



## Short communication

Enhanced electrochemical performance of the solid oxide fuel cell cathode using  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ 

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## ABSTRACT

This paper reports on the electrochemical performance of an SOFC cathode for potential use in intermediate-temperature solid oxide fuel cells (IT-SOFCs) using the oxygen non-stoichiometric misfit-layered cobaltite  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  or composites of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  with  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ ). Electrochemical impedance spectroscopy revealed that symmetric cells with an electrode of pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  exhibit a cathode polarization resistance ( $R_p$ ) of  $12.4 \Omega \text{cm}^2$ , at  $600^\circ\text{C}$  in air. Strikingly,  $R_p$  of the composite CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  with 50 vol.% CGO was reduced by a factor of 19 (i.e.  $R_p = 0.64 \Omega \text{cm}^2$ ), the lowest value reported so far for the  $\text{Ca}_3\text{Co}_4\text{O}_9$  family of compounds. These findings together with the reported thermal expansion coefficient, good compatibility with CGO and chemical durability of this material suggest that it is a promising candidate cathode for IT-SOFCs.

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## 1. Introduction

The high efficiency of solid oxide fuel cells (SOFCs) in converting chemical energy to electrical energy [1] offers a promising way of energy production. However, the cost and material issues confronted at the typical SOFC operation temperature of above  $750^\circ\text{C}$  outweighs its potential as a commercialized energy-conversion device. The focus in the SOFC research has been to lower the operation temperature to the  $550\text{--}750^\circ\text{C}$  range obtaining the so called intermediate temperature SOFCs (IT-SOFCs) [2]. This range of temperature facilitates the use of low cost seals and interconnects in addition to expected improvement in the long-term stability of the cells. With the decrease of the operating temperature, however, it is known that electrolyte ohmic losses increase and the electrochemical performance of the electrodes also decreases. Thus, a continuous search and development of component materials for IT-SOFCs is needed.

In the case of cathodes, by far, most of the reported candidate materials for IT-SOFCs consists of mixed-ionic electronic conductors (MIECs) and are of the perovskite type  $(\text{Ln,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ , ( $\text{Ln} = \text{La-Yb}$ ) [3], typically  $(\text{La,Sr})(\text{Fe,Co})\text{O}_{3-\delta}$  (LSCF) [4–7]. These materials have been investigated intensively because of their good catalytic activity for oxygen reduction, high oxide ion conductivity, and high electronic conductivity. However, the disadvantages

of these types of materials are their known chemical reactivity with zirconia-based electrolytes and their thermal expansion mismatch (e.g.  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ ,  $\text{TEC} \sim 20 \times 10^{-6} \text{K}^{-1}$  [8]) with that of commonly used SOFC electrolytes such as yttria stabilized zirconia ( $\text{TEC} \sim 10 \times 10^{-6} \text{K}^{-1}$  [9]), gadolinia doped ceria ( $\text{TEC} 12.5 \times 10^{-6} \text{K}^{-1}$  [10]), and  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$  ( $\text{TEC} 10 \times 10^{-6} \text{K}^{-1}$  [11]).

Recently, the misfit-layered cobaltite  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ , which are extensively used as a thermoelectric material [12] has also been investigated as a candidate cathode material for IT-SOFCs [13,14]. In addition to its matching thermal expansion coefficient ( $9\text{--}10 \times 10^{-6} \text{K}^{-1}$ ) and its good chemical stability with standard CGO IT-electrolyte, the composite of  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  and CGO was found to exhibit an electrochemical performance not prohibitively high for use in IT-SOFCs [13]. This misfit-layered structure can be described as  $[\text{Ca}_2\text{CoO}_3]_{b1/b2}[\text{CoO}_2]$  consisting of alternate stacking of a rocksalt-type  $\text{Ca}_2\text{CoO}_3$  layer and a  $\text{CdI}_2$ -type  $\text{CoO}_2$  layer with two different periodicities  $b1$  and  $b2$  along the  $b$  axis, respectively [15]. The perceived mixed ionic and electronic conductivity of this material originating from the electronic conduction in  $\text{CoO}_2$  blocks and ionic conduction in rock-salt blocks has been initially demonstrated by Nagasawa et al. [13]. Electrochemical tests on symmetrical cells at  $700^\circ\text{C}$  in air showed an electrode polarization resistance,  $R_p$ , of  $4 \Omega \text{cm}^2$  for a  $40 \mu\text{m}$  thick layer. This was, however, improved with the addition of 30 wt.% CGO leading to an  $R_p \sim 1 \Omega \text{cm}^2$  [13]. Continuous work by Rolle et al. [14] has focused on cathode processing optimization in order to decrease the cathode polarization resistance. While some interesting

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findings such as the effects of sintering temperatures and including various current collectors have been demonstrated in the said work, the  $R_p$  was still higher than those reported for common SOFC cathode materials such as LSCF in Refs. [4–7] which have  $R_p$  values in the range  $0.19\text{--}1\ \Omega\ \text{cm}^2$  at  $600\ ^\circ\text{C}$  in air depending on the LSCF volume fraction and the microstructure. Thus, there is still a need for new and improved cathode materials for IT-SOFCs.

In this work, misfit-layered cobaltite  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ( $\delta > 0$ ) has been studied as a candidate material for SOFC cathodes. The effects of sintering conditions for the pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  cathode as well as the addition of CGO on the electrochemical performance were investigated in detail. Cathode symmetric cells were fabricated on a dense CGO electrolyte by screen printing followed by firing. The microstructure of the cathodes was analyzed by scanning electron microscopy while the polarization resistances at various temperatures were measured using electrochemical impedance spectroscopy.

## 2. Experimental

$\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  material was synthesized by the solid-state reaction. Precise amounts of  $\text{CaCO}_3$  (99.5%, Johnson Matthey AS<sup>-1</sup>, Denmark) and  $\text{Co}_3\text{O}_4$  (99.7%, Alfa Aesar, Germany) powders were mixed by ball milling with ethanol for 36 h. The resulting mixture was dried and then calcined at  $950\ ^\circ\text{C}$  for 24 h in air. CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  composites were prepared by adding commercially available  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (Rhodia, France). In this study, pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and two composite compositions,  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  mixed with 22 vol.% of CGO (22CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ ) and 50 vol.% of CGO (50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ ) were selected to compare with the reported investigations on the same and the state of the art materials e.g. LSCF. The 22 vol.% CGO corresponds to about 30 wt.% CGO, the composition reported by Nagasawa et al. [13] and Rolle et al. [14]. Also, with the increased amount of CGO up to 50 vol.%, it is possible to have a comparative look on the difference in the electrochemical performance of 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  with that of the commonly used composite cathode in SOFCs—LSCF/CGO where the amount of CGO is 40–50 vol.%. Composition calculations are based on the theoretical densities of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and CGO,  $4.68\ \text{g cm}^{-3}$  [15] and  $7.29\ \text{g cm}^{-3}$  [16], respectively.  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  composite inks consisting of powder–dispersant–binder mixture were prepared and screen printed onto both sides of a  $5\ \text{cm} \times 5\ \text{cm}$ , dense  $290\ \mu\text{m}$  thick CGO electrolyte (KERAFOL, Germany). The screen printed samples were sintered at 700, 850, 900 and  $950\ ^\circ\text{C}$  in air for 2 h in order to determine the optimum sintering conditions. The resulting layer thickness after sintering is about  $60\ \mu\text{m}$  as determined from scanning electron microscope images.

Electrochemical measurements of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  composite cathodes were performed in air at various temperatures on square samples with an approximate size of  $6\ \text{mm} \times 6\ \text{mm}$  by electrochemical impedance spectroscopy on symmetric cells using a Hioki 3522–50 impedance analyzer in the frequency range 70 mHz to 100 kHz under open circuit conditions with 50 mV amplitude AC signal. In all cases, Pt paste (Ferro GmbH, Germany) and Pt mesh were used for current collection. The impedance arising from the series inductance of the rig (80–100 nH), determined by measurements with samples removed was subtracted from the data. The measured data were normalized to the geometrical area of the cell and were divided by two to account for the symmetric structure of the cell. The microstructures of the cathodes were analyzed using a Zeiss Supra 35 scanning electron microscope (SEM). The powders and the deposited layers on dense CGO electrolyte were characterized using a Bruker D8 Bragg–Brentano diffractometer with Cu K $\alpha$  radiation. The absolute oxygen content of the pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$

powder was determined by iodometric titration. The titration method is based on dissolution of the sample (45–50 mg) in acidic solution (1 M HCl) and subsequent reduction of  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{IV}}$  with  $\text{I}^-$  ions. The experimental details were as described in Ref. [17].

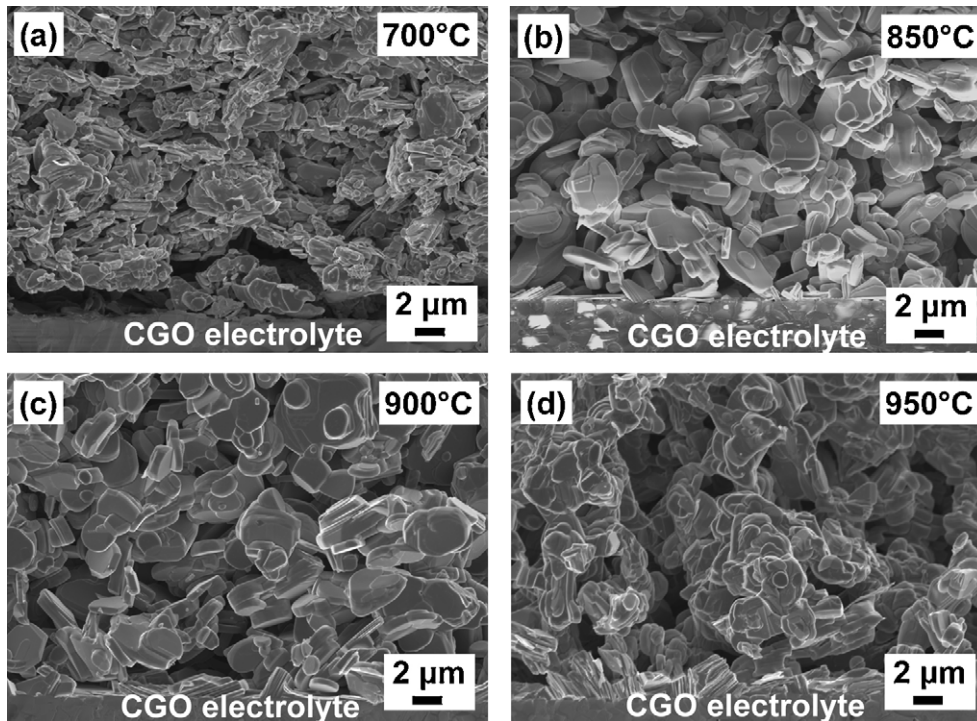
## 3. Results and discussion

### 3.1. Phase and microstructure

X-ray diffraction (XRD) analysis of the as prepared powders and deposited layers of the pure material shows phase purity within the XRD detection limit corresponding to the JCPDS card PDF# 21–0139 for  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ( $\delta > 0$ ) material (Figs. S1 and S2 in the Supporting Information, respectively). For the CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  mixture, no reaction products between CGO and  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  are found from the XRD patterns irrespective of the CGO content (Fig. S3 in the Supporting Information). This is in agreement with previous reports [13,14]. The titration results for our prepared powder revealed that  $\delta$  is determined to be 0.25 (Table S1 in the Supporting Information). The misfit layered cobaltite can be more accurately described by the formula  $[\text{CoO}_2]_{1.62}[\text{Ca}_2\text{CoO}_{3-x}]$ , where the oxygen nonstoichiometry takes place in the rock-salt blocks [15]. Based on the titration measurements this formula can therefore be written as  $\text{Ca}_3\text{Co}_4\text{O}_{9.25}$  which gives  $[\text{CoO}_2]_{1.62}[\text{Ca}_2\text{CoO}_{2.93}]$ . Shimoyama et al. [18] have shown that the smallest composition tolerated by this system is  $\text{Ca}_3\text{Co}_4\text{O}_{9.15}$  corresponding to  $x=0.14$  in the formula  $[\text{CoO}_2]_{1.62}[\text{Ca}_2\text{CoO}_{3-x}]$ .

SEM images of fracture cross sections of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  sintered at various temperatures are shown in Fig. 1. The areas examined were focused near the cathode layer–CGO electrolyte interface. It is clear from Fig. 1 that the morphology of the films changed with increasing sintering temperature from 700, 850, 900 to  $950\ ^\circ\text{C}$ . For the film, which was sintered at  $700\ ^\circ\text{C}$ , the morphology looks as if the grains have just begun to sinter, i.e. some large grains surrounding with many small ones, which are separated and poorly faceted (Fig. 1a). Moreover, it appears as if the adhesion between the dense CGO and the deposited layer is very poor as illustrated by the air-gaps (Fig. 1a). Poor adhesion of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  to the CGO electrolyte when the sample was heated at  $700\ ^\circ\text{C}$  was also clearly evidenced as the cathode layer delaminated when the symmetric cell was fractured. Interestingly, Nagasawa et al. [13] have reported a good adherence between CGO and  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  interface when the cathode layer is heated at a maximum of  $700\ ^\circ\text{C}$ . The consequences of this disparity will be assessed in the following discussion on the electrochemical performance of the tested cells. With increasing sintering temperature e.g. to  $850\ ^\circ\text{C}$ , the grains started growing forming a plate-like morphology (Fig. 1b). The evolution of the microstructure became more pronounced with increasing sintering temperature at  $900\ ^\circ\text{C}$  (Fig. 1c) and  $950\ ^\circ\text{C}$  (Fig. 1d). All investigated films exhibit a similar porous structure, and the films sintered at  $950\ ^\circ\text{C}$  show some lamella-like grains, particularly the grains at the region close to the substrate surface. In addition to the evolution of morphology, for the film sintered at  $950\ ^\circ\text{C}$ , it seems that the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  grains began to be sintered together forming a connective structure (Fig. 1d). This entails better connectivity compared to the samples sintered at lower temperatures. Good connectivity is a necessity for efficient transfer of ions and electrons. It is important to note that only those heated at  $950\ ^\circ\text{C}$  were tested since the adhesion to the dense CGO electrolyte of the other samples sintered at lower temperatures was insufficient to allow them to be mechanically cut. No suitable sample sintered below  $950\ ^\circ\text{C}$  was left for testing due to extensive delamination.

Fig. 2a and b shows SEM micrographs of the fractured surfaces of the 22CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  composites sintered at  $950\ ^\circ\text{C}$ , respectively. In both cases the CGO grains are about



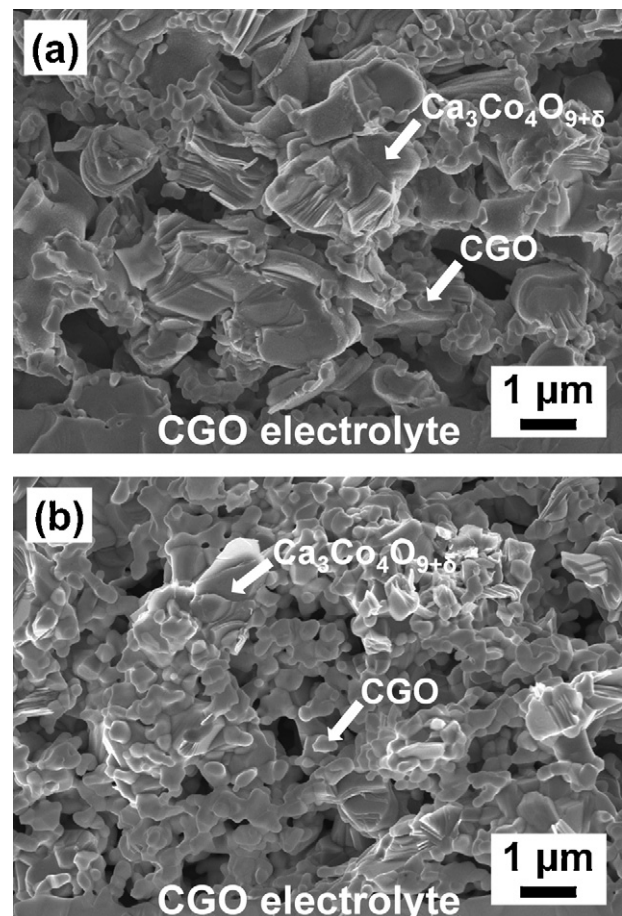
**Fig. 1.** SEM micrographs of the fractured cross sections of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  layer screen printed on the dense CGO electrolyte and sintered at various temperatures. (a) 700 °C, (b) 850 °C, (c) 900 °C, and (d) 950 °C.

200 nm in diameter and are covering the surface of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  network. For the 22CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ , a large number of CGO grains end up as isolated particles in the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  network (Fig. 2a). If the amount of CGO is larger, i.e. in the case of 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  (Fig. 2b), the CGO grains form a more continuous network. This structure is preferred as the oxide ions can be transported in the CGO phase without a significant associated increase in the polarization resistance.

### 3.2. Electrochemical performance

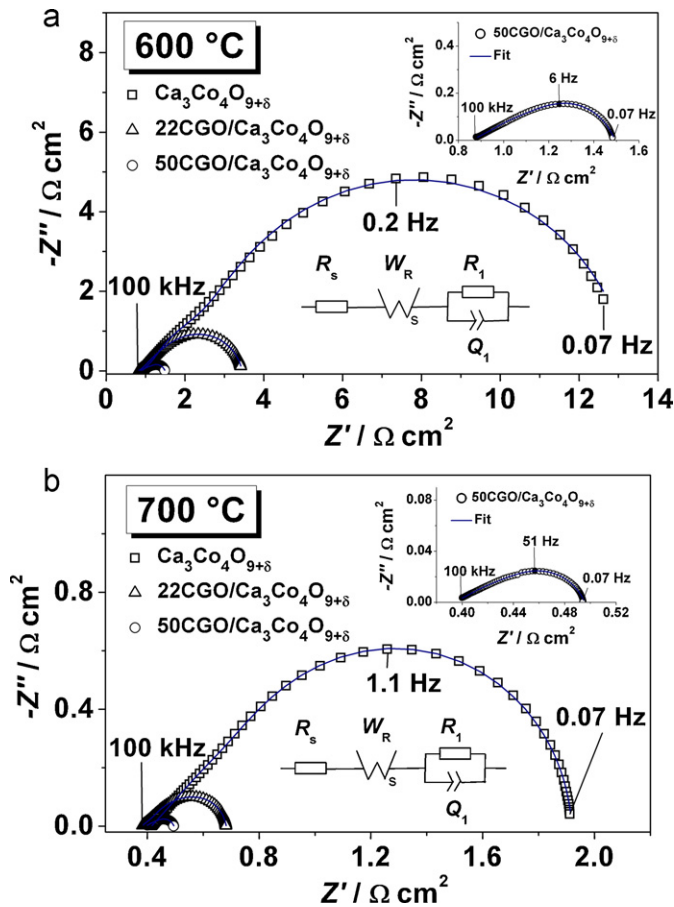
The complex plane plots at 600 and 700 °C in air of the symmetric cells of pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  composites are shown in Fig. 3. We have adopted the equivalent circuit model previously reported by Nagasawa et al. [13] with the inductance subtracted to fit the impedance spectra. The series resistance,  $R_s$ , consists of mainly the electrolyte resistance with additional contributions from the interfacial resistance at the electrode/electrolyte and electrode/current collector interfaces. The cathode polarization resistance, referred to as  $R_p$  in this study, consists of the resistance,  $W_R$ , associated with the high frequency electrode response represented by a Warburg element, and  $R_1$  associated with the low frequency electrode response represented by a constant phase element (Q). No attempt was made in this paper to attribute the equivalent circuit elements to their respective electrode process. Nagasawa et al. [13] have provided explanation on the designation of the circuit elements to the corresponding electrode processes. The data in the present study, however, is insufficient to verify the claims of the said work. We only use the total value,  $R_p$ , to compare with previous works.

The shape of impedance arcs in Fig. 3 of the composite materials seems to remain similar to that of pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ . This suggests that the addition of CGO affected both the high and low frequency processes associated with the electrode. In a SOFC cathode, oxygen reduction is generally perceived to be confined close to the electrode/electrolyte interface, where the gas has simultaneous access



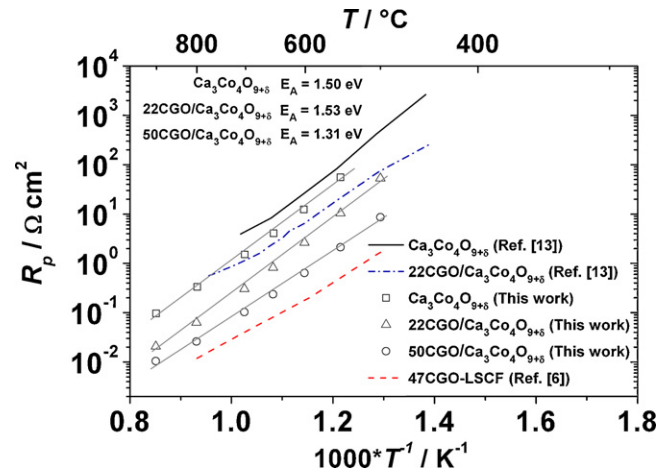
**Fig. 2.** SEM micrographs of the fractured cross sections of (a) 22CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and (b) 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  deposited on the dense CGO and fired at 950 °C.  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and CGO grains are labeled.





**Fig. 3.** Complex plane plots at (a) 600 °C and (b) 700 °C in air of the symmetric cells of pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  composites. The insets show the impedance spectra of the 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ . The equivalent circuit models to fit all the data are also shown. The solid lines are the fit. The lowest frequency data points correspond to 0.07 Hz.

to both the electronically and ionically conductive phases [19]. It is conceivable that the addition of CGO mainly extended this electrochemical reaction zone from the electrode/electrolyte interface. At 600 °C, The addition of 22 vol.% CGO to  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  decreased  $R_p$  from 12.4  $\Omega\text{cm}^2$  for the pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  to 2.63  $\Omega\text{cm}^2$ . Particularly,  $R_p$  was further reduced to 0.64  $\Omega\text{cm}^2$  with the addition of 50 vol.% CGO in the case of the 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ . This reduction in  $R_p$  could be attributed to the formation of a CGO network that conducts oxide ions with a very low resistance. In the case of 22CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ , it can be clearly seen that the amount of CGO was insufficient to promote connectivity among the CGO phase in the entire electrode. A CGO phase that is not percolated but still in contact with the electrocatalyst is not necessarily inactive in transporting oxide ions. This is especially true in composites of CGO and materials with considerable ionic conductivity such as LSCF, where the oxide ion can be transferred in both phases and between them. Evidently,  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  has limited ionic conductivity [13]. Thus, the great disparity in the ionic conductivity of CGO and  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  makes the percolation of the CGO phase more important. It is important to note that even with the low amount of CGO, the decrease in  $R_p$  of the pure material was significant. It is highly likely that although many of the CGO particles are disconnected within the electrode structure, some of the CGO phase near the electrolyte could still be percolated up to a certain length inside the electrode structure. These high ionic conducting percolated areas serve to increase the electrochemical reaction zone and enhance the oxide ion transport towards the electrolyte thus decreasing the  $R_p$ . With



**Fig. 4.** Polarization resistance ( $R_p$ ) as a function of the reciprocal absolute temperature and the corresponding activation energies ( $E_A$ ) for all the symmetric cells tested in air. Data from Ref. [13] of the same material and data from Ref. [6] for the 47 vol.% LSCF–CGO cathode are also shown for comparison.

further addition of CGO, a point will be reached such that the entire CGO phase in contact with the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  is percolated in the entire electrode structure. In this case, the sites for oxygen reduction reaction are more available thereby decreasing  $R_p$ . This is most likely the case in 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ .

The measured polarization resistances in air plotted against inverse absolute temperature are shown in Fig. 4. Data from previous works are also plotted for comparison. The activation energy of the pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  was determined to be about 1.50 eV, which is in good agreement with the previous investigation in this family of materials [13]. The activation energy was only lowered to 1.31 eV with the addition of 50 vol.% CGO. The key results from this study are the remarkable performance compared to that of previous work and the promising  $R_p$  values obtained. The difference in  $R_p$  values at 600 °C of the present study from that of the work of Nagasawa et al. [13] for the pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  is about a factor of two and about a factor of three for the 22CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ . These results also indicate that the microstructure and processing are important parameters when preparing electrodes with this material. The measured  $R_p$  values for the 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  can be compared to the standard SOFC cathodes, particularly LSCF–CGO composite cathodes, although it is understood that it is not entirely correct to compare cathodes of different (or even the same) materials with different microstructures.  $R_p$  only serves as a measure of performance. The  $R_p$  value of 0.64  $\Omega\text{cm}^2$  for 50CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  at 600 °C is an order of magnitude lower than the values reported in Ref. [13]. The value is comparable to the composition 36CGO/LSCF (<1  $\Omega\text{cm}^2$  at 590 °C) reported by Dusastre and Kilner [4] but higher than the 50CGO/LSCF (0.33  $\Omega\text{cm}^2$  at 600 °C) reported by Murray et al. [5]. The lowest reported  $R_p$  values for an LSCF–CGO composite are those by Wang and Mogensen [6] for the composition 47CGO/LSCF (0.19  $\Omega\text{cm}^2$  at 600 °C) which are also shown in Fig. 4 for comparison. Certainly, the CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  composite cathode is open for optimization. This study only demonstrates a significant step in processing route that can be adopted in making the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  material a viable cathode for IT-SOFCs.

For the pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and the 22CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ , the sintering temperature is most likely the main difference between the present study and that of Nagasawa et al. [13] (or Rolle et al. [14]). Although low sintering temperature is usually preferred for grain size reduction/surface area maximization, it should not be low such that the adhesion and connectivity between grains is compromised. Examination of the SEM micrographs in Fig. 1 showed that sintering the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  layer at 950 °C may have

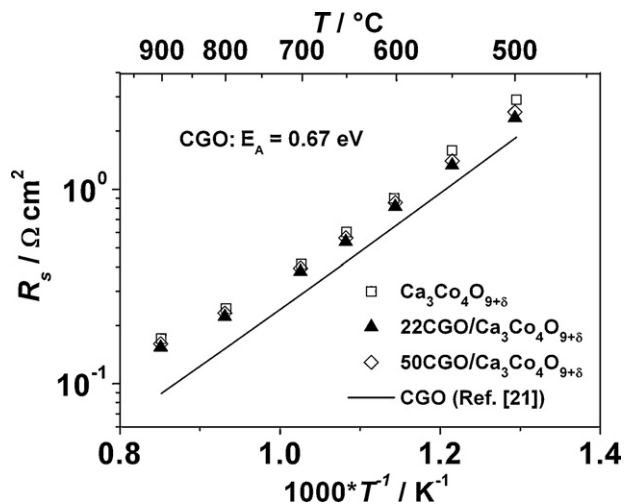


Fig. 5. Series resistance ( $R_s$ ) as a function of the reciprocal absolute temperature for all the symmetric cells tested in air. The straight line represents the calculated series resistance of a 290  $\mu\text{m}$  CGO electrolyte [21].

not only enhanced the adhesion of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  to the CGO electrolyte but also promoted a well sintered structure that entails connectivity of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  grains. We speculate that this sintering temperature might already be the optimum for this cathode system since sintering at higher temperatures, e.g. 1000 °C, promotes the decomposition of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  into  $\text{Ca}_3\text{Co}_2\text{O}_6$  which has significantly lower electronic conductivity than the parent phase [20].

A way to examine the quality of the electrode/electrolyte and electrode/current collector interfaces is through the  $R_s$ . From the reported values of CGO electrolyte conductivity [21], we have calculated  $R_s$  and compared it with the experimental values as shown in Fig. 5. In all the cases, the  $R_s$  values are only slightly higher than the calculated values of resistance from a 290  $\mu\text{m}$  CGO suggesting that sufficient adhesion and connectivity between the CGO grains was attained.

#### 4. Conclusions

Pure  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  and CGO/ $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  composite cathodes with enhanced electrochemical performance are presented as viable candidates for an IT-SOFC cathode. By improving the processing conditions, specifically by optimizing the sintering temperature of the screen printed layers, the present  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  based cathodes show a significant improvement comparing to that of previous works reported on the same material. The sintering temperature at 950 °C resulted in a well adhering cathode layer into

the CGO electrolyte with well connected grain microstructure. Notably, the addition of 50 vol.% CGO to  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  resulted in a remarkable reduction of  $R_p$  to about 0.64  $\Omega\text{cm}^2$  which is the lowest value reported so far for this family of materials. The excellent performance is attributed to the high ionic conducting CGO phase which extended the electrochemical reaction zone from the electrode/electrolyte interface. These findings together with the reported thermal expansion match and chemical stability of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  with CGO should encourage further work on this material.

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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.2011.08.110.

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