

# The Electrochemical and thermal performances of $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$ as a cathode material for IT-SOFCs

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With the aim of application to cathode material in IT-SOFC, 2D misfit layered calcium cobalt oxide  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  was studied using XRD, SEM, thermal dilatometry and impedance spectroscopy. Chemical reactivity of  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  with electrolyte indicated good compatibility with CGO against generating impurity phase  $\text{CaZrO}_3$  with YSZ. Thermal expansion coefficient of pure  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  exhibited  $10.0\text{-}11.0 \times 10^{-6} \text{ K}^{-1}$ , which is similar to that of CGO electrolyte. Indeed, we verified a good adherence between electrode thin layer and the electrolyte. Electrochemical property of  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  pellet showed good performances, i.e. ASR values are 3.0 and 24.5  $\Omega\text{cm}^2$  at 700 and 600 °C in ambient air respectively, in our experimental conditions.

## Introduction

Solid oxide fuel cells (SOFCs) have received considerable attention due to high conversion efficiency in several fuel cell types, without adding of catalytic agent to improve the kinetics. Recently, the intermediate temperature SOFCs (IT-SOFCs) operating at 600-800 °C are of interest for improvement of temperature controllability and longer operation time of materials. In the background, it put forward that gadolinium-doped ceria (CGO) for electrolyte material shows higher ion conductivity at intermediate temperature (under 800 °C) in comparison with that of conventional yttria-stabilized zirconia (YSZ) used in the high temperature region (900-1000 °C) (1-2).

Previous studies on cathode materials for SOFC have already recently focused on Perovskite cobalt-based oxide such as  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSM) (3-5),  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  (LSC) (6-8) and  $\text{Sm}_{1-x}\text{Sr}_x\text{CoO}_3$  (SSC) (9-11), showing promising performances. At the same time, it is known that perovskite cobalt oxide has incompatible aspect with electrolytes such as thermal expansion coefficient, and chemical reactivity with zirconia.

Layered calcium cobalt oxide  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  is most known for thermoelectric material due to the high figure of merit  $ZT$  ( $ZT=S^2\sigma T/\kappa$  where  $S$ ,  $\sigma$ ,  $T$  and  $\kappa$  are seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity respectively) (12-14). The crystal structure is constituted of stacking rock-salt type  $[\text{Ca}_2\text{CoO}_3]$  layers and  $\text{CdI}_2$  type pseudo hexagonal  $\text{CoO}_2$  layers alternately. The constitutional formula can be represented  $[\text{Ca}_2\text{CoO}_3]_p\text{CoO}_2$  ( $p$  value represents  $b_H/b_{RS}$ , where  $b_H$  and  $b_{RS}$  are  $b$  axis of pseudo hexagonal and rock-salt layer respectively with  $p \sim 0.62$ ) (15-16). Furthermore, the misfit between each subseat along the  $b$  axis results in

an incommensurate modulated structure between elements of each seat adequately described using the 4D superspace formalism.

From the oxygen deficient nature of the rock-salt layers and from the excellent electric transport of similar  $[\text{CoO}_2]$  layers in superconducting sodium-cobalt bronzes (17),  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  could be considered as a natural intergrowth between electronic and potential  $\text{O}^{2-}$  conducting units. We surmise that this new candidate for IT-SOFC cathode is well from the point of view of electrochemistry, thermal expansion and chemical stability. Those several points constitute the purpose of this study.

## Experimental

Polycrystalline  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  was synthesized using the conventional solid state reaction. The stoichiometric mixture sample was prepared from reagent grade  $\text{CaCO}_3$  and  $\text{Co}_3\text{O}_4$  powders as precursors and calcined at 880 °C for 12 h in air. The obtained sample was pelletized by uniaxial pressing at 10 MPa and sintered at 880 °C for 24 h in air.

Impedance measurements were performed on symmetrical cells with CGO electrolyte. CGO pellets were formed by uniaxial pressing at 2.5 MPa, and sintered at 1200 °C for 2 h in air.  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  ink was deposited on both side of the pellet by brush and dried at room temperature. The samples were heat treated in three steps: the step was heated up from room temperature to 500 °C during 12 h, next was up to 700 °C during 2 h and last was down to room temperature at 6 h. The cylindrical cell after heat treating was 10.57 mm in diameter and 1.73 mm in thickness.

XRD measurements (Siemens, D8) were carried out the powder or pellet samples at the condition of  $2\theta=6-70^\circ$  and  $0.02^\circ$  step using  $\text{Cu-K}_\alpha$  radiation. The lattice parameters refinements were carried out using JANA2006 program (18).

Thermal dilatometry was performed for examining thermal expansion coefficient (TEC) of cathode materials. The measurements were carried out the temperature range from 150 °C to 820 °C.

Cross-section scanning electron microscopy (SEM, Hitachi Ltd, S-4700) was performed for observation of the electrode/electrolyte interface, at 15 kV.

Impedance spectroscopy measurements were performed using the Solartron SI 1260 analyzer. Here, the cells were slightly pressed between golden plates used as current collectors. Measurement temperature and oxygen partial pressure conditions were carried out from 760 to 540 °C at 50-60 K step and from 1 to  $3.7 \times 10^{-5}$  atm respectively. The applied AC-amplitude was 50mV, under zero DC polarization, in a frequency range from 1.0 mHz to 1.0 MHz.

## Results and discussion

The XRD pattern of powder  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$ , which was refined by Rietveld analysis, is shown in Figure 1. The superspace group was supposed to be  $X2/m(0,p,0)s0$ , and cell parameters resulted in high fitting at  $a \sim 4.8249 \text{ \AA}$ ,  $b \sim 2.8247 \text{ \AA}$ ,  $c \sim 10.831 \text{ \AA}$ ,  $\beta \sim 98.065^\circ$  and  $p \sim 0.6182$  which obtained good agreement of  $R_p \sim 3.57 \%$  and  $R_{wp} \sim 5.22 \%$ . About the two unidentified peaks at  $2\theta=12.9$  and  $18.0^\circ$ , Grebille *et al.* had mentioned that they correspond to new satellite reflections in RS layer (19). On the other hand, Ling *et al.* suggested that they might be small-unidentified impurities (20).

Previous studies have already shown the incompatibility between zirconia-based electrolyte and perovskite cobaltite/manganate,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  (LSC) or  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSM), leading to the formation of low conductive  $\text{La}_2\text{Zr}_2\text{O}_7$  or  $\text{SrZrO}_3$  by reaction with

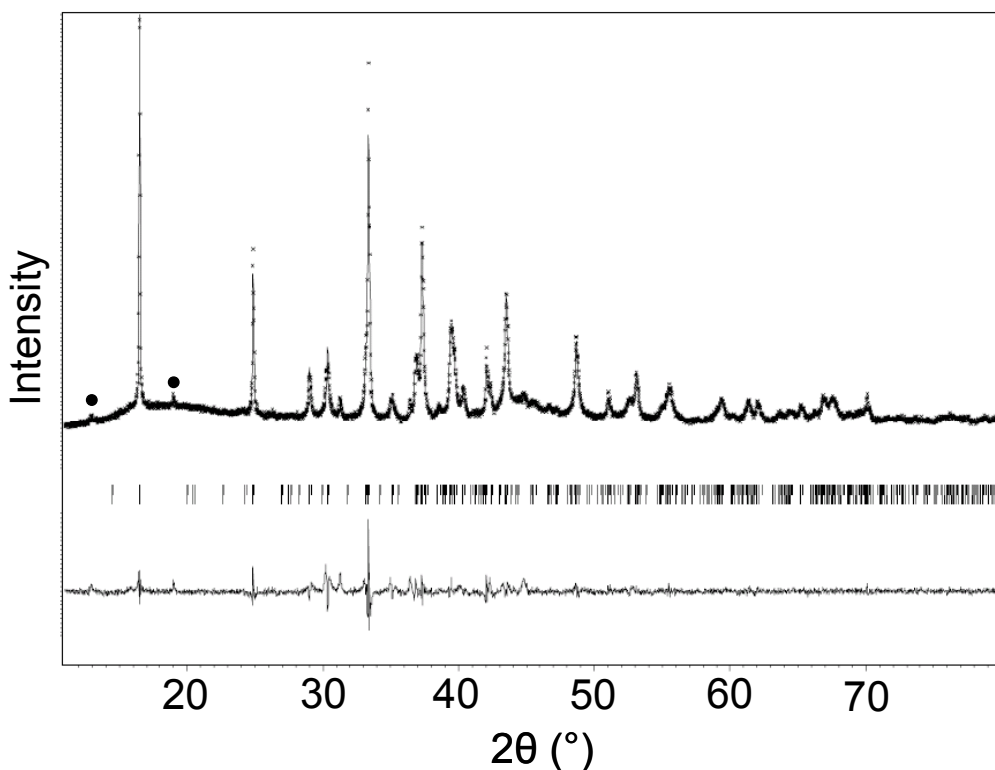


Figure 1. X-ray diffraction patterns of polycrystalline  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  and calculated profile by rietveld refinement. Filled circle marks indicate unrecognized peaks (see text).

YSZ (21). Then, we carried out preliminary chemical reactivity tests between layered  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  and several electrolytes.  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  powders were mixed in 50 mass% with CGO or YSZ, pelletized by uniaxial pressing at 10 MPa and heat-treated for 100 h at 750 °C. Figure 2 shows corresponding XRD patterns. In the case of YSZ electrolyte, XRD pattern clearly showed  $\text{CaZrO}_3$  and  $\text{Co}_3\text{O}_4$  impurity peaks in addition to  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  and other cobaltites. In other words, the reaction with YSZ electrolyte leads to the

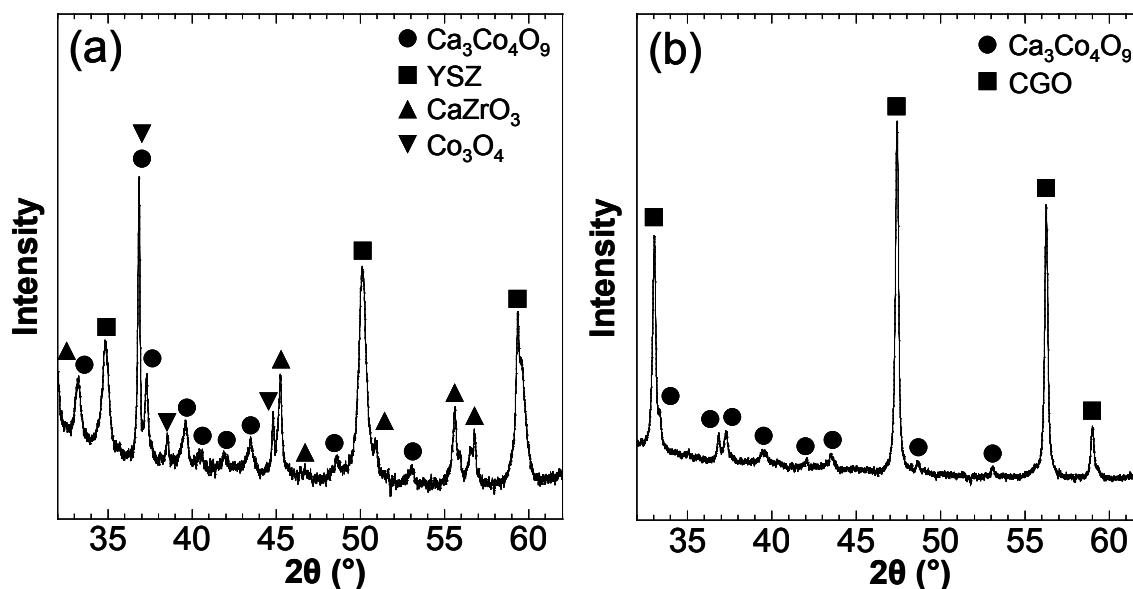


Figure 2. X-ray diffraction pattern in reactivity tests between  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  and YSZ (a) or CGO (b).

decomposition of  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$ . On the other hand, no impurity phase was observed between  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  and CGO electrolyte, confirming a good compatibility between them.

After deposition of the electrodes on CGO using the method described in ref. (22), the cross section was analyzed. Then,  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  layer deposited on CGO pellet were fixed by resin after the heat treating and sliced. Typical SEM image of the cross section is shown on Figure 3. It was observed that the adherence between the electrode and electrolyte is good without any evidence for surficial cracks. The porosity appears of medium quality. The thickness of cathode cross section is estimated to about 30-40  $\mu\text{m}$ .

The comparison of TEC between electrode and electrolyte is constitutive attribute along with electrochemical properties. Figure 4 is shown the linear thermal expansion and TEC for  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$ . It yields TEC values of about  $10.0\text{-}11.0 \times 10^{-6} \text{ K}^{-1}$  in the investigated region. On the other hand, Du et al. (23) and Kharton et al. (24) mentioned TEC values for CGO electrolyte of 11.1, 11.5 and  $12.0 \times 10^{-6} \text{ K}^{-1}$  at 400, 600 and 800  $^\circ\text{C}$  respectively. In fact, this apparently good mechanical compatibility is a contributing factor for IT-SOFC cathode application.

We carried out the impedance spectroscopy measurements for  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  electrode deposited CGO electrolyte. Figure 5 shows Nyquist plots in dependence of several oxygen partial pressures or temperatures. The fitting analysis of impedance spectra was used by Zview 3.1 program. Due to the symmetrical cells geometry, the area specific resistance (ASR) was calculated from the total polarization resistance  $R_p$  and electrode surface area  $S$  using the following:  $\text{ASR} = (R_p * S) / 2$ . In ambient air, the resulting ASR values are 3.0 and 24.5  $\Omega\text{cm}^2$  at 700 and 600  $^\circ\text{C}$  respectively. It is remarkable that these resistances values are obtained without any particular effort provided to optimize the microstructure and porosity of the electrode layers. This result indicates that the layered  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  has the enough capability to candidate of new cathode material in IT-SOFC. In addition, it was checked by XRD after polarization (Temperature: from room temperature to 800 $^\circ\text{C}$ ;  $p_{\text{O}_2}$ : from 1 to  $10^{-5}$  atm.; total experimental time  $\sim$  1month) that the electrode remains unchanged.

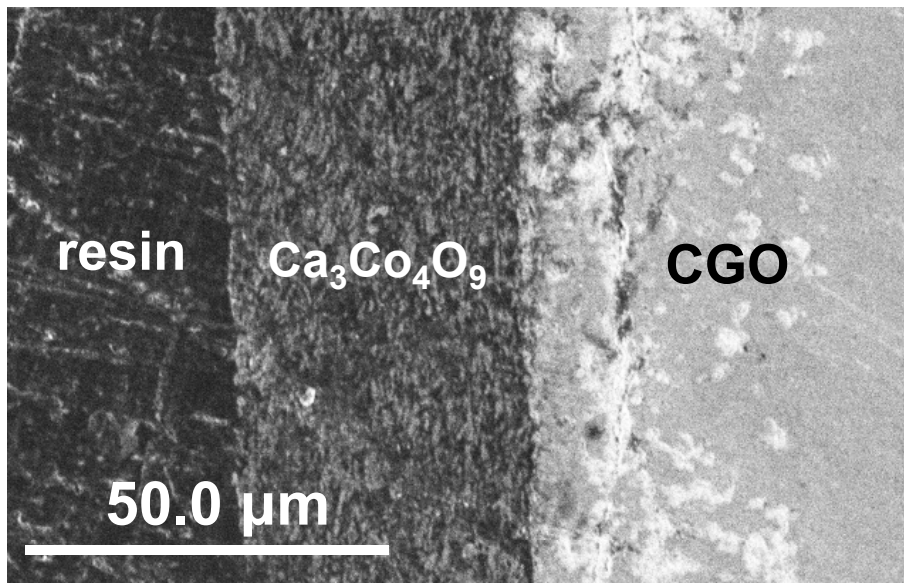


Figure 3. Scanning electron micrograph of cutting cross section of  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  deposited CGO pellet.

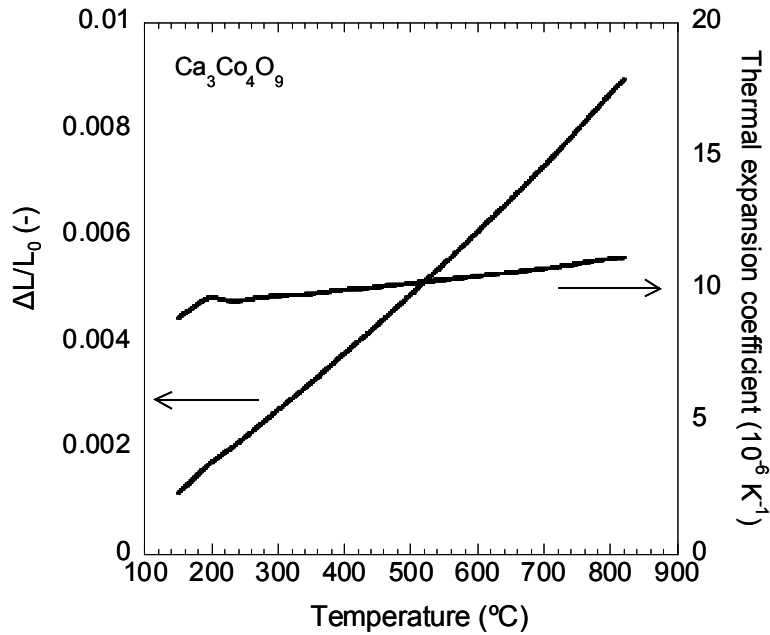


Figure 4. Liner thermal expansion and thermal expansion coefficient of  $\text{Ca}_3\text{Co}_4\text{O}_9$ .

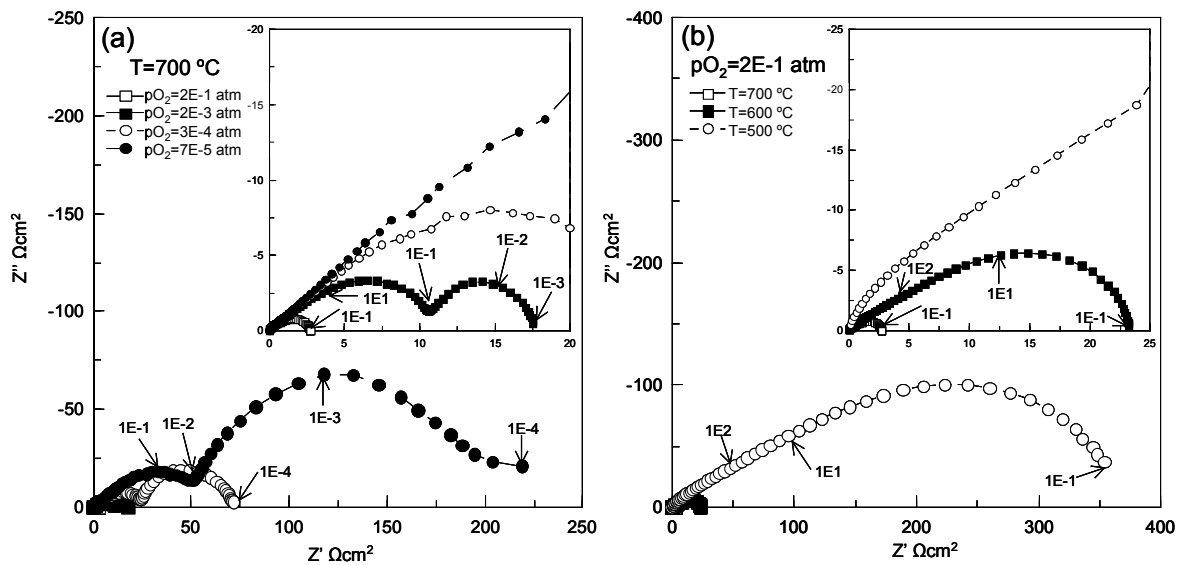


Figure 5. Oxygen partial pressure (a) or temperature (b) dependence of impedance spectra of  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  deposited CGO pellet.

### Conclusions

Electrochemical and thermal properties of layered cobaltite  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  were investigated for applying to cathode material of IT-SOFC. Chemical compatibility with CGO is good, however incompatible with YSZ as well as other perovskite cobaltite. Polarization resistance of  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  cathode showed comparable value to other conventional cathode materials. It was understood that the background of striking

impedance spectra was considerable near TEC values between electrode and electrolyte. From a comprehensive standpoint, we revealed that 2D misfit layered calcium cobalt oxide  $\text{Ca}_3\text{Co}_4\text{O}_{9.8}$  inherited the possibility of cathode material in IT-SOFC.

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