



## Research Paper

# Distributed relaxation times technique for the determination of fuel cell losses with an equivalent circuit model to identify physicochemical processes

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## ABSTRACT

This paper shows the developments of an equivalent circuit model adopted to interpret the deconvoluted electrochemical impedance spectra of an Ni-YSZ/YSZ/GDC/LSCF solid oxide fuel cell obtained by varying the operating temperature and the oxygen partial pressure under a fixed load. This allowed to unfold the physicochemical processes occurring within the anode supported cell and to identify which elements are responsible for major polarization losses. Furthermore, this model has proved to be effective even in the high frequency region, which is often beset by the onset of troublesome artifacts, as underlined by the comparison with the galvanic current interruption technique.

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## 1. Introduction

In the modern energy production framework, the use of renewable fuels appears crucial in the highly efficient generator systems. Solid oxide fuel cells coupled with biomass source offer an highly efficient combined heat and power generation [1–4]. SOFCs have proved to be promising energy conversion systems although the high operating temperature, considerable concerns about the mechanical and chemical stability of the materials which constitute the entire cell assembly [5]. One of the main drawbacks for SOFC systems is related to trace compounds impact [4,6–11]. Moreover, SOFC systems still require high operating temperature to guarantee an adequate ionic conductivity of the electrolyte. Other drawbacks concern the thermal expansion mismatch and slow start-up and shut-off procedure [12]. Therefore, given the recent trend to operate at intermediate temperature conditions, the contribution to the overall cell performance drop due to ohmic losses as well as electrodes ones must be carefully assessed.

In fact, the electrodes overpotentials are a limiting factor for the cell power density especially at intermediate temperature

(600–800 °C) [13]. At this operating level the electrocatalytic activity reduction is remarkable [14] and the ohmic resistance increases. A viable way for diminishing the resulting losses is to spread out the active sites required for the electrochemical reactions. A major portion of polarization losses arise from the ORR [15], located at the cathode electrode where the mixed electronic-ionic conductor is extended from the 3PB up to the two phase interface (2PB). However, the employment of the  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (LSCF) oblige to place a thin layer of doped ceria material between the YSZ electrolyte and the perovskite-type electrode to prevent unfavorable reactions and consequent deterioration of cell performance [16] resulting in an increase of overall resistance.

The current-voltage characteristic curve is ineffective to decouple the total cell losses and to assess the relative contribution due to activation, concentration and ohmic phenomena since it provides only accurate information of the overall performance.

The EIS, on the other side, is a well proven *in-situ* diagnostic technique able to provide information of the cell behavior [4]. This technique is able to establish a correlation between the operating conditions and the relative losses contribution due to the elements which constitute the PEN [17,18]. The latter is achievable through the analysis, at each frequency, of the relative amplitude and the

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**Nomenclature**

2PB	two phase interface	P <sub>3A</sub>	anodic concentration polarization
3PB	three phase boundary	P <sub>1C</sub>	cathodic activation process
ASC	Anode Supported Cell	P <sub>2C</sub>	cathodic concentration phenomena
ASR	Area Specific Resistance	PEN	Positive Electrolyte Negative
C/V	Current density versus voltage curve	pO <sub>2</sub>	oxygen partial pressure
CEM	Controller Evaporator Mixer	R <sub>1A</sub>	anode resistance related to P <sub>1A</sub>
CNLS	Complex Non-Linear Least Square	R <sub>2A</sub>	anode resistance related to P <sub>2A</sub>
DRT	Distributed Relaxation Times	R <sub>3A</sub>	anode resistance related to P <sub>3A</sub>
D <sup>δ</sup>	chemical bulk diffusion coefficient	R <sub>an</sub>	total anodic polarization resistance
ECM	Equivalent Circuit Model	R <sub>cc</sub>	ohmic resistance of current collectors
EDS	Energy-dispersive X-ray Spectroscopy	R <sub>chem</sub>	chemical resistance related to P <sub>1C</sub>
EIS	Electrochemical Impedance Spectroscopy	R <sub>conc</sub>	concentration resistance related to P <sub>2C</sub>
GCI	Galvanic Current Interruption technique	rds	rate determining step
GDC	Gadolinia-Doped Ceria layer	R <sub>el</sub>	ohmic resistance of electrode
k <sup>δ</sup>	chemical oxygen surface exchange	R <sub>GDC</sub>	ohmic resistance of GDC interlayer
LSCF	La <sub>1-x</sub> Sr <sub>x</sub> Co <sub>1-y</sub> Fe <sub>y</sub> O <sub>3-δ</sub>	R <sub>int</sub>	ohmic resistance of interdiffusion layer
MFC	Mass Flow Controller	R <sub>ohm</sub>	ohmic resistance of the cell
MIEC	Mixed Ionic Electronic Conductors	RQ	resistance condenser element
OCV	Open Circuit Voltage	R <sub>YSZ</sub>	ohmic resistance of YSZ electrolyte
ORR	Oxygen Reduction Reaction	SEM	Scanning Electron Microscopy
P <sub>1A</sub>	TPB charge transfer process (anode)	SOFC	Solid Oxide Fuel Cell
P <sub>2A</sub>	transport of oxygen ions through the electrolyte phase (anode)	t <sub>chem</sub>	characteristic time constant
		Z <sub>i</sub>	imaginary part of the complex impedance
		ω	angular frequency
		τ	relaxation time

phase shift between the applied sinusoidal current (or voltage) stimulus and the corresponding voltage (or current) response [18]. However, the decoupling process can exploit an equivalent circuit model, previously determined by means of DRT technique. This is done to assign a specific part of the impedance spectra to the corresponding physicochemical process [17]. This procedure allows to overcome the well-known issue related to the non-uniqueness of the equivalent model adopted to fit the experimental data through a CNLS approach [19]. In literature are available several circuit models [20–23], each with its specific features and then not always suitable for a generalized analysis, which aim to describe the mass transport phenomena, reaction kinetics and ohmic losses. Alternative methods for obtaining a distribution function of relaxation times involve the adoption of Fourier transform with an adjustable windowing function as in [24], the use of a Bayesian approach [25] or the reconstruction through an adaptive genetic evolution method, which is not consequential to the determination of a regularization parameter, as explained in [26]. This wide variety of methods, each with its flaws, confirms amply the need for further investigations. Moreover, as pointed out by Klotz in [27], the accurate evaluation of total ohmic resistance via impedance analysis is always a challenging task due to the need to adopt high frequencies even up to 1 MHz. This is difficult to achieve without observing the onset of troublesome artifacts that should not be underestimated due to miscalculation or at worst a misinterpretation of real phenomena taking place inside the cell. To overcome the latter limitation in this work, the GCI has been adopted. This technique is considered to be complementary to the EIS for the investigation of SOFCs behavior [28].

In this work the adopted equivalent circuit is validated through experimental results under a wide range of temperature and oxygen partial pressures, as proposed in [29], and maybe used to analyze in detail all the losses imputable to the electrodes and the electrolyte with the ultimate aim to improve the cell performance.

However, differently from previous works approaching the

same topic [20,21], this paper focus on electrochemical impedance spectroscopy performed under load rather than at OCV.  $t_{\text{us}}$  attempting to provide valuable insight into specific mechanisms of solid oxide fuel cell in real applications, especially concerning the ORRs at the MIEC. At the same time this paper wants to establish a comparison basis for future works based on SOFCs fed by syngas, for which the operating voltage plays an important role on kinetic reactions.

## 2. Experimental and methods

### 2.1. ASC specimen tested

The SOFC analyzed in this work is an anode supported cell, made by Solidpower spa (Italy) with a circular shape with a surface area of 47 cm<sup>2</sup> composed of a cermet anode (Ni – YSZ8% mol) with a thickness of 240 μm, an MIEC cathode (La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>) of 42 μm, a solid electrolyte (8%mol YSZ) of 8 μm and a buffer layer (Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-x</sub>) of about 4/5 μm (depending on the analyzed cell). These geometrical values were obtained from SEM images (FEI Inspect, Philips 525 M) of the cross section of the ASC, while the chemical composition was verified by means of EDS (SW9100 EDAX), see Appendix A in Supplementary material.

### 2.2. Test setup

All the tests were carried out on the single planar cell and performed at the IN.TE.S.E laboratory (Innovation Technologies for Energy Sustainability) of the Energy Department of Politecnico di Torino, as described also elsewhere [2,6,9,30–32]. The test station consists of a furnace where the single cell is placed, flanges for the fuel and oxidant distribution flows are adopted, both realized with inert ceramic material (Al<sub>2</sub>O<sub>3</sub>). The latter ensure air and fuel heating. The inert ceramic housing has a sealless configuration. This unavoidably implies a contact between the cathodic and anodic

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