



A distributed real-time model of degradation in a solid oxide fuel cell, part I: Model characterization



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HIGHLIGHTS

- A real-time distributed model of degradation in a SOFC was implemented.
- Degradation was related to local current density, temperature, and fuel utilization.
- Degradation was represented as an increment in ohmic resistance.
- Distributed profiles of key cell parameters during degradation were analyzed.

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ABSTRACT

Despite the high efficiency and flexibility of fuel cells, which make them an attractive technology for the future energy generation, their economic competitiveness is still penalized by their short lifetime, due to multiple degradation phenomena. As a matter of fact, electrochemical performance of solid oxide fuel cells (SOFCs) is reduced because of different degradation mechanisms, which depend on operating conditions, fuel and air contaminants, impurities in materials, and others. In this work, a real-time, one dimensional (1D) model of a SOFC is used to simulate the effects of voltage degradation in the cell. Different mechanisms are summarized in a simple empirical expression that relates degradation rate to cell operating parameters (current density, fuel utilization and temperature), on a localized basis. Profile distributions of different variables during cell degradation are analyzed. In particular, the effect of degradation on current density, temperature, and total resistance of the cell are investigated. An analysis of localized degradation effects shows how different parts of the cell degrade at a different time rate, and how the various profiles are redistributed along the cell as consequence of different degradation rates.

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1. Introduction

Several mechanisms of degradation affect high temperature fuel cells, from electrode delamination and electrolyte cracking to electrode poisoning and microstructure coarsening [1–4]. Some mechanisms cause a decrement in power output at constant current and others can result in catastrophic failure of the cell. The nature of these mechanisms is different, and many models have been developed to analyze different types of degradation, causes and possible corrective actions [5–10]. In the work from Verda et al., a CFD model of a SOFC is developed in order to simulate the degradation of anode, cathode, and electrolyte due to instabilities

or electrolyte delamination [5]. Virkar models different degradation phenomena to investigate the effect of a single cell failure in a stack [6]. The effect of trace species in the anode is studied by Ryan et al., where different degradation mechanisms are classified based on their physical effect on the cell [7]. Gazzarri and Kesler develop a finite elements model of a SOFC to analyze the impact of different degradation mechanisms on the impedance, proposing a method for degradation modes identification [8]. A correlation between open circuit voltage and sulfur concentration in the fuel is proposed by Nagel et al., who investigate the impact of reforming activity on cell performance [9]. A model of different degradation processes is used by Nakajo et al. to study the effect of operating conditions on SOFC lifetime [10]. In this work, a simplified model is developed for real-time applications that takes into account localized degradation in the fuel cell. This work is critical for cyber-physical hardware simulations of hybrid system performance and impact on fuel cell

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Nomenclature			
FU	fuel utilization	r_d	degradation rate [%·kh ⁻¹]
LSM	lanthanum – strontium – manganite	r_{sr}	reformed methane rate [mol·s ⁻¹]
PEN	positive side – electrolyte – negative side	R_g	ideal gas constant [J·mol ⁻¹ ·K ⁻¹]
SOFC	solid oxide fuel cell	T	temperature [K]
TPB	triple phase boundary	t	time [h]
WGS	water gas shift	th	thickness [m]
YSZ	yttria-stabilized zirconia	V	voltage [V]
$A_{channel}$	cross-sectional area of the channel for conduction heat transfer [m ²]	x	mole fraction
A_{gas}	area of convective heat transfer between gas and solid [m ²]	Symbols	
A_{react}	area of reaction [m ²]	α	charge transfer coefficient
c_p	specific heat [J·kg ⁻¹ ·K ⁻¹]	η	electrochemical loss [V]
F	Faraday's constant [C·mol ⁻¹]	ρ	resistivity [Ω·m]
G	Gibbs free energy [kJ]	ρ_s	solid density [kg·m ⁻³]
K_p	equilibrium constant	Subscripts	
i	current density [A·cm ⁻²]	act	activation
i_0	exchange current density [A·cm ⁻²]	an	anode
n	number of electrons transfer per reaction	ca	cathode
p	partial pressure [Pa]	dif	diffusion
R	area specific resistance [Ω·m ²]	el	electrolyte
		irr	irreversible
		ohm	ohmic

operability.

Although the variety of degradation phenomena, all the diverse mechanisms and degradation modes are affected by operating parameters such as current density, temperature and fuel utilization, which can be controlled [4,11–16]. For example, it was observed that high operating temperature promoted lower cell degradation by reducing cathode overpotential [10]. In addition, temperature distribution governs the location of the highest current density zone, where a stronger degradation is induced [16]. Fuel utilization affects the distribution of fuel composition over the active area of the cell, resulting in different localized degradation distributions [10,17]. High fuel utilization can lead to oxidation of the anode material at the anode-electrolyte interface [18].

In a previous work, the effect of overall degradation of a SOFC was modeled for real-time applications [19,20]. An empirical function for the degradation rate (in terms of percentage of voltage drop per 1000 h of operation) was previously extrapolated from experimental data and incorporated in the SOFC model, first at a global level [19] and then on a localized basis, taking into account also the effect of the temperature [21]. A simple algebraic expression, a function of current density, temperature, and fuel utilization, was used to achieve real-time performance of the model, with the final goal of coupling the fuel cell model with the hardware components of a fuel cell gas turbine hybrid emulator. It has been posed that the common effect of all degradation mechanisms can be seen as an increment in the area specific resistance (ASR) of the cell [17,18,22]. For simplicity, the degradation rate was incorporated in the model as an incrementing factor in the ohmic resistance.

In this work, the effect of localized degradation in a SOFC is analyzed using a real-time distributed model. In Part I, the degradation model and the employed methodology are described. The behavior of the main parameters during cell degradation is analyzed. In the Part II, a more detailed analysis of several fuel cell parameters is presented, along with the effect of degradation on heat generation, temperature gradients, and overpotential [23]. In this second part, the possible causes of failure are pointed out, in order to determine a future control strategy that can mitigate

degradation effects.

2. SOFC model

A 1D, real-time model is used to simulate a co-flow, planar anode-supported SOFC, composed of a Ni doped yttria-stabilized zirconia (Ni-YSZ) anode, a YSZ-lanthanum strontium magnetite (LSM) cathode, and YSZ electrolyte [24]. The model employed in this work was previously developed with the goal of integrating it into a SOFC gas turbine hybrid system emulator [25]. Maintaining real-time capability while capturing the localized degradation effects is the main objective of this work.

The model employs a coupled approach of finite difference and finite volume, respectively for thermal and electrochemical equations. Since the electrochemistry models do not use differential equations, the finite volume approach is more appropriate. For heat transfer, the only way to meet the real-time requirement is to use a finite difference method. A mixed approach is necessary to meet both the accuracy and real-time requirements. The cell is discretized in 20 volumes (or nodes) in the direction of fuel and air flows. Properties such as temperature, pressure, and concentration are assumed to be uniform in each control volume. Variables such as current density, Nernst potential, temperatures and fuel composition are calculated on a distributed basis, in each node and for each sample time. The following equations are used in the model to calculate Nernst potential (Eq. (1)), cell voltage (Eq. (2)), and overpotentials (Eqs. (3)–(5)). The Butler-Volmer equation for the activation losses is approximated in Eq. (4) according to the approach presented by Noren and Hoffman [26]. Since each electrode contributes to the activation polarization, Eq. (4) is applied to both anode and cathode. The expressions for exchange current densities, i_0 , are illustrated in Eqs. (6) and (7).

$$V_{NERNST} = -\frac{\Delta C_{H_2O}^0}{nF} + \frac{R_g T}{nF} \ln \left(\frac{p_{H_2} \sqrt{p_{O_2}}}{p_{H_2O}} \right) \quad (1)$$

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