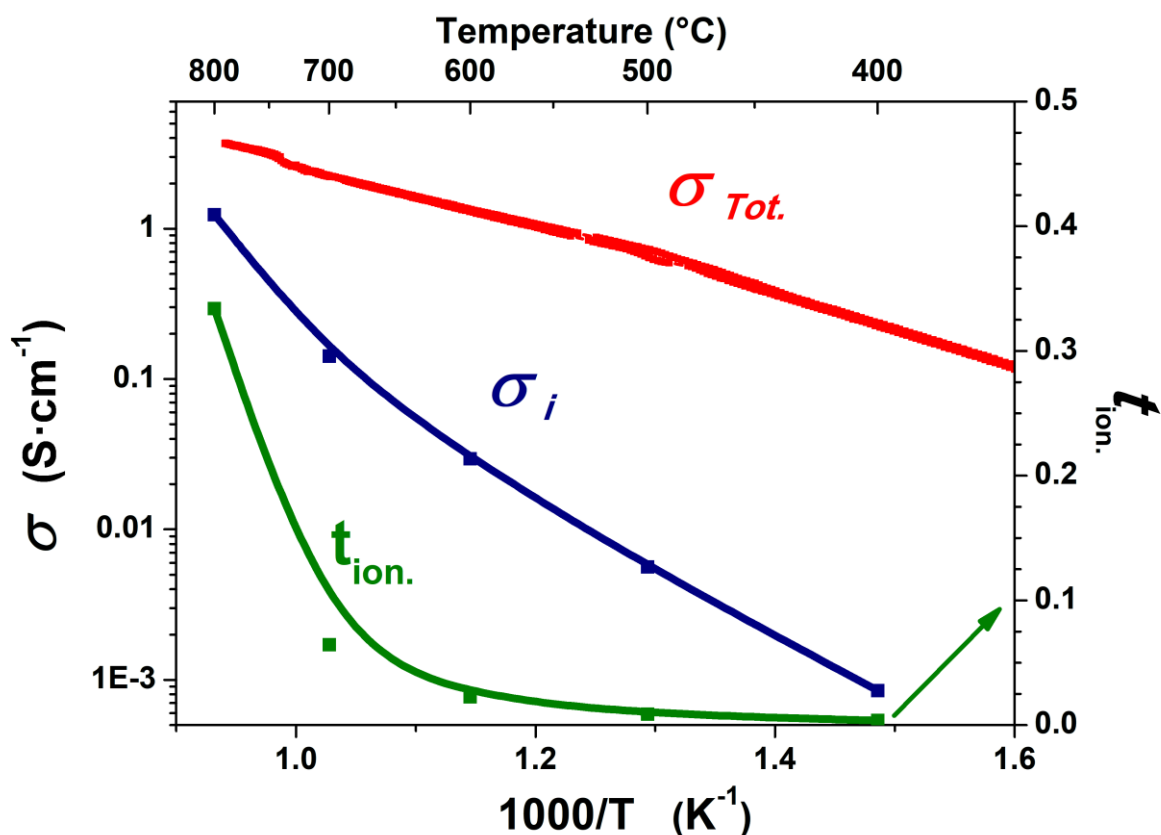


Figure 8. Temperature dependences of ionic [this work] and electronic conductivities [35] (left Y axis) and ionic transport number (right Y axis) for Pr_6O_{11} .

Conclusions

Pr_6O_{11} is a recently developed very efficient SOC oxygen electrode material which has been much studied during the last five years, mainly as a composite with gadolinium doped ceria (deposited using an infiltration way). This oxide can be expected to have good ion transport properties but, to our knowledge, no results published to date have confirmed this point. A reason could be the issues which are encountered when sintering the Pr_6O_{11} pellets (in order to obtain a relative density $\geq 94\%$). It is indeed a limiting step prior to the determination of electronic and ionic transport properties, with respect to the easy formation of phases such as Pr_9O_{16} , Pr_7O_{12} and / or Pr_2O_3 , having different oxygen stoichiometries depending on the temperature and surrounding atmosphere. Indeed, such phase transitions induce dimensional variations which lead to the formation of cracks and possibly to the break of the pellet.

In this context, the sintering of a commercial Pr_6O_{11} powder has been carefully studied, in particular by varying the thermal cycles and the nature of the atmosphere according to the various phase

transitions. The combination of two thermal cycles, a first one performed at high temperature (1370°C) under oxygen, followed by a second one at 700°C under air in order to recover the stoichiometry of oxygen led to dense Pr₆O₁₁ pellets with a relative density of 95%.

Then, D* and k* coefficients were determined in the temperature range 400 - 800°C. The results confirm that the oxygen mobility (*i.e.* the oxygen diffusion coefficient) is very high in the structure of Pr₆O₁₁ and especially at low temperature, significantly higher than the one of usual oxygen electrode materials, such as Pr₂NiO_{4+δ} or La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ}. Besides, the oxygen surface exchange coefficient is also higher than the ones of Pr₂NiO_{4+δ} and La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} at low temperatures, with a low activation energy, close to 0.7eV. The exceptional electrochemical performances of Pr₆O₁₁ as oxygen electrode materials for SOC applications is obviously linked to the oxygen transport properties of Pr₆O₁₁, showing high D* and k* coefficients at low temperature (600-400°C).

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Figure captions

- Fig. 1 *Dilatometric behavior in air of a Pr_6O_{11} green pellet ($d_{\text{rel}} = 59\% d_{\text{th}}$) (a) linear shrinkage and (b) sintering rate as a function of time and temperature (derivation of the curve 1-a with respect to the time) during (b) heating and (c) cooling as a function of temperature.*
- Fig. 2 *Linear shrinkage of a Pr_6O_{11} green pellet heat-treated under argon, air and oxygen as a function of temperature ($5^\circ\text{C}/\text{min}$ heating and cooling rate).*
- Fig. 3 *SEM cross section micrographs of Pr_6O_{11} pellets sintered :
(a) at $1450^\circ\text{C}/1\text{h}$ under O_2 (cycle 5, $d_f = 87\% d_{\text{th}}$),
(b) at $1370^\circ\text{C}/15\text{h}$ under O_2 followed by a rapid cooling to 700°C under air with a 7 h stage (cycle 10, $d_f = 95\% d_{\text{th}}$).*
- Fig. 4 *a) Mapping of the ^{18}O concentration around a micro-crack area, observed after an oxygen isotopic exchange performed at $T = 600^\circ\text{C}$ during 4920s; b) Mapping of the ^{18}O concentration in a dense area, without crack, observed after an oxygen isotopic exchange performed at $T = 400^\circ\text{C}$ during 15420 s.*
- Fig. 5 *^{18}O diffusion profile recorded by TOF-SIMS analysis on a Pr_6O_{11} pellet after oxygen isotopic exchange performed at $T = 400^\circ\text{C}$ during 15420 s.*
- Fig. 6 *Arrhenius plot of the D^* coefficient vs. $1/T$ determined for Pr_6O_{11} . Comparison with the corresponding values determined for $\text{Pr}_2\text{NiO}_{4+\delta}$ [31], and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ [32].*
- Fig. 7 *Arrhenius plot of the k^* coefficient vs. $1000/T$ determined for Pr_6O_{11} . Comparison with the corresponding values determined for $\text{Pr}_2\text{NiO}_{4+\delta}$ [31], and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ [32].*
- Fig. 8 *Temperature dependences of ionic [this work] and electronic conductivities [35] (left Y axis) and ionic transport number (right Y axis) for Pr_6O_{11} .*