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Combined experimental and modeling study of interaction between LSCF and CGO in SOFC cathodes

Rémi Costa (1), Roberto Spotorno (1), Claudia Repetto (1), Zeynep Ilhan (1,2) and Vitaliy Yurkiv (1,2)
(1) German Aerospace Centre (DLR), Institute of Technical Thermodynamics,
Pfaffenwaldring 38-40, 70569 Stuttgart, Germany
(2) Institute of Thermodynamics and Thermal Engineering (ITW), Universität Stuttgart,
Pfaffenwaldring 6, 70550 Stuttgart, Germany

Tel.: +49-711 6862-733
Fax: +49-711-6862-747
Contact: remi.costa@dlr.de

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Abstract

The development of a high-performance oxygen electrode for SOFCs in order to achieve high power density at a stack level is still challenging. It is important to emphasize the factors controlling the efficiency of the cathode. Over the intrinsic electro-catalytic activity of the cathode material itself toward the oxygen reduction, the microstructural parameters such as the porosity, the tortuosity or the particle size are of major importance in the definition of the electrochemical active surface area.

In this paper we focus on the behavior of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ (LSCF)-$Ce_{1-x}Gd_xO_{2-\alpha}$ (CGO) composite cathodes with different development and characterization of composite cathodes produced by suspension spraying and sintering, with or without further surface modification by infiltration either LSCF or CGO nano-particles.

Different symmetrical cells were produced by varying the LSCF/CGO ratio with an active surface area of about 12.57 cm^2. Cells were contacted with a fine platinum mesh without any contacting paste and electrochemical impedance spectra (EIS) were recorded in static ambient air in the frequency range 10 mHz – 100 kHz between 500 °C and 800 °C. The serial resistance (Rs) and the total polarization resistance (Rp) were both quantified.

The developed kinetic model of oxygen reduction at LSCF/CGO cathode, which incorporates elementary heterogeneous chemistry and electrochemical charge-transfer processes at two different electrochemical double layers, transport in the porous composite electrode, as well as gas supply, is used to explain the non-intuitive interaction between LSCF and CGO phases. This allows a mechanistic interpretation of the origin of different chemical, electrochemical and transport phenomena occurring in composite cathodes.

Introduction

The objective of this paper is to explore the performance of SOFC cathodes by investigating interaction between $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) with CGO ($Ce_{0.9}Gd_{0.1}O_{2-\alpha}$) when combining them in a composite cathode layer. However, although being widely investigated [1,2], the microscopic details of the LSCF and CGO interaction in the SOFC cathode, occurring at the different boundaries (surface/gas and bulk/bulk phases), are not yet fully resolved. Yet, the knowledge of elementary kinetics of SOFC cathode (electro-) chemistry is important because the understanding at the fundamental level yields better predictive capability of LSCF/CGO phases interaction, which allows optimal design and operation of new fuel cell systems.

In the present work, our previously developed elementary kinetic model of oxygen reduction [3] is applied to analyze recent in-house experimental data, which were conducted using well-defined and thoroughly characterized variety of LSCF/CGO composites.

1. Scientific Approach

Different symmetrical cells were produced by wet ceramic processing/sintering by varying the LSCF:CGO volume ratio (100:0 – 70:30 – 50:50 – 30:70) with an active surface area of about 12.57 cm^2. Cells were contacted with a fine platinum mesh without contacting paste and electrochemical impedance spectra (EIS) were recorded in static ambient air in the frequency range 10 mHz – 100 kHz between 775 K and 1075 K. The serial resistance (R_s) and the total polarization resistance (R_p) were both quantified. Microstructure characteristics of the samples were investigated by means of SEM and Image analysis and porosimetry measurement through mercury intrusion.

In order to understand the impact of CGO, small modification of the surface is done by infiltration 5wt% CGO related to the mass of the deposited cathode. The infiltration of CGO is performed by dispersing the CGO nano-particles at the surface of the backbone. This process is summarized in Figure 1.

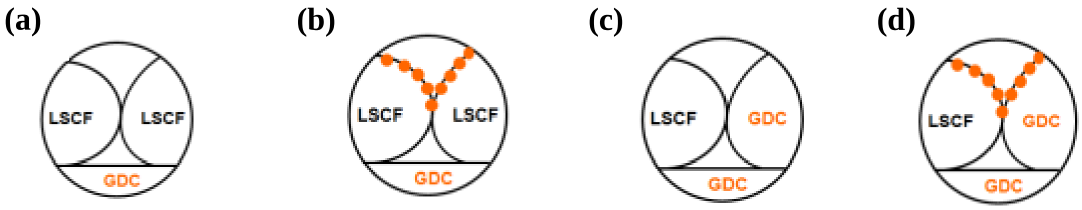

Figure 1: Different cathode design used in this work: LSCF (a), LSCF impregnated with 5wt% CGO (b), LSCF:CGO 50:50 (c), and LSCF:CGO 50:50 impregnated with 5wt% CGO (d).

Based upon these experiments, elementary kinetic model is developed and validated on the basis of experimental results in order to physically understand the behavior of the different cathode materials. The modeling framework has been used in our previous study on oxygen reduction at LSCF/CGO cathodes [3]. We use transport model, reaction kinetics and thermodynamics datasets from later reference as parameter base for the present work.

2. Results

2.1 Experimental results

The geometrical features (average pore diameter and total pore surface area) of the different LSCF/CGO cathodes as experimentally determines in the present work are shown in Table 1.

Table 1: Morphological characteristics of porous cathode with and without surface modification by infiltration of CGO

Cathode	***Average pore diameter [nm]***	***Total pore surface area [m²/g]***
LSCF	≈ 221	≈ 3.79
LSCF impregnated with 5wt% CGO	≈ 197	≈ 4.40
LSCF:CGO 50:50	≈ 212	≈ 2.95
LSCF:CGO 50:50 impregnated with 5wt% CGO	≈ 183	≈ 4.08

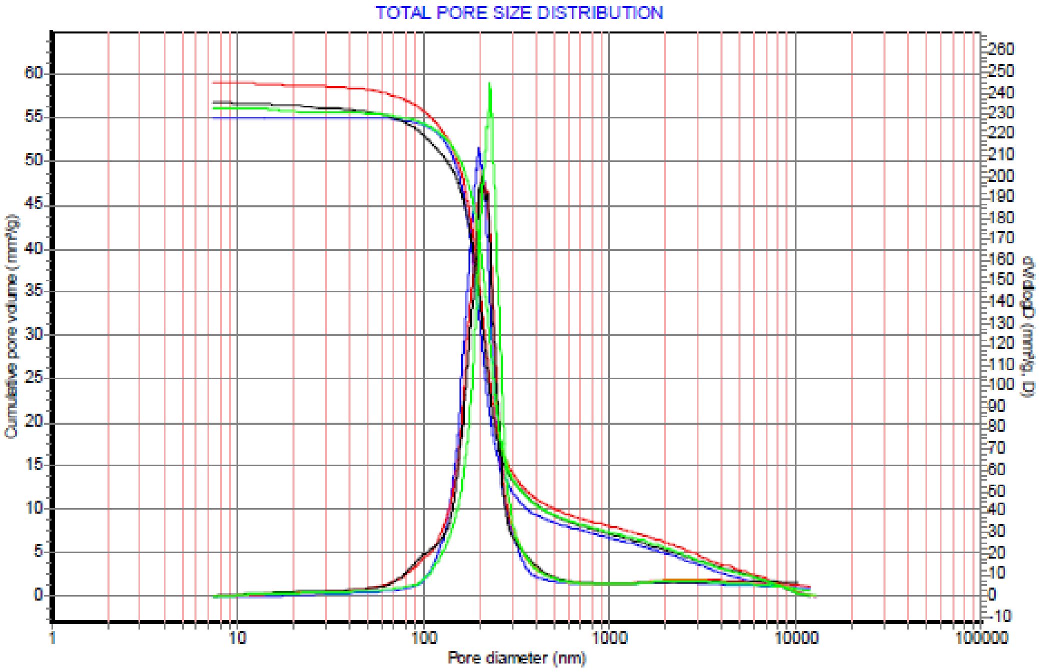

Figure 2: Pore distribution for **LSCF**, **LSCF impregnated with GDC**, **LSCF 50%vol/GDC 50%vol**, **LSCF 50%vol/GDC 50%vol impregnated with GDC.**

An Arrhenius plot of area-specific resistance versus inverse temperature is shown in Fig. 3. As it is briefly mentioned above in the present experiments, the temperature was varied in the range between 775 K and 1075 K for different cathode composites. All experiments show one linear temperature regime over whole temperature region. At any given temperature, different data sets scatter by almost one order of magnitude, which indicates that electrode performance is a strong function of individual preparation parameters.

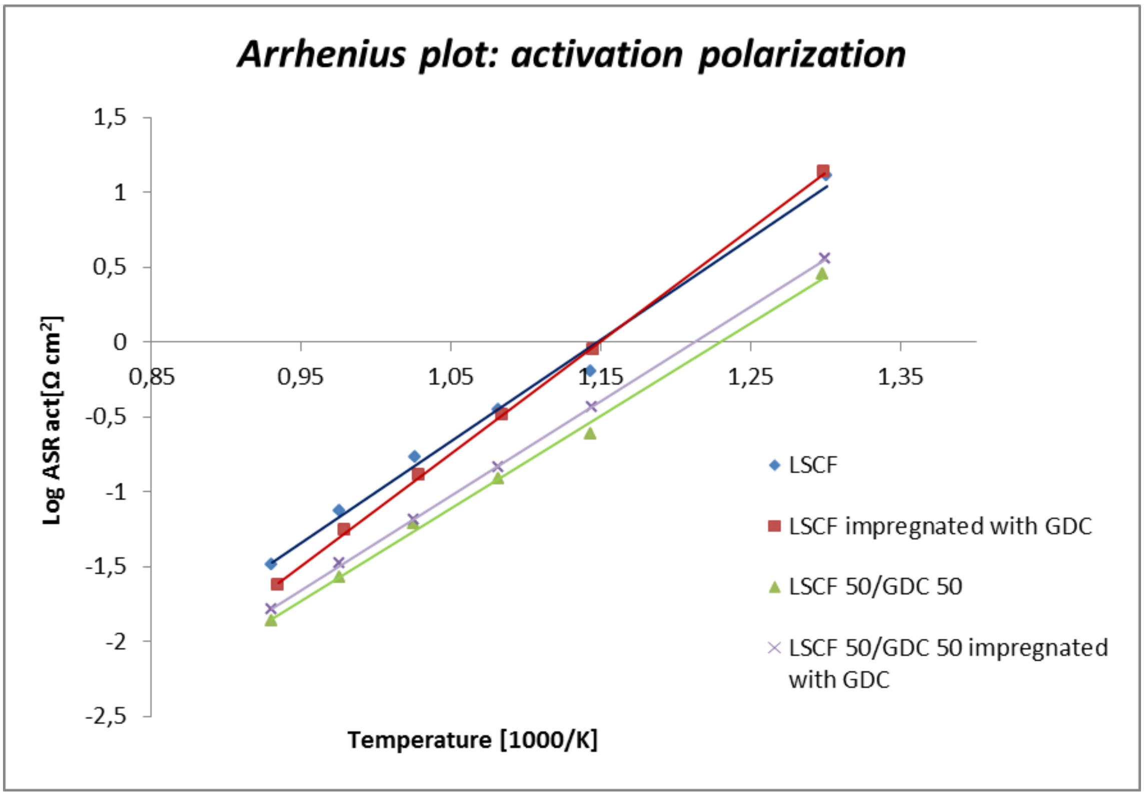

Figure 3: Arrhenius plot for ASR of LSCF and LSCF: CGO 50:50 composite cathodes with and without addition of 5wt% CGO.

2.2 Modeling and simulation results

Based upon numerical impedance simulations, experimental EIS data were successfully reproduced over a wide range of operating temperatures (775 K–1075 K). Using model reduction studies, the three experimentally observed features of the impedance spectra could be attributed to (*i*) gas conversion in cathode gas supply volume (low frequencies), (*ii*) electrochemical oxygen reduction on the LSCF surface (intermediate frequencies) and (*iii*) charge-transfer of double negatively charged oxygen through two-phase boundary between LSCF and CGO (high frequencies) [3].

In order to further interpret the behavior of ASR as function of electrode and operational parameters, a sensitivity analysis was performed for two different temperatures (775 K and 1075 K). The results of performed sensitivity analysis are shown in Fig. 4. A sensitivity of unity means that ASR is directly proportional to the parameter. Negative sensitivities mean that a parameter increase leads to a decrease of ASR. Sensitivities close to zero mean that the ASR does not depend on the parameter, and hence, the process represented by the parameter is not rate-determining. The performed sensitivity analyses show that only charge-transfer reactions (C1 and C2) are rate-limiting. All other reactions are fast and not rate co-limiting. This also means that the accuracy of the rate coefficients has a minor influence on the simulation of the overall oxygen reduction process. Correspondingly, the thermodynamic data of species involved in CT reactions, particularly O^{1-}_{LSCF}, has also have a high influence on ASR.

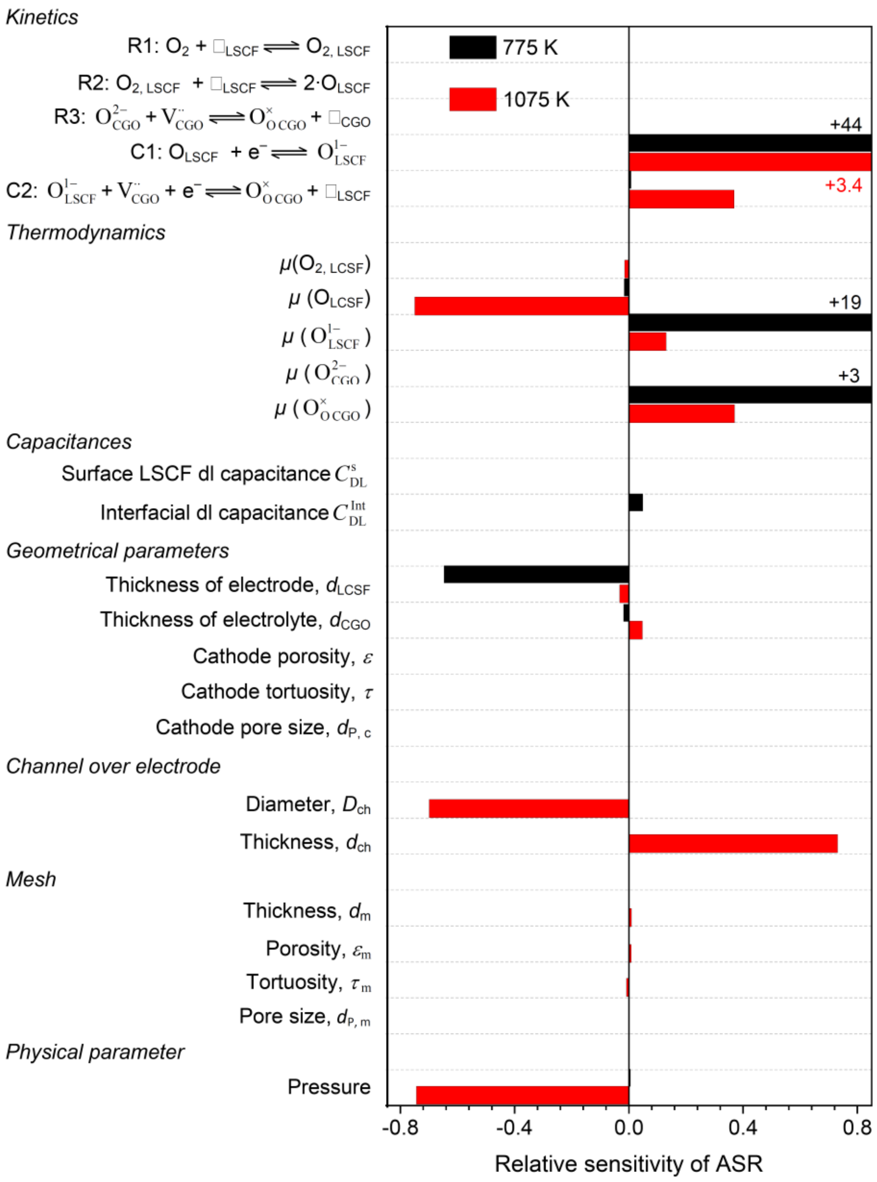

Figure 4: Sensitivity analysis of the area-specific resistance (ASR) of the LSCF/CGO composite cathode 70:30 at two different temperatures

References

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