

Short communication

Plasma spray synthesis of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ as a new electrolyte for intermediate temperature solid oxide fuel cells

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Abstract

The apatite-type lanthanum silicate films were successfully synthesized by modified atmosphere plasma spraying using lanthanum oxide and silicon oxide mixed powders and precalcined hypereutectic powders in the size range 1–3 μm and 5–8 μm , respectively, as starting feedstock materials. The films differed not only in microstructural scale, but also in the characteristic of the degree of film densification. A detail describing the evolution of microstructure has been discussed. A considerable improvement in densification of the $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte films has been observed.

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1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) have attracted lots of worldwide attention because of their potential long-term stability and economical competitiveness for many (including residential and automotive) applications [1]. Today the discovery of a new solid electrolyte for IT-SOFCs is a grand challenge for SOFC community. The most technologically promising intermediate temperature ionic conducting electrolyte seems to be a ceramic with apatite-type structure, which, potentially, meets most of the requirements for IT-SOFCs working temperature range 600–800 °C [2–8]. This structure, with the general chemical formula $\text{M}_{10-x}(\text{RO}_4)_6\text{O}_{3-1.5x}$, where M is a metal such as a rare earth or alkaline earth (M = La, Mg, Ca, Sr or Ba) and R is a p-block element (R = Si or Ge), is well known for its great chemical and physical stability [9–12]. Several critical issues still remain, however, including electronic conductivity and uncertain mechanical integrity under fuel cell operation conditions.

Apatite-type lanthanum silicates are promising candidates as electrolytes for IT-SOFCs because of their low activation energy and high ionic conductivity in a reduced atmosphere [12–22]. One of the major challenges for this type of ionic conductor is a proper compromise conductivity and stability. For example, $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte exhibits the highest conductivity among the investigated apatite-type materials, but the chemical and physical stability in an working temperature is inadequate for fuel cell applications due to that $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ is not an equilibrium phase [17,23–25].

$\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ does not sinter easily, and the highest conductivities can be obtained only when sintering occurs at or approaching 1600 °C by conventional solid state reaction [26–28]. This high sintering temperature is a major issue for the fabrication methods of the required low cost thin films, and densification is not expected below 1500 °C. Because of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$, it is possible to use modified atmospheric plasma spraying (APS) to form apatite-type structure that exhibits both adequate ionic conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel cell operation. Moreover, direct synthesis of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte film has not so far been performed. Here, we present a new mixing process, modified APS, a thermal spraying process carried out under atmospheric pressure to elaborate $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte film, that greatly increases

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stability and improves sinterability without impairing conductivity at suitable temperature for IT-SOFCs manufacture.

2. Experimental

2.1. Preparation of the starting feedstock powders

Non-precipitated powders were prepared by a simple mechanical mixing method. Stoichiometric amounts of high-purity lanthanum oxide (La_2O_3) and silicon oxide (SiO_2) powders were mixed and blended with appropriate amounts of polyvinyl alcohol (PVA) (10 wt.%). The resultant mixtures were then dried and calcined at 250°C in air for 2.5 h to form the agglomerate powders. The mixed powders were milled and sieved to meet the requirements of feedstock powders. The whole process was repeated until appropriate both mixture size and density powders were obtained. Precalcined powders were prepared by a solid state reaction method. The stoichiometric amounts mixed powders were calcined at 1300°C in air for 48 h. The calcined mixed powders were repeated milled and calcined until the intra-agglomerate pores with different grain sizes were eliminated.

2.2. Preparation of the electrolyte films

APS system with a Sulzer-Metco F4 torch gun was used to deposit the ceramic powders onto low carbon mild steel coupons which had been grit blasted and degreased immediately prior to deposition. Details of the operation of the system are given elsewhere. In this work hydrogen and argon were used as fuel gases with argon also as a powder carrier gas. Flat substrates approximately $10\text{ mm} \times 10\text{ mm} \times 3\text{ mm}$ thick were coated using the following procedure. The APS gun was placed in front of the fixed coupons at a standoff distance of 80 mm and traversed vertically at 400 mm s^{-1} . The other spraying parameters employed are summarized in Table 1. Additional cooling was supplied during coating by four air jets aimed radially on the back of coupons at a pressure of 6 bar.

2.3. Films characterization

X-ray diffraction (XRD) analysis of films was carried out on a Simens D5000 automatic diffractometer with a copper anticathode and a wavelength of 1.5406 \AA to determine phase purity and measure crystal parameters. Overall particle size analysis was measured using a Malvern laser diffraction granulometer (Mastersizer 2000). Microstructural characterization of the spray formed structure was performed by a JSM5800LV (JEOL, Japan) scanning electron microscopy (SEM) combined

with EDX analyzer. For powders, an EDX analysis was carried out in order to highlight a possible evolution of the composition after spraying. The densities of the sintered samples and sprayed films were obtained from the mass and geometric dimensions.

3. Results and discussions

The apatite-type lanthanum silicate films were successfully prepared by APS using La_2O_3 and SiO_2 mixed powders and precalcined hypereutectic powders as starting feedstock materials. (Hereafter the film fabricated with non-precipitated La_2O_3 and SiO_2 mixed powders by a APS process will be described simply as $n\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film, and the film fabricated with precalcined hypereutectic powders by APS as $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film.) Polyvinyl alcohol (PVA) adhesive is used in La_2O_3 and SiO_2 mixed powders in order to control both mixture size and density. An average mixed particle size of $20\text{--}40\text{ }\mu\text{m}$ was selected to achieve the optimum flowability of powders during spraying. The effect of grain size distribution on spraying properties has been discussed later in this paper.

Whilst the nominal $n\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film, did not become complete apatite-type structure phase, $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film by the APS process was apatite-type hexagonal structure phase after using the hypereutectic powders precalcined at 1300°C for 48 h (heating rate 4°C min^{-1}). In order to investigate the chemical stability of lanthanum silicate films in atmosphere, samples of both compositions were exposed to air for 1 week. XRD patterns were used to identify the phase formation, which are shown in Fig. 1. Obviously, two phases can be observed in XRD patterns, which are $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ and La_2SiO_5 . The $n\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film (Fig. 1b) is not well crystallized, which is due to the incomplete reaction in APS process using the non-precipitated mixed powders as starting feedstock materials. It is definitely because that $n\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film (Fig. 1b) is still a compound, containing mostly La_2SiO_5 . Moreover, the different positions of La_2SiO_5 in the two spectra are due to the combination and overlapping of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ and La_2SiO_5 peak positions. The apatite-type structure phase could be seen for $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film (Fig. 1a), crystallization improved, with the hexagonal structure. The obtained $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film from well crystallized sample was refined by standard least square procedures in order to determine the symmetry and the space group of the apatite-type structure. It has been confirmed that the room-temperature structure is hexagonal, space group $P6_3$, with the following lattice parameters: $a = 9.684(3)\text{ \AA}$, $c = 7.184(4)\text{ \AA}$. $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film results in good crystallization with apatite-type hexagonal phase. This result suggests that the chemical stable $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film can be synthesized using the precalcined hypereutectic powders as starting feedstock materials by the APS process.

Because electrolyte/electrode interfacial polarization resistances often cause significant power losses in SOFCs, it is very important to develop catalytically active electrode materials for the intermediate temperature operation of SOFCs [29]. The primary function of the anode in a fuel cell based on an ionic conducting electrolyte is to facilitate fuel oxidation: $1/2\text{ H}_2 \rightarrow \text{H}^+ + \text{e}^-$ (assuming H_2 as the fuel). Ni has been a par-

Table 1
Spraying parameters of APS

Parameters	$\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$
Voltage (V)	55
Current (A)	600
Spray distance (mm)	80

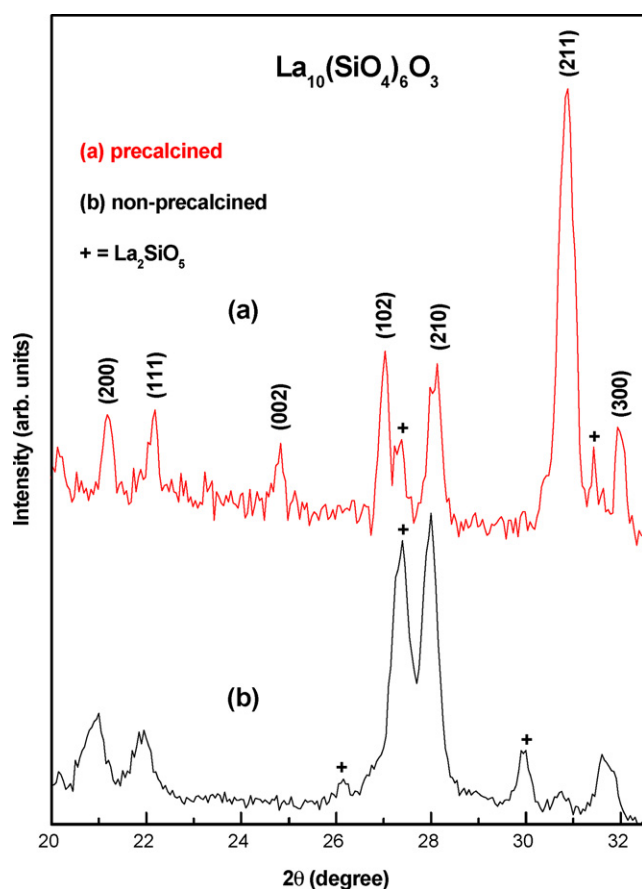


Fig. 1. XRD patterns for $n\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ and $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ films exposed to air for 1 week.

ticularly successful catalyst for the anode reactions in YSZ- or GDC-based ionic conducting electrolyte SOFCs. Therefore, we used Ni- $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ as the anode in our initial study. Lanthanum silicate films prepared from non-precalcined La_2O_3 and SiO_2 mixed powders and precalcined hypereutectic powders were fabricated by modified APS under identical conditions. Here we employed the simple low carbon mild steel as the substrate to reveal the characteristics of lanthanum silicate films.

Fig. 2 shows a typical cross-section image of the electrolyte/substrate bilayer fabricated by a modified APS process. The image 2a indicates that the $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte film appears sufficiently dense, without any noticeable connected pores, using precalcined hypereutectic feedstock powders. The image shown in Fig. 2b reveals that the $n\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte film is not well-adhered to the substrate, with some cracking or delamination, using non-precalcined La_2O_3 and SiO_2 mixed powders. The $n\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film prepared from non-precalcined mixed powders displays a microstructure with many micron-sized pores, whereas the use of precalcined powders resulted in a dense microstructure. For $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film made from the latter material only occasional pores were found. Density measurements revealed a clear advantage in the use of precalcined feedstock powders as $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film exhibited a higher density of 5.32 g cm^{-3} , which is 94% of the theoretical density of 5.66 g cm^{-3} .

Employing precalcined hypereutectic powders of 20–40 μm size as starting feedstock and controlled plasma processing parameters can result in dense film formation. Plasma parameters would be precisely controlled to ensure a larger degree of melting in the outer zone and partial melting/heating in the core of the powder. Hence, the densification in the outer zone will occur via melting and the resolidification whereas the core will experience consolidation via solid state precalcining. The degree of melting can be monitored by the direct measurement of the temperature (T) and velocity (v) of the exiting particles from the plasma jet using an *in situ* process diagnostic technique.

The preparation of dense electrolyte films on porous electrodes is an important step in the fabrication of high performance SOFCs, due to the requirements of gas tightness. $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ synthesized via solid state reaction from the component oxides have to be heated up to 1600 $^\circ\text{C}$ to achieve the desired densities, because of the poor reactivity arising from the prolonged heating at elevated temperatures (such as 1500 $^\circ\text{C}$ for 48 h). The simple and cost effective process has been expected. We fabricated the $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte film by modified APS method, allowing us to fabricate crack-free film. The film was uniform, and the thickness could be readily controlled by varying the amounts of powders used or time and distance of spraying. The implementation of this simple and cost effective fabrication method may enable significant cost reductions in SOFCs fabrication. Furthermore, this technique is equally applicable to the fabrication of other devices based on ceramic films, for example, YSZ electrolyte of SOFCs for gas separation.

The ability for sintering of starting powders before APS is an important precondition for the application of these materials in SOFCs electrolyte. Precursors prepared from La_2O_3 and SiO_2 powders were mixed with 10 wt.% PVA and $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ precursors were sintered at 1300 $^\circ\text{C}$ for 48 h (heating rate $4 \text{ }^\circ\text{C min}^{-1}$). For the precalcined powders, sintering at 1300 $^\circ\text{C}$, lead to an obvious grain growth and significant structural densification. The fractures made from non-precalcined and precalcined powders are shown in Fig. 3a–d. The microstructure of the mixed powders adhered from 10 wt.% PVA showed grain size 1–3 μm (Fig. 3a and c). The precalcined hypereutectic powders are monodisperse and an average grain size is 5–8 μm with distinct grain boundaries (Fig. 3b and d).

On the other hand, the particle size of the starting materials is of prime importance when applied as feedstock powders in APS process. PVA adhesive is used in La_2O_3 and SiO_2 mixed powders in order to control both mixed particle size and density. An average particle size of 20–40 μm was selected to achieve the optimum flowability of powders during spraying. Coarser powder particles (>50 μm) often remain unmelted or partially melted, which subsequently results in high porosity and weak bonding in the spray deposited structure. Finer particles (<1 μm) suffer from poor and inconsistent flow, resulting in the clogging of the plasma spray gun and porosity in the spray deposit. It is difficult for the smaller particles (<20 μm) to arrive at the substrate since most of them were blown off by compressed air during the APS process. Here the spraying conditions were further optimized to reach higher particle velocities and temperature. Therefore, a chosen 35:12 Ar/ H_2 ratio is only one part of

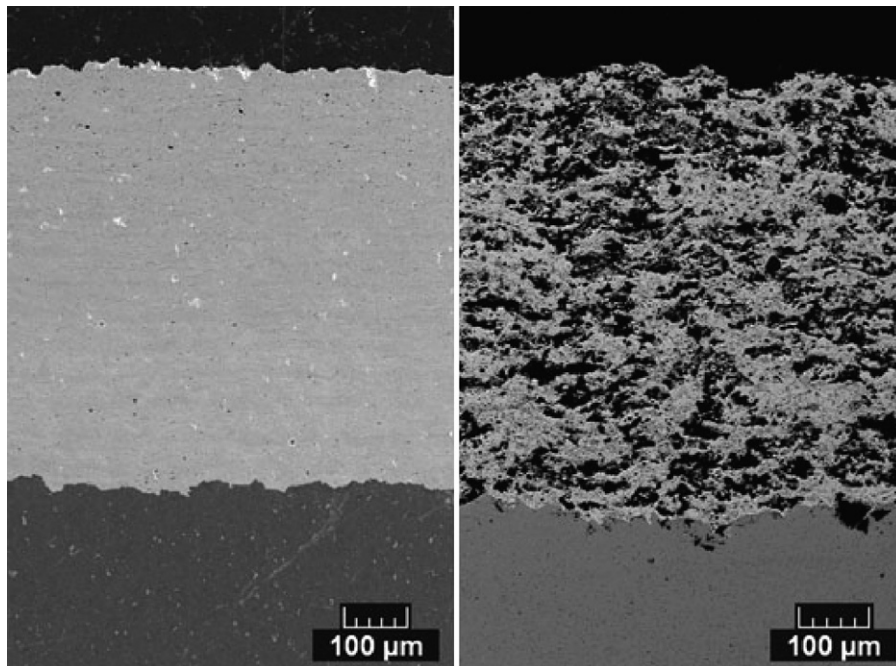


Fig. 2. Cross-sectional microstructure images of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte films supported by a stainless steel substrate. (a) $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte film with APS process using the hypereutectic powders precalcined at 1300°C for 48 h (as-prepared). (b) $n\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ electrolyte film using the non-precalcined feedstock powders.

the optimization process. In addition, the other part of this process was the slight reduction of the spraying distance (80 mm). On the other hand, a feasible grain size ($5\text{--}8\ \mu\text{m}$) was chosen for this work. The obvious improvement of the densification by

about 20% was shown in Fig. 2. The precalcined hypereutectic powders exhibit a higher densification than simply mixed powders, which is due to the growth of grains and the elimination of intra-agglomerate pores in the precalcined process.

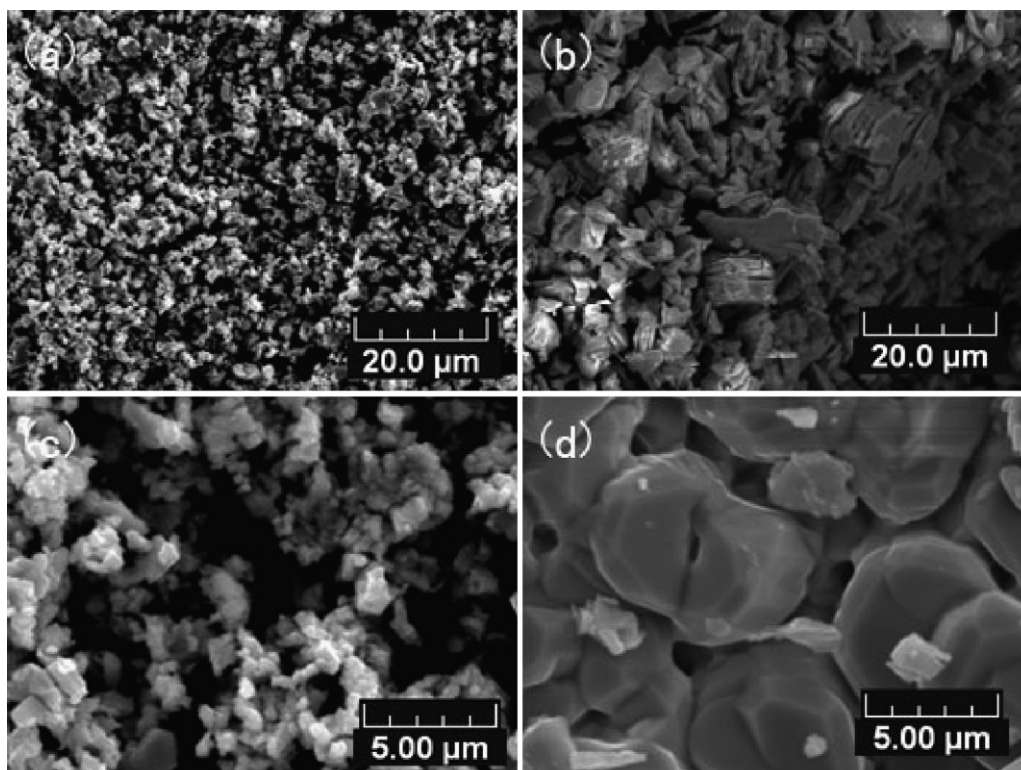


Fig. 3. SEM images of the fracture precursors of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$. The powders were prepared (a) via a mechanical mixing with 10 wt.% PVA adhesive and (b) by the precalcining route at 1300°C for 48 h. (c) and (d) are the corresponding topical images.

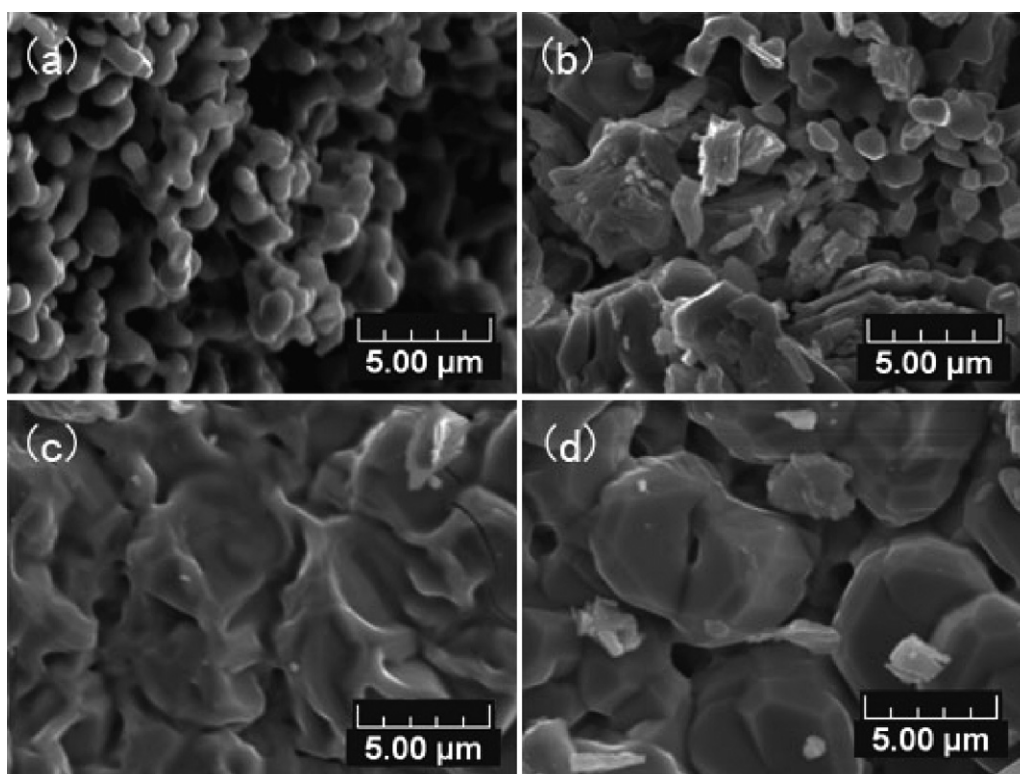


Fig. 4. SEM images of the fracture precursors of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C and (d) 1300 °C.

The complete densification of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film is ascribed to the precursor grain size and the presence of agglomerate in grains. To quantify the effect of the sintering temperatures on the microstructure of precursor powders, several sintering temperature have been used ranging from 1000 °C to 1300 °C (Fig. 4). It can be observed that the grain size changes with the sintering temperature. As the temperature increases, the grain size tends to increase too. At 1000 °C, the grain size is about 1 μm and increases up to 6 μm after heating at 1300 °C for 48 h. It can be noticed that (Fig. 4a), at 1000 °C, the sintering process starts: necks between grains can be observed. The low temperature (1100 °C) corresponds to the elimination of the intra-agglomerate pores with different grain sizes while the high temperature (1300 °C) is attributed to the inter-agglomerate pores removal, following the particles rearrangement. The precursor powders undergo two sintering steps up to 1300 °C. Indeed, a fast increase of the grain growth at high temperature appears during the intra-agglomerate and partly inter-agglomerate pores elimination, giving rise to the stabilization. Whilst the necks of grains become wide and gradually disappear (Fig. 4b), and the intra-agglomerate pores are eliminated (Fig. 4c). The present study on the precursor powders demonstrates the importance of internal situation in grains on the coating process.

4. Conclusions

Lanthanum silicate films were fabricated successfully using precalcined hypereutectic powders by modified atmospheric plasma spraying. Effective precalcined at high temperatures of

precursor powders is demonstrated to be sufficient to achieve very high dense lanthanum silicate films. The introduction of precalcined hypereutectic powders into the APS process and the preparation of fully densification $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ film have proved the development of the electrolyte membrane concepts that are essential to the efficient utilization of ionic-conducting ceramics in intermediate temperature devices.

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