



Short communication

## Optimisation of the Solid Oxide Fuel Cell (SOFC) cathode material $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$

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### ABSTRACT

This paper focuses on the electrochemical potentialities of the 2D misfit compound  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ , so far mainly investigated for its thermoelectric properties. Its expansion coefficient ( $\text{TEC} = (9-10) \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ ) and its chemical stability are compatible with standard CGO IT-electrolyte and the first optimisation steps of the deposited cathode have been performed with the aim to minimise the ASR and increase the cell durability. Particular attention has been paid on the effect of thickness and microstructure for pure and composite cathodes. The electrode reaction was performed on symmetrical cells. The preliminary results presented here show that the composite (70 wt.%  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO) gives the lowest ASR values compare to single-phased electrodes. Strikingly, the ASR values increase for thinner deposited layers. The effect of various current collectors (gold grid vs. platinum paste) has been also checked.

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### 1. Introduction

A good suite of materials are currently available for SOFC operation at high temperatures (800–1000 °C); however, possible issues with long-term stability and availability of suitable, low cost seals and interconnects have focused considerable attention for intermediate-temperature (IT) SOFCs, working below 800 °C [1]. The decrease of the operating temperature mainly reduces electrochemical performances at the cathode, thus providing a critical source of electrical loss [2]. Therefore, it is of great importance to develop new powerful prototypes at lower temperature, which involves the optimisation of the thermodynamic and kinetic aspects of the electrochemical process, for example through the search for new cathode materials. The main requirements for SOFCs cathodes are (i) high electronic conductivity with a possible anionic contribution, (ii) a good stability under oxidative conditions, (iii) a significant catalytic activity towards oxygen dissociation, and (iv) long-term chemical/thermal/mechanical stabilities in the concerned thermal range with the electrolyte and other contact components.

In this topic, the most commonly investigated materials are 3D-perovskites (Sr-doped  $\text{LaMO}_{3-\delta}$  (M = Mn, Co, Fe),  $\text{SmCoO}_{3-\delta}$ ), which display good performances due to their mixed ionic-electronic conductivity (MIEC) [3]. More recently, layered double perovskites with ordering of oxygen vacancies such as  $\text{LBaCo}_2\text{O}_{5+\delta}$  (L = lanthanide) [4] have also been presented as promising cathode materials, as well as Ruddlesden–Popper phases ( $\text{La, Sr}_{n+1}\text{MO}_{3n+1}$  (M = Ni), highlighting the important role of extra oxygen path within their 2D-structural characteristics. It turns out that the necessity to provide new ionic-electronic conductors is a strategic area within the SOFC research community.

The 2D misfit compound  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  (Ca349) has been investigated for its relatively high thermoelectric performances observed in the field of oxide compounds [3–5]. Its structure can be described as alternating  $[\text{CdI}_2]$ -type and oxygen deficient rock-salt slabs according to the formula  $[\text{CoO}_2][\text{Ca}_2\text{CoO}_{3-\delta}]_{0.62}$ . Here, each sandwiching block would individually play a role for efficient electronic ( $[\text{CdI}_2]$  type blocks) and ionic transport (rock-salt blocks) [6]. From this scheme, Ca349 could be considered as a regular intergrowth between electronic and  $\text{O}^{2-}$  conducting units, which inspired the possibility of MIEC properties and potentially high performance as SOFC mixed conducting cathode [6].

Its matching thermal expansion coefficient ( $\text{TEC} = (9-10) \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ ) and its good chemical stability provides compatibility with standard CGO IT-electrolyte. Preliminary

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electrochemical measurements of pure Ca349/CGO and composite (70 wt.%  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO)/CGO show attractive performances [6].

With the aim to minimise the polarisation resistance and to understand the cathode electrochemical response, a first stage of optimisation has been performed, by screening the effects of the thickness and microstructure on various supports (dense CGO, dense YSZ protected by a CGO layer). The effect of various current collectors (gold grid vs. Pt paste) has been also considered. Our study yields the evidence of the most limiting factors to improve in the future use of this innovating electrode material.

## 2. Scientific approach

We prepared several cathode inks for deposition by screen-printing on various electrolytes. The microstructures of the deposited layers have been characterised by Scanning Electron Microscopy (SEM) after various thermal treatments. In order to identify and understand the phenomena involved in the conducting process as well as the influence of the cell configuration in the pure Ca349 and the composite (70 wt.%  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO)/CGO cathode reaction, symmetrical cells are then prepared and studied using Electrochemical Impedance Spectroscopy upon thermal cycles.

## 3. Experiments

Single-phase Ca349 was prepared by solid state reaction at 880 °C from  $\text{CaCO}_3$  (JMC puratronic grade 2) and  $\text{Co}_3\text{O}_4$  (Alfa Aesar  $\geq 99.7\%$ ). The Ca349 based inks consist of a powder–dispersant–binder mixture. Since we already established the good chemical stability of Ca349 with CGO, while it reacts with YSZ (6) leading to  $\text{CaZrO}_3$  and  $\text{Co}_3\text{O}_4$  at 800 °C after 100 h [6], our layers have been deposited on various supports including dense CGO and dense YSZ protected by a CGO porous layer, by screen-printing using a DEK 248 screen-printer. Various calcination temperatures were considered in order to determine the optimal thermal treatments, i.e. 800 °C, 900 °C and 1000 °C. The deposited layers were characterised on pelletised samples using a D8 Bruker AXS diffractometer ( $\text{CuK}\alpha = 1.54 \text{ \AA}$ ). The microstructure of the cathodes surface and along their cross-section was analyzed using the Hitachi S3400N and the JEOL JSM 5600 scanning electron microscopes. Impedance spectroscopy data were collected on symmetrical cells with a SI1260 Solartron in various frequency ranges with an applied ac voltage of 50 mV. The set-up was heated at 750 °C and then two cooling–heating cycles were performed. Data were collected every 50 °C and 2 h stabilisation times were considered between each temperature change, which corresponds to a drifting of less than 5%. For comparison purpose, platinum paste or gold grids were used as current collectors on different cell configurations. The data were fitted using the ZView 3.1 software.

## 4. Results and discussion

### 4.1. Optimisation of the treatment temperature

In this study we focussed on two ink-compositions: (80 wt.%  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –20 wt.% cellulose) and (70 wt.%  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO), in view to evaluate the effects of the pore former and of the compositional ratio. Whatever the electrolyte support is (dense CGO or dense YSZ protected by a porous layer of CGO), X-ray diffraction reveals the conservation of the initial XRD pattern (Fig. a, presented in supplementary data) after all thermal treatments (at 800 °C and 900 °C). However, we also verified that at 1000 °C, Ca349 decomposes into  $\text{Ca}_3\text{Co}_2\text{O}_6$ .

### 4.2. Microstructural characterisations

We have considered different cell configurations, which are reported in Table 1. Particular attention was paid to the thickness, microstructure, porosity and adherence on the dense electrolytes. The SEM images of the surface of several layers are reported in Fig. 1 while cross-sections are shown in Fig. 2.

*Analysis of surfaces.* The screen-printed cathode layers mainly consist on platelets. In general, the cathodes thermally treated at 800 °C have a heterogeneous microstructure (Fig. 1(a), (b), (e) and (f)). For the pure cathodes PC800c and PY800c samples (Fig. 1(a) and (b)), the platelets are randomly oriented. The cellulose has indeed a disordering effect, leading to very disturbed surfaces. Layers treated at 900 °C (Fig. 1(c), (d), (g) and (h)) show a denser surface with a broad distribution of grain sizes ( $\sim 0.5$ – $5 \mu\text{m}$ ). The surface is more homogeneous than after the 800 °C treatment. The same trend is evidenced for pure (P) and composite cathodes (C), on all substrates.

*Cathode on YSZ/CGO substrates.* Because of the reactivity of Ca349 towards YSZ, a protective CGO layer was screen-printed on a dense YSZ pellet prior to the cathode deposition (PY800/900 and CY800/900 samples). One can notice the increased density of the CGO interlayer between 800 °C and 900 °C sintering temperatures, while conserving small grains. However, the reached density is far to be sufficient for exploitable impedance measurements, not performed on any of these samples. We note that the adhesion between CGO ( $\sim 10 \mu\text{m}$  thick) and YSZ is correct, and is improved at 900 °C. For the concerned samples, the thicknesses of the cathodes are between 5 and 20  $\mu\text{m}$ , Fig. 2.

*Cathode on CGO substrates.* For pure Ca349 cathodes on CGO, SEM images of the cross-section confirm the disorganisation of the layer after decomposition of cellulose, but the pore former properties of the cellulose are not clearly efficient here. Indeed, the porosity of the pure Ca349 cathodes (PC samples) and those of the cellulose-free composites (CC-samples) shows no significant difference. Only for the latest ones, one should note well stacked platelets with a rather regular and plane surface.

The thicknesses of all samples have been estimated from cross-sections (Fig. 2) and are listed in Table 1. They are included in between 5 and 10  $\mu\text{m}$ . To further evaluate the impact of the thickness on the electrochemical reaction, we also prepared a thicker composite layer (CC800<sub>20</sub>), close to 20  $\mu\text{m}$ , by two successive screen-printing passages with an intermediate drying (Fig. 2(f)).

For all samples, the adhesion of the cathode layers on the substrate is correct. In any case, the aspect of the grains is similar. These microstructures are different to the ones reported in Ref. [6] for hand-painted layers, which were more porous and thicker, of about 40  $\mu\text{m}$  and 15  $\mu\text{m}$ , for pure  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  and (70 wt.%  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO) composite, respectively.

### 4.3. Electrochemical characterisations

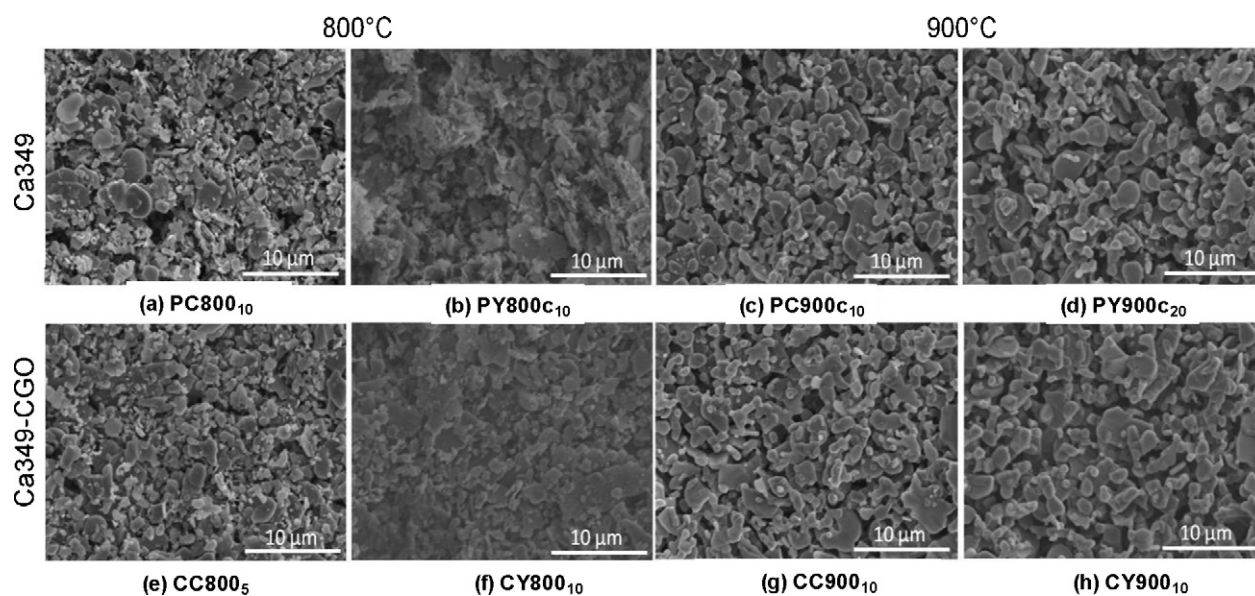
*Effect of the cathode composition and type of collector.* Impedance spectra evolutions with temperature are given in Fig. 3. Particular attention was paid to the cells with dense CGO support: CC800<sub>5</sub> and PC800<sub>10</sub> with a gold grid current collector (Fig. 3(a) and (b)) and CC800Pt<sub>5</sub> mounted with a platinum paste current collector Fig. 3(c). After subtraction of the series impedance, the plotted impedance spectra correspond to the polarisation part only.

The electrochemical response of the pure cathode PC800<sub>10</sub> (Fig. 3(a)) consists of one semi-circle, composed of several contributions. Whatever the temperature is, it could be fitted by the equivalent circuit given in Fig. 3 in a first approach, similar to the one previously used for pure and composite hand-painted cathodes [6]. Fit results are given in Table a in supplementary data. The same trend is observed for the composite cathode CC800<sub>5</sub> (Fig. 3(b)). As already evidenced in Ref. [6] for hand-painted cells, the compos-

**Table 1**

Considered cell configurations: cathode composition, thermal treatment, electrolyte support, thicknesses and current collector.

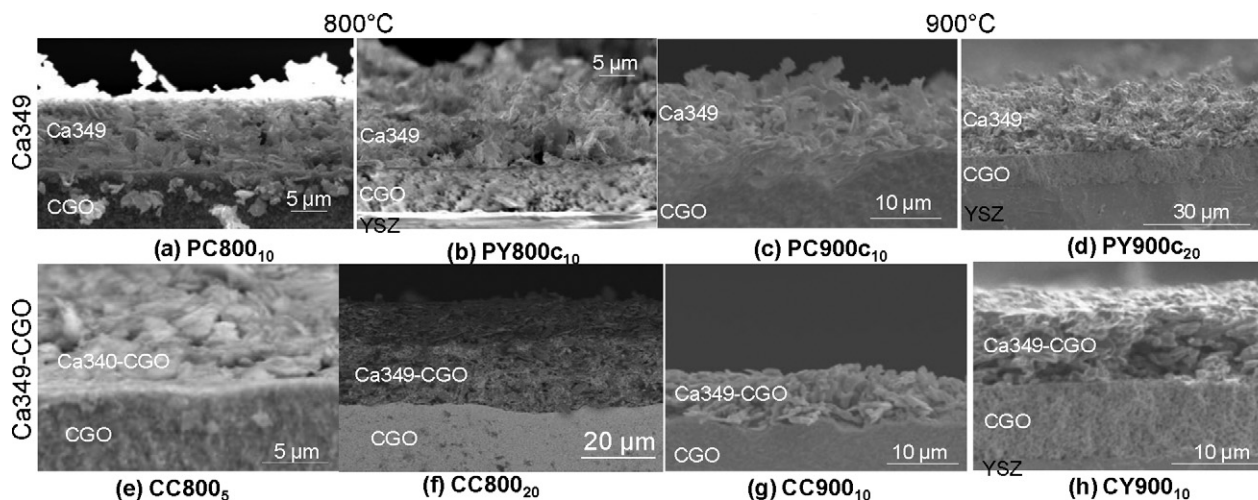
Composition	Treatment $T$ (°C)	Support	Current collector	Thickness ( $\mu\text{m}$ )	Name
Pure $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ + 20 wt.% cellulose	800	Dense CGO	Au grid	5–10	PC800c <sub>10</sub>
Pure $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ + 20 wt.% cellulose	800	Porous CGO layer on dense YSZ	Au grid	~10	PY800c <sub>10</sub>
Composite 70 wt.% $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO	800	Dense CGO	Au grid	~5	CC800 <sub>5</sub>
Composite 70 wt.% $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO	800	Dense CGO	Pt paste	~5	CC800Pt <sub>5</sub>
Composite 70 wt.% $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO	800	Dense CGO	Au grid	~20	CC800 <sub>20</sub>
Composite 70 wt.% $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO	800	Porous CGO layer on dense YSZ	Au grid	5–10	CY800 <sub>10</sub>
Pure $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ + 20 wt.% cellulose	900	Dense CGO	Pt paste	5–10	PC900cPt <sub>10</sub>
Pure $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ + 20 wt.% cellulose	900	Porous CGO layer on dense YSZ	Pt paste	~20	PY900cPt <sub>20</sub>
Composite 70 wt.% $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO	900	Dense CGO	Pt paste	5–10	CC900Pt <sub>10</sub>
Composite 70 wt.% $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ –30 wt.% CGO	900	Porous CGO layer on dense YSZ	Pt paste	~10	CY900Pt <sub>10</sub>

**Fig. 1.** SEM images of the surface of pure (PC800c<sub>10</sub> (a), PY800c<sub>10</sub> (b), PC900c<sub>10</sub> (c), PY900c<sub>20</sub> (d)) and composite (CC800<sub>5</sub> (e), CY800<sub>10</sub> (f), CC900<sub>10</sub> (g), CY900<sub>10</sub> (h)) cathodes layers deposited on various electrolyte with calcination temperatures of 800 °C and 900 °C.

ite cathode has a smaller ASR value than the pure Ca349 cathode, ASR ~ 2.5 and 4  $\Omega\text{cm}^2$  at 750 °C, respectively.

For composite cathode with platinum paste collector CC800Pt<sub>5</sub> (Fig. 3(c)), one can notice an additional semi-circle at low frequency, called the *D* arc. This could be attributed to the platinum paste response. Considering an eventual surface reaction or its high coverage, which could block the access to porosity, the additional

semi-circle might be related to surface phenomena associated to a limiting gas diffusion or concentration effect [7]. This contribution can be fitted by adding the element circuit: (R//CPE). Then the total electrochemical response embraces the intrinsic cathode one at high/medium frequency (*B*+*C*) and the surface reaction, at low frequency (*D*). As shown on Fig. b of supplementary data, the same trend is also observed when platinum

**Fig. 2.** SEM images of the cross-sections of P800c<sub>10</sub> (a), PY800c<sub>10</sub> (b), PC900c<sub>10</sub> (c), PY900c<sub>20</sub> (d), CC800<sub>5</sub> (e), CC800<sub>20</sub> (f), CC900<sub>10</sub> (g) and CY900<sub>10</sub> (h) layers.

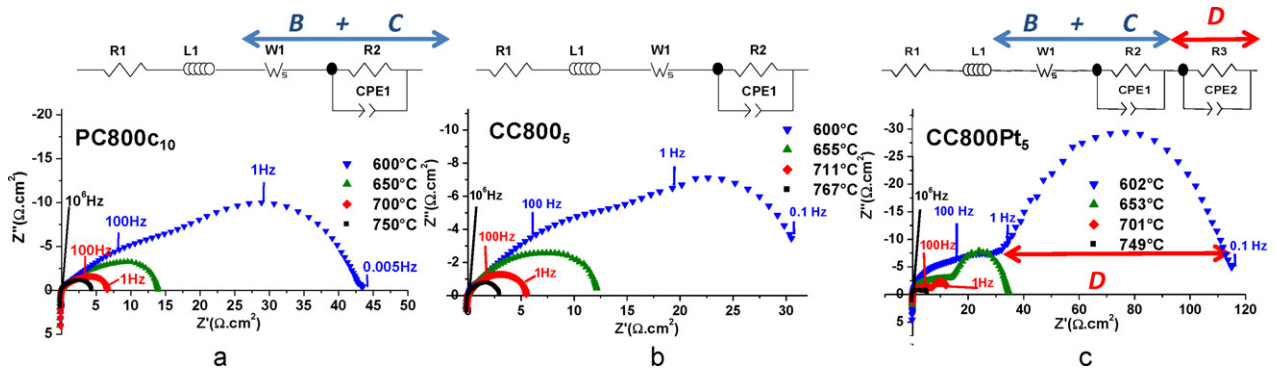


Fig. 3. Cathode composition and collector effect: temperature evolution of the impedance spectra of pure (PC800c<sub>10</sub> (a)) and composite (CC800<sub>5</sub> (b)) cathode with gold grid collector and the same composite cathode measured with platinum paste collector (CC800Pt<sub>5</sub> (c)). All cells are thermally treated at 800 °C.

paste is used as collector of pure Ca349 cathode treated at 900 °C (PC900cPt).

**Frequencies analysis.** An analysis of the frequencies of each component of the impedance spectra has been carried out on the basis of the work of Jorgensen et al. on LSM/YSZ [7]. In the high and medium frequency range, whatever the sample (PC800c, CC800, CC800Pt or PC900cPt), the spectra can be decomposed into two overlapped contributions: the so-called “C arc (medium frequency)”, overlapping a small part of “B arc (high frequency)” [7]. At high temperature, their frequencies are too close to establish clearly distinct electrochemical processes. However, according to Ref. [7], the processes involved in the C arc could be assigned to the competitive reactions at the TPB: adsorption, transfer of species and surface diffusion. The B arc can be assigned to the transport of O<sup>2-</sup> ions and intermediates species, through the cathode and at the cathode/electrolyte interface. Ca349 being potentially ionic conductor, the oxygen ions can migrate through the cathode across Ca349 grains, as well as CGO ones in the composite case.

In the PC900cPt case (Fig. b supplementary data) fired at 900 °C and pasted with platinum, the B + C frequencies extend to a broader range, which shows a sensitive effect of the thermal treatment on the driving mechanism. Indeed the B arc being sensitive to the microstructure, it is affected by the densification. In fact, for all Pt pasted samples (PC900cPt and CC800Pt) (Fig. 3(c)), the appearing of the additional large semi-circle evidenced at low frequency (*f* < 1 Hz) (D arc) might be attributed, according to the Jorgensen description, to phenomena related to gas diffusion limitation at the surface. This phenomenon can be clearly attributed to the effect

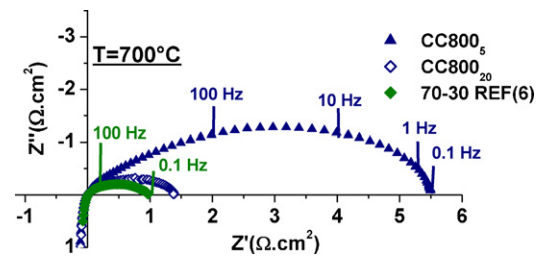


Fig. 4. Thickness effect: electrochemical response of composites CC800<sub>5</sub> (5 μm) and CC800<sub>20</sub> (20 μm) at 700 °C compared to composite 70–30 of Ref. [6] (15 μm).

of the platinum paste current collector deposited on the cathode surface. Studies are currently under investigation for a better understanding of the involved processes.

**Effect of the thickness on the impedance spectra.** The comparison of the data at 700 °C, for the same composites (CC800) deposited on dense CGO with two different thicknesses (5 and 20 μm thick) with the hand-painted composite layer of Ref. [6] (15 μm thick) is given in Fig. 4. The frequency ranges associated with the electrochemical processes are similar for all samples. Nevertheless, the hand-painted material show lower ASR (~1 Ω cm<sup>2</sup> at 700 °C) than screen-printed ones (~1.5 Ω cm<sup>2</sup>/20 μm and 4.5 Ω cm<sup>2</sup>/5 μm), which might imply differences in diffusion effects because of the different grains size and the smallest porosity of the latest. Considering the screen-printed cathodes, one can notice that the thinner layer gives the worst ASR values.

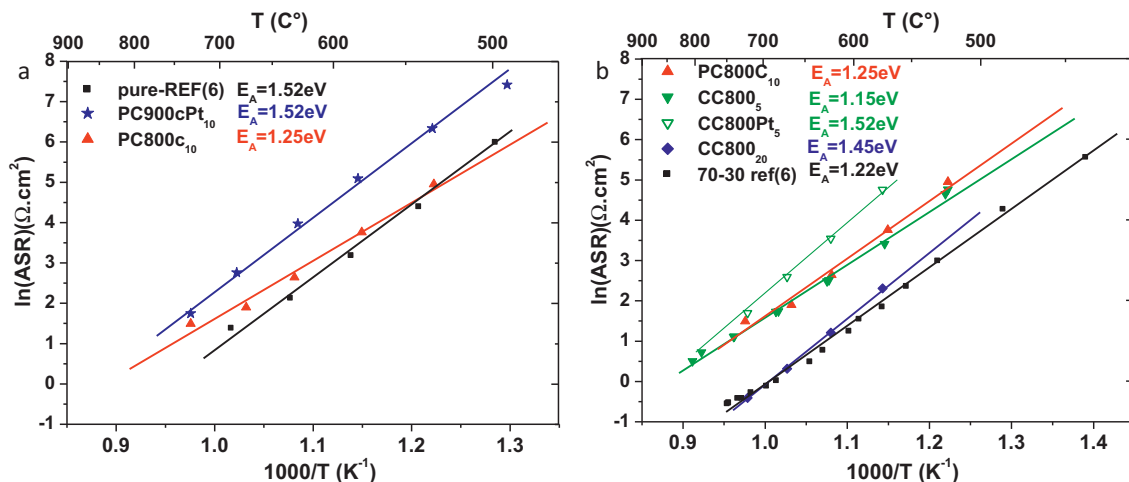


Fig. 5. ASR evolution with temperature and corresponding activation energies (*E<sub>A</sub>*) of pure (a) (PC800c, PC900c) and composite (b) (CC800<sub>5</sub>, CC800<sub>20</sub>, CC800Pt<sub>5</sub>) cathodes layers, compared to Ref. [6].

**ASR thermal evolution.** The Fig. 5(a) shows the thermal evolution of ASR of three different layers with their activation energies. The lowest activation energy ( $E = 1.25$  eV) is obtained after screen-printing compared to hand-painting ( $E = 1.52$  eV), even if ASR values for the latter are slightly lower at low temperatures. It pictures well the compromise to access by tuning several parameters, such as the cathode porosity, the effect of the thickness. . . About the penalizing effect of the Pt-paste collector, it is clear that the corresponding layers shows both larger ASR values assorted with a high activation energy ( $E = 1.52$  eV). Similar behavior has been observed for platinum-pasted composite CGO–Ca349 layers (Fig. 5(b)). Here, once more, the best performances of rather thick layers is comforted since CC800<sub>20</sub> (20  $\mu\text{m}$ ) and the layer of Ref. [6] (15  $\mu\text{m}$ ) show the smallest ASR values and rather low activation energies (1.22–1.45 eV).

To improve the ASR, many parameters need to be further optimised, not only the microstructure of the layers, their composition, but also their thickness. The effect of the cathode thickness on the polarisation resistance is indeed a parameter which has been discussed on various composite cathodes [8–11], because of the Triple Phase Boundary point length. In our case, it seems to affect the Ca349 cathode response, showing that screen-printed cathodes, thinner than the hand-painted ones, give worst performances.

## 5. Conclusions

This study is focused on the optimisation of the potential cathode material  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  on various supports (dense CGO, dense YSZ protected by a CGO porous layer). The phase remains stable until 900 °C. For the considered inks, the best microstructural properties are obtained for layers treated at 900 °C. The electrochemical improvement using cellulose as a pore-former has not been evidenced in this study. From the microstructural point of view, the cellulose decomposition might be violent and induces a disorganisation of the layer. Further study should be performed to evaluate the effect of various cellulose amounts, as well as to envisage other

pore former, such as carbon black. The effect of the thermal treatment should also be considered.

It was pointed out that, in case of  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ , the current collector affects strongly the electrochemical response. Surprisingly, the platinum paste current collector is inappropriate, since it induces an additional electrochemical response probably connected to surface phenomena. The effect of other current collectors is currently under investigation. With the aim to improve  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  properties for potential use as cathode material for SOFC, optimisations of the microstructure, porosity, thickness, etc. are currently under progress.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jpowsour.2011.02.030](https://doi.org/10.1016/j.jpowsour.2011.02.030).

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