



# Effect of low temperature in-situ sintering on the impedance and the performance of intermediate temperature solid oxide fuel cell cathodes



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## HIGHLIGHTS

- LSC based cathodes are highly suitable for low temperature in-situ sintering.
- LSC based 800 °C in-situ sintered cathode showed an ASR of 0.05  $\Omega \text{ cm}^2$  at 650 °C.
- LSCF showed poor low temperature in-situ sintering capabilities.
- Poor cathode grain connectivity may distort the high frequency EIS response.
- Poor cathode adhesion may be detected by an additional EIS high frequency arc.

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## ABSTRACT

The effect of in-situ sintering temperature and time on the electronic conductivity, impedance and performance of IT-SOFC cathodes were studied. The studied cathodes were for comparison ( $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  (LSC), ( $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3\text{:Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (LSC:CGO),  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF) and  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3\text{:Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (LSCF:CGO). The LSCF-based cathodes showed poor sintering capabilities compared to the LSC-based cathodes in the studied temperature range of 650–950 °C. The poor necking between individual LSCF grains lower the electronic conductivity. Furthermore, poor cathode/electrolyte adhesion was seen as an additional high frequency impedance arc, which gradually disappeared as the LSCF cathodes were sintered at increasing temperature. Effects on the impedance shape from poor cathode grain connectivity was shown through impedance simulations to result in a possible increase in the high frequency slope of the characteristic Gerischer impedance response of porous mixed ionic and electronically conducting (MIEC) cathodes. In contrast to LSCF, the LSC-based cathodes showed excellent sintering capabilities, electronic conductivity and performance. Scanning electron microscopy investigations showed that significant interaction already takes place at 750 °C between the LSC-based cathodes and the electrolyte. The polarization resistance ( $R_p$ ) of the LSC based cathodes was 0.05  $\Omega \text{ cm}^2$ , which to our knowledge is the best performance reported in the literature for a low temperature 800 °C in-situ sintered cathode.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are promising electrochemical energy conversion devices due to high efficiency, fuel flexibility, low pollutant emissions and stack scalability. The last decade of research has to a large extent focused on lowering the SOFC operating temperature. This has some clear advantages, such as increased durability and the possibility of a significant wider choice of materials, which increases the chances of the SOFC technology to

lower cost and become sufficiently competitive. The mixed ionic electronic conductors (MIEC) and composites with a good ionic conducting material, such as gadolinium doped ceria (CGO), is the common type of cathodes considered for 600–800 °C intermediate temperature SOFC (IT-SOFC). These types of cathodes are traditionally sintered above 1000 °C. In-situ cathode sintering offer a potential lowering of the cost since the high temperature cathode sintering step is avoided. Furthermore, the fabrication route of metal supported SOFCs (MS-SOFC) requires an in-situ cathode sintering below 900 °C due to corrosion [1]. Despite the extensive research in MIEC based cathodes very little is actually known about the effect of sintering temperature on the performance and thus

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impedance of MIEC-based cathodes. Some of the requirements for a low temperature in-situ sinterable cathode are:

- Good electrocatalytic activity
- Good electrical properties
- High sinterability
- Mechanical stability towards thermal cycling

The stability towards thermal cycling depends in practise on numerous parameters. As a first approximation it depends on matching of the Thermal Expansion Coefficients (TEC) of the various cell components. However, in practise an exact TEC match and a similar TEC temperature dependency of the various components is not possible. Temperature gradients will also always be present, which induces stresses. Furthermore, the adhesion of the cathode to the electrolyte, the thickness of the cathode, and the temperature history and range of operation also affects the mechanical robustness of the cathode. Nevertheless, all requirements mentioned above must be fulfilled for a successful in-situ sintered cathode.

A few studies have demonstrated that in-situ and low temperature sintering of various potential SOFC cathodes such as  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF),  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3:\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (SSC:SDC),  $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5-\delta}:\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.9}$  (SBSC:CGO) and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) is feasible on button cell level [2–5]. Baek et al. compared the properties of in-situ sintered SBSC:CGO and BSCF cathodes with conventional cathodes such as  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  (LSM82),  $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$  (LSF82), LSCF and SSC:SDC [5]. Despite these studies the knowledge is sparse about the implication of poor connectivity of the cathode grains and poor cathode/electrolyte adhesion on the electrical conductivity, the serial resistance, the electrochemical performance, and hence the impedance response of low temperature in-situ sintered cathodes.

The focus of the present study is to systematically study the effect of low temperature in-situ sintering on the performance and the impedance response of MIEC and MIEC:CGO composite cathodes in the temperature range 650–950 °C. The MIEC materials and MIEC:CGO composites studied are  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ ,  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3:\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ ,  $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3$  and  $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3:\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ . Of convenience, these compositions will in the following be referred to as LSCF, LSCF:CGO, LSC and LSC:CGO. These material combinations are expected to have different properties such as sinterability, electronic and ionic conductivity, which consequently should be reflected in the performance. Thus, a comparison of these cathodes is expected to shed further light on the importance of these properties.

## 2. Theory

The porous structure of the MIEC based cathodes can be modelled as columns as illustrated in Fig. 1 [6,7]. Each column can be described by the general transmission line depicted in Fig. 1 with the following general solution [8–11]:

$$Z = \frac{\chi_1\chi_2}{\chi_1 + \chi_2} \left( L + \frac{2\lambda}{\sinh(L/\lambda)} \right) + \lambda \frac{\chi_1^2 + \chi_2^2}{\chi_1 + \chi_2} \coth\left(\frac{L}{\lambda}\right) \quad (1)$$

with

$$\lambda = \sqrt{\frac{\zeta}{\chi_1 + \chi_2}} \quad (2)$$

Here  $L$  is the thickness of the electrode and  $\lambda$  is the characteristic AC penetration length or equivalent the electrochemical utilization thickness of the electrode. Eq. (1) represents the impedance (in  $\Omega$ ) of a single column shown in Fig. 1, but in principle the porous

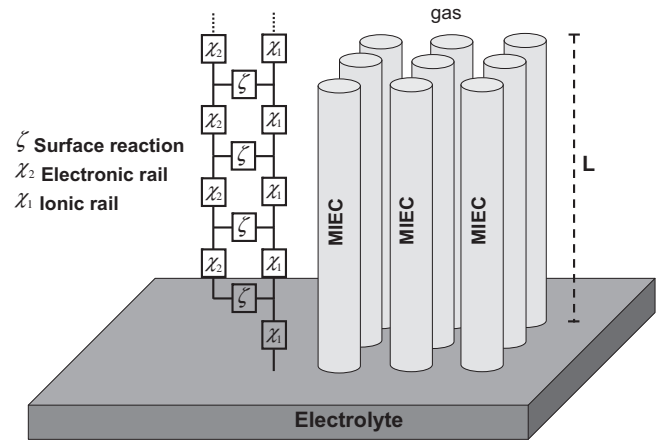


Fig. 1. The porous MIEC electrode is modelled as columns, which can be described by the general transmission line.

electrode consists of  $n$  columns pr. area. However, it is difficult to determine the exact number of columns pr. area in the porous electrode. A much easier and equivalently informative approach is to consider the porous electrode effectively as one column pr. area. This enables a direct application of Eq. (1). For the case where the cathode grains are sintered well together, the well known Gerischer response can be obtained by making the reasonable assumption that the electronic conductivity is significantly higher than the ionic conductivity  $\chi_2 \ll \chi_1$ , which results in Eq. (1) being simplified to:

$$Z = \lambda\chi_1 \coth\left(\frac{L}{\lambda}\right), \text{ with } \lambda = \sqrt{\frac{\zeta}{\chi_1}} \quad (3)$$

The transport of oxide ions via diffusion in the MIEC column can be modelled as a resistor pr. unit length (in  $\Omega \text{ cm}^{-1}$ ):

$$\chi_1 = r_{\text{gi}} \quad (4)$$

Finally the impedance of the surface reaction  $\zeta$  (in  $\Omega \text{ cm}$ ) can be modelled as a simple parallel combination between a resistor  $r_r$  and a constant phase element  $q_r$  (CPE):

$$\zeta = \frac{r_r}{1 + r_r q_r (j\omega)^{\alpha_r}} \quad (5)$$

The unit of the impedance  $\zeta$  is  $\Omega \text{ cm}$  because it is the area specific impedance of the column surface (in  $\Omega \text{ cm}^2$ ) divided by the perimeter of the column. For thick cathodes  $L \gg \lambda$  and  $\coth(L/\lambda) \rightarrow 1$ , which implies, that the Gerischer impedance response has the shape of a skewed semicircle. The expression originating from Eq. (3) with the assumptions in Eq. (4) and Eq. (5) is in accordance with the following Finite-Length-Gerischer (FLG) expression derived in Ref. [6]:

$$Z = \frac{RT}{4F^2 C_V^0} \sqrt{\frac{A}{D_V^{\text{eff}} k_0}} \frac{\coth\left(\frac{(L/\lambda_0)\sqrt{1+j\omega/k_0}}{\sqrt{1+j\omega/k_0}}\right)}{\sqrt{1+j\omega/k_0}}, \text{ with } \lambda_0 = \sqrt{\frac{AD_V^{\text{eff}}}{k_0}} \quad (6)$$

$R$  is the gas constant,  $T$  is the temperature,  $F$  is faradays constant,  $C_V^0$  is the concentration of oxygen vacancies,  $A$  is the thermodynamic enhancement factor,  $D_V^{\text{eff}}$  is the effective oxygen vacancy diffusion coefficient,  $k_0$  is the surface reaction rate constant and  $L$  is the thickness of cathode. For further explanation the reader is referred

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