



A durability model for solid oxide fuel cell electrodes in thermal cycle processes

Yanxiang Zhang, Changrong Xia*

CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, 96 Jinzhai RD, Hefei, 230026 Anhui, China

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ABSTRACT

Despite the intense interest in solid oxide fuel cells, many details of their durability remain a mystery. Here, we present the insight see on electrode degradation in thermal cycle processes. Our model interprets the degradation to the stresses induced by thermal expansion mismatch of the electrocatalyst and electrolyte in a composite electrode that undergoes a temperature change. Such stresses might break the particle–particle interfaces (grain boundaries), thus reduce oxygen-ionic conductivity, electronic conductivity, and three-phase boundaries within the electrode, and consequently, degrade its performance. The model formulates the degradation rate as a function of cycle number, thermal expansion coefficient, composition, and particle size, providing a remarkable ability to balance thermal expansion restriction and catalytic activity of electrode materials, to optimize the electrode structure and composition, and to predict thermal-cycle durability. The model explicitly demonstrates that, in addition to their excellent electrochemical activity, nanostructured electrodes exhibit exceptional durability in thermal cycle processes.

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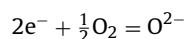
1. Introduction

Solid oxide fuel cells (SOFCs) are a forward looking technology for highly efficient, environmental friendly power generation [1–5]. A SOFC is a multilayer structure consisting of at least three functional components: anode, electrolyte and cathode. All components have to show a well matched thermal expansion behavior so that the multilayer structure could function well in thermal cycle processes including start-up and shut-down [6]. Unfortunately, thermal expansion coefficients (TECs) of electrocatalysts such as lanthanum strontium manganite, lanthanum strontium cobaltite, and nickel are usually different from that of electrolytes. Therefore, there is always electrode degradation in the thermal cycle processes. However, details of the degradation process are still not available for electrodes with different TECs and various structures.

The present work provides the insight into electrode durability in thermal cycle processes. A model is developed to quantitatively predict the electrode performance in terms of interfacial polarization resistance with respect to thermal cycle number, electrocatalyst TEC, temperature change, and electrode characteristics including composition, microstructure, and particle size. The model is interpreted here with the cathode but can also be used to evaluate the anode durability. In addition, the model is applicable to other solid-state electrochemical devices that undergo temperature changes.

2. Model description

In the cathode, oxygen is electrochemically reduced to oxygen ion via the overall half-cell reaction,



Therefore, the reaction occurs at so-called three-phase boundary (TPB) where oxygen-ion, electron, and oxygen are available [7]. In a porous composite cathode consisting of an electrocatalyst and an electrolyte, TPB is created when an oxygen-ionic conducting (the electrolyte, *i* phase) particle is bonded to an electronic conducting (the electrocatalyst, *j* phase) particle, forming an *i*–*j* interface between the two phases (Fig. 1). The TPB is active if only the electrocatalyst particle is connected to the percolated electronic phase through forming a *j*–*j* interface (grain boundary) with its adjacent electrocatalyst particle that belongs to the electronic conducting network. Similarly, to activate the TPB, an *i*–*i* interface (grain boundary) must be formed between the electrolyte particle and its neighboring electrolyte particle that belongs to the ionic conducting network of the composite cathode. The reaction will not happen if any of the three interfaces breaks: the *i*–*j* interface breaking destroys the TPB, the *i*–*i* breaking blocks the oxygen ion transportation route, and the *j*–*j* breaking terminates the electron supply. These interfaces are usually formed with high temperature related processes and often strong enough to withstand the harsh SOFC operating conditions. When thermal expansion coefficient (TEC) of the electrolyte (α_i) and the electrocatalyst (α_j) are different, the interface could be broken by a misfit strain ($\Delta\varepsilon$) resulted from a temperature change, ΔT (positive for heating and negative

* Corresponding author. Tel.: +86 551 3607475; fax: +86 551 3601592.
E-mail address: xiacr@ustc.edu.cn (C. Xia).

Nomenclature

D	degradation rate (%)
\tilde{E}	Young's modulus for dense materials (GPa)
\tilde{E}	effective Young's modulus (GPa)
I	current density (mA cm^{-2})
L	electrode thickness (μm)
m	Weibull parameter
N	cycle number
P	survival probability
p	percolation probability
R	resistance (Ωcm^{-2})
r	particle radius (μm)
ΔT	temperature change ($^{\circ}\text{C}$)
V	voltage (V)
W	power density (mW cm^{-2})
Z	coordination number

Greek letters

α	thermal expansion coefficient (K^{-1})
$\Delta\varepsilon$	misfit strain
ϕ	volume fraction
ν	Poisson ratio
ρ	resistivity (Ωcm)
Σ	Weibull parameter ($\text{N cm}^{-11/15}$)
σ	stress (GPa)

Superscripts

eff	effective value
E	electrolyte
C	cathode
A	anode

Subscripts

ave	average value
g	pore
i	ionic conducting phase
j	electronic conducting phase
s	survival

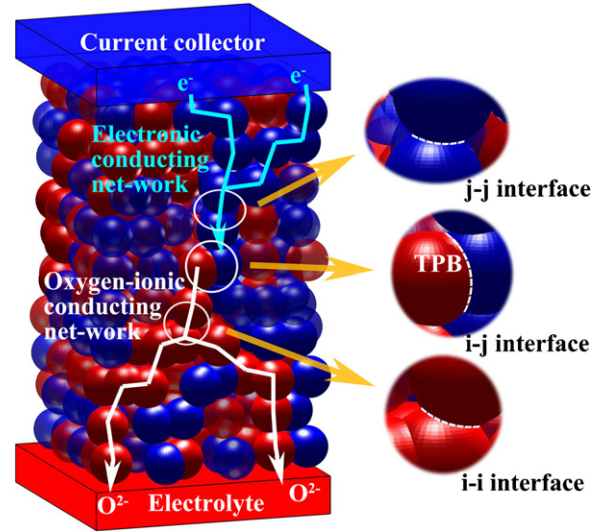


Fig. 1. Illustration for a three-phase boundary (TPB), particle–particle interfaces, and conducting networks, in a composite cathode consisting of electrocatalyst (blue), electrolyte (red), and pores (transparent). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

as [9],

$$\alpha_{\text{ave}} = \frac{\alpha_i \tilde{E}_i + \alpha_j \tilde{E}_j}{\tilde{E}_i + \tilde{E}_j} \quad (4)$$

The interfaces between the two phases are assumed to belong to either the ionic phase or the electronic phase. That is, the stress in the interfaces of the two phases, σ_{i-j} , is equal to σ in absolute value, and its direction is set to be the same as ionic phase. It is the stresses that break the interface, resulting in the reduction of TPB, and consequently, degradation in electrochemical performance with respect to temperature change processes such as thermal cycle. Fortunately, the interface may survive sometimes. The survival probability, $P_{s,i-j}$, under positive stress σ can be estimated with Eq. (5), which is derived from the Weibull weakest-link theory [10,11],

$$P_{s,i-j}(\sigma) = \exp\left(-r_{i-j}^2 \left(\frac{\sigma}{\Sigma_{i-j}}\right)^{m_{i-j}}\right) \quad (5)$$

where Σ_{i-j} and m_{i-j} are Weibull parameters corresponding to the interface between i and j phase, r_{i-j} is the smaller particle radius of i and j phase, i.e., the size of the nanosized particles in case of nanostructured electrodes. Eq. (5) suggests high survival probability is associated with smaller size. For simplification, the effect of electrolyte layer on electrode-structure failure is attributed to Σ_{i-j} , and the validity is shown in Fig. 2a. After N thermal cycles, the number of effective contacts (survival interfaces) between an i phase particle and j phase particles, $Z_{i-j,N}$, is given by,

$$Z_{i-j,N} = Z_{i-j} P_{s,i-j}^N \quad (6)$$

Z_{i-j} denotes the initial interface number (coordination number), which is a function of electrode composition and particle sizes. Eq. (6) reveals an exponentially decreasing rule of survival coordination numbers as a function of thermal cycle number. The interfacial polarization resistance, R_p , strongly depends upon the interface number according to the particle-layer model [12],

$$R_p = \sqrt{\frac{\rho_{\text{TPB}}^{\text{eff}} \rho_i^{\text{eff}}}{\ln_i p_i p_j Z_{i-j,N}}} \coth\left(L \sqrt{\frac{\rho_i^{\text{eff}} \ln_i p_i p_j Z_{i-j,N}}{\rho_{\text{TPB}}^{\text{eff}}}}\right) \quad (7)$$

for cooling),

$$\Delta\varepsilon = (\alpha_j - \alpha_i)\Delta T \quad (1)$$

At a stress balance state, imposition of this misfit strain results in a couple of equal and opposite stresses, σ_i in the electrolyte phase and σ_j in the electrocatalyst phase, holding $\sigma_i = -\sigma_j = \sigma$. So,

$$\Delta\varepsilon = \sigma \left(\frac{1}{\tilde{E}_i} + \frac{1}{\tilde{E}_j}\right) \quad (2)$$

where \tilde{E}_i and \tilde{E}_j are the effective modulus of electrolyte and electrocatalyst phases, respectively. According to the power law expression [8], they can be simplified as,

$$\tilde{E}_i = \frac{E_i}{1-2\nu} \phi_i (1-\phi_g) \quad (3-a)$$

$$\tilde{E}_j = \frac{E_j}{1-2\nu} \phi_j (1-\phi_g) \quad (3-b)$$

where ϕ_g represents the cathode porosity, ϕ_i and ϕ_j denote the volume fraction of ionic and electronic phases relative to the total solid materials, with the porosity ϕ_g specified independently. E_i and E_j are the Young's modulus corresponding to fully dense materials. ν is the Poisson ratio. The TEC of the whole cathode can be estimated

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