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A distributed real-time model of degradation in a solid oxide fuel cell, part II: Analysis of fuel cell performance and potential failures

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HIGHLIGHTS

• Degradation in a SOFC was studied with a real-time distributed model.

• A degradation rate incremented the ohmic resistance of the cell during time.

• Variables distributed profiles during 12,000 h of degradation were analyzed.

• Issues related to thermal management of the cell were highlighted.

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ABSTRACT

Solid oxide fuel cells are characterized by very high efficiency, low emissions level, and large fuel flexibility. Unfortunately, their elevated costs and relatively short lifetimes reduce the economic feasibility of these technologies at the present time. Several mechanisms contribute to degrade fuel cell performance during time, and the study of these degradation modes and potential mitigation actions is critical to ensure the durability of the fuel cell and their long-term stability. In this work, localized degradation of a solid oxide fuel cell is modeled in real-time and its effects on various cell parameters are analyzed. Profile distributions of overpotential, temperature, heat generation, and temperature gradients in the stack are investigated during degradation. Several causes of failure could occur in the fuel cell if no proper control actions are applied. A local analysis of critical parameters conducted shows where the issues are and how they could be mitigated in order to extend the life of the cell.

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1. Introduction

Durability of high temperature fuel cells, such as solid oxide fuel cells, is significantly impacted by diverse mechanisms of degradation, which reduce the fuel cell performance during time and can cause the failure of the stack. Many are the causes and the direct consequences of degradation mechanisms in the cell: impurities in the fuel can cause electrode poisoning delamination, coarsening of nickel particles, or carbon deposition in the anode; presence of water vapor in the cathode stream can induce materials segregation; operating conditions can cause phase separation within the anode, electrolyte cracking, or other detrimental effects [1-7]. Most of the studies present in the literature focus on the effect of fuel contaminants on cell performance degradation [8-11]. However,

http://dx.doi.org/10.1016/j.jpowsour.2016.01.027 0378-7753/Published by Elsevier B.V. the direct effect of fuel cell operating parameters, such as current density and temperature, on degradation mechanisms has been observed in the literature [2,12–18]. For this reason, a simplified, real-time model of degradation was developed in this work, where the voltage degradation rate per 1000 h of operation is related to three operating parameters: current density, fuel utilization and temperature. Relating degradation to controllable parameters, rather than non-observable degradation mechanisms, allows to use control actions to mitigate degradation effects during the cell lifetime.

In Part I of this paper the real-time, one dimensional model of a SOFC with localized degradation was described and the behavior of the main parameters during degradation was shown [19]. All the details about the model and the employed empirical expression of the degradation rate were presented in Part I. In this Part II, an analysis of polarization distributions is performed. Local current density and temperature profiles, shown in the previous part, affect

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Nomenclature		r _d P	degradation rate [% khr ⁻¹] ideal gas constant [$I \mod^{-1} K^{-1}$]
FU	Fuel utilization	К _g T	temperature [K or C where specified]
ISM	Lanthanum_Strontium_Magnetite	t	time [hr]
DEN	Positive side Electrolyte Negative side	V	voltage [V]
FLIN	Solid ovido fuel cell	v	voltage [v]
JULC		X	
IPB	Iriple phase boundary		
WGS	Water gas shift	Symbols	
YSM	Yttria-stabilized zirconia	α	charge transfer coefficient
A _{react}	Area of reaction [m ²]	Δ	difference
F	Faraday's constant [C mol ⁻¹]	η	electrochemical loss [V]
G	Gibbs free energy [kJ]		
K_p	equilibrium constant	Subscrip	ts
i	current density [A cm ⁻²]	act	activation
<i>i</i> 0	exchange current density [A cm ⁻²]	diff	diffusion
п	number of electrons transfer per reaction	irr	irreversible
р	partial pressure [atm]	ohm	ohmic
R	area specific resistance [Ωm^2]	PEN	positive side-electrolyte-negative side
Roxide	resistance of the channels $[\Omega m^2]$		-

cell overpotential, which mainly drives degradation phenomena [12,13]. The paper also focuses on the control issues that arise when the cell degrades, in terms of performance losses, thermal management, and safe operability of the stack. Analyzing localized effects of degradation, it is possible to have a qualitative idea of what issues need to be controlled (for example, temperature gradients along the cell or heat generation distribution) when the cell is degrading, in order to develop appropriate control strategies. The cell lifetime can be predicted more accurately, since part of the cell degrades faster than others, and the necessary control actions can be evaluated. The results presented in Part I and this Part II are consistent with the ones proposed by Nakajo et al. [12,13], where a very detailed model of several degradation mechanisms was employed to predict the parameters distribution along the cell and the global lifetime.

2. SOFC model and test procedure

The 1D, real-time model of a co-flow, planar SOFC used in this work is described in detailed in the Part I of this paper [19]. A coupled approach of finite difference and finite volume is employed to solve respectively thermal and electrochemical equations [20]. The cell is discretized in 20 volumes of calculation in the direction of fuel and air flows. Distributed profiles of all the main fuel cell parameters are calculated at each sample time of 80 ms, which is chosen as the optimal compromize between short computational time and accuracy in capturing the transients. The constraints related to the real-time performance of the model are primarily due to its applications. As such, the SOFC model is normally coupled with hardware components of a fuel cell emulator [21]. Ongoing activities focus on the impact of cell degradation on a SOFC gas turbine hybrid system, hence the importance of ensuring short computational time while capturing the effects of local degradation [22].

Degradation rate is calculated according with Equation (1) and incorporated into the total resistance of the cell as shown in Equations (2) and (3). The algebraic expression of Eq. (1) was extrapolated from experimental data using a curve fitting approach [23]. The data set referred to experiments performed at different values of current density, fuel utilization, and temperature. Material set and fuel composition considered in this work are the same as those employed for the aforementioned experiments.

$$r_d = \frac{0.59FU + 0.74}{1 + \exp\left(\frac{T - 1087}{22.92}\right)} \left(e^{2.64i} - 1\right) \tag{1}$$

$$R = \left(R_{PEN} + R''_{oxide} + R_{irr}\right) \cdot \left(1 + r_d \cdot \frac{t}{1000}\right)$$
(2)

$$R_{irr=\sum_{time}} \left(R_{PEN} + R_{oxide}^{''} \right) \cdot \frac{r_d}{1000}$$
(3)

The effect of degradation is an increment in the ohmic resistance $R_{PEN} + R^{''}_{oxide}$, which is a function of temperature. Degradation contribution is expressed in terms of the coefficient r_d (percentage of voltage drop per 1000 h of operation) and with the term R_{irr} , which represents the irreversible contribution of degradation and whose value is updated at each sample time.

Water-gas shifting (WGS) reaction is taken into account and considered at the equilibrium. The equilibrium constant for WGS reaction is presented in Equation (4). As shown in Table 1, the employed fuel is a typical coal-derived syngas containing a significant amount of hydrogen, steam, and carbon monoxide.

$$K_{p,shift} = \frac{pH_2pCO_2}{pH_2OPCO} = \exp\left(\frac{4276}{T} - 3.961\right)$$
(4)

The operating parameters considered for this test are reported in Table 1.

Table 1		
Nominal	operating	conditions.

Cathode air flow	1.00 kg/s
Cathode inlet temperature Cathode inlet pressure	690 °C 0 kPag (1 atm)
Current	200 A
Fuel flow	0.095 kg/s
Fuel utilization	80%
Average cell temperature	820 °C
Anode inlet temperature	800 °C
Fuel composition	29.1% H ₂ , 27.1% H ₂ O, 28.6% CO, 12% CO ₂ , 3.2% N ₂

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