



Understanding degradation of solid oxide electrolysis cells through modeling of electrochemical potential profiles



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ARTICLE INFO

Article history:

Received 16 October 2015

Received in revised form 2 December 2015

Accepted 9 December 2015

Available online 17 December 2015

Keywords:

SOEC

degradation

bi-layer electrolyte

modeling

electrochemical potential profiles

ABSTRACT

Establishing the spatial distribution of the various chemical and electrochemical potentials in an operating SOEC is critical as several degradation mechanisms are tightly connected to them, but at the same time very challenging to achieve experimentally. Such distributions are presented here on the basis of a two dimensional bi-layer electrolyte SOC model including for both electrodes a description of activation, concentration, and conversion losses. An extensive parametric study is reported to illustrate the influence of the electrode polarization resistances, the ionic and electronic conductivities in the electrolyte, the gas composition, temperature, and pressure on the current density distribution over the cell and the oxygen activity distribution within the electrolyte. The developed model is further used to simulate long-term durability experiments during different stages of operation, thereby helping to rationalize microstructural and chemical changes observed in post-mortem analysis. Finally, measures to mitigate degradation by changing conditions of operation, material or electrode properties or overall cell geometry are suggested.

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1. Introduction

High temperature solid oxide cells (SOCs) can be reversibly operated as fuel cells (SOFCs) or as electrolysis cells (SOECs) for steam electrolysis or syngas production. SOECs offer high production rates, high energy conversion efficiencies [1,2], fast power cycling, and low manufacturing cost, thereby being attractive for conversion and storage of renewable electricity and for production of synthetic fuels [3].

SOC performance and durability depends on cell architecture, materials selection, cell processing, particle sizes, particle size grading, porosity, tortuosity, as well as on operating parameters (e.g. temperature, pressure, gas composition, gas flow rates, cell voltage, current density), rendering optimization of cell design and operation control a complex task. Furthermore, several critical operating parameters such as the current density, temperature, chemical and electrochemical potentials are in fact functions of position within the cell and their spatial distribution is very difficult to access experimentally.

As a consequence mathematical modeling of SOFCs has attracted intense research efforts the last two decades with the

aim to optimize performance and to establish efficient control strategies for SOFC stacks. Different aspects of this extensive body of work have been collected in review papers [4–8], offering a good overview of the field. On the contrary, little modeling work has focused on SOEC operation, summarized in a recent review paper [9]. Despite the obvious similarities, the substantially different potential ranges and gradients involved, influence performance and long-term stability in very different ways.

Modeling efforts so far (both in SOFCs and SOECs) have mainly aimed i) at establishing a link between performance prediction and cell construction and/or operating parameters, thereby being used as tools for rational cell development, and ii) at assessing thermal gradients established within a SOC during operation, a very critical issue for SOFCs as it can lead to thermal stress induced mechanical failure. In-plane thermal gradients are significantly less pronounced in SOECs due to the endothermic nature of the steam and/or carbon dioxide reduction [10]. Less effort has been directed so far to the estimation of chemical and electrochemical potential profiles within SOCs. Nevertheless, this is very important information as several degradation mechanisms as well as microstructural and/or compositional changes are associated with the oxygen activity ($a_{O_2} = p_{O_2}/1atm$) reaching too low or too high a value in the cell. The elevated oxygen activity near the oxygen electrode/electrolyte interface in SOEC operation has been shown to result in “oxygen bubble” formation in the YSZ electrolyte grain

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List of symbols

F	Faraday constant
R	Ideal gas constant
T	Temperature
p	pressure
p_i	Partial pressure of species i
a_i	Activity of species i
J_i^{in}	Inlet flow rate of species i
R_{conc}	Concentration resistance
R_{conv}	Conversion resistance
R_{elc}	Electrochemical polarization resistance
R_{ion}	Resistance to oxide ionic transport
R_{et}	Resistance to electronic transport
R_{ect}	Electronic charge transfer resistance
σ_{ion}	Oxide ion conductivity
D_i	Diffusion coefficient of species i
c_i	Concentration of species i
K_{eh}	Electron-hole intrinsic equilibrium constant
ΔH_O°	Equilibrium enthalpy of oxidation
ΔS_O°	Equilibrium entropy of oxidation
ϕ	Galvani potential
μ_i	Chemical potential of species i
η_i	Electrochemical potential of species i
V	Cell voltage
V_{eq}	Nernst voltage
i_i	Current density of species i
j_i	Flux of species i
z_i	Charge of species i
u	speed
r	Ratio of ionic to electronic current density
x	Distance from H ₂ electrode in the electrolyte
L	Electrolyte thickness
L_i	Thickness of electrolyte layer i
ξ	Reduced electrolyte thickness
d	Particle size diameter
t	Thickness
ε	Porosity
τ	Tortuosity
A	Area
y	3-valent dopant fraction
y^0	Initial homogeneous 3-valent dopant fraction
γ	Ratio of the diffusion coefficient of the host to that of the 3-valent substituent
V^m	Molar volume

boundaries [11–16] and/or delamination of the oxygen electrode [16–19]. The reduced oxygen activity near the Ni/YSZ fuel electrode/electrolyte interface in operating SOECs results in formation of zirconia nanoparticles due to dissolution of Zr into Ni, followed by bulk or surface diffusion and formation of ZrO₂ nanoparticles where the activity of O₂ is higher (e.g. at the interface between Ni-Ni or in a Ni pore) [20]. Si poisoning of the H₂-electrode and SiO₂ inclusions in Ni grains near the Ni/YSZ interface have also been observed after long-term SOEC durability studies and associated with the reduced oxygen activity prevailing there [20,21]. Furthermore, the large span in oxygen activity and electrochemical potential of the electrons across the electrolyte promotes kinetic demixing and can result in compositional and microstructural changes [15–23], as has recently been observed in long-term operated SOEC [15]. Although emphasis is placed here on degradation mechanisms directly related to absolute values or gradients in activity of O₂, it should be mentioned in passing that Ni

coarsening [21,24] and contamination of active sites by impurities such as Cr, Si, and Al among others act as additional causes of degradation [12,21,25].

Experimental determination of the oxygen activity profile within real operating SOCs is very difficult, and therefore modeling can prove very valuable in this context. Several approaches to solving the transport equations in mixed ionic electronic conductors (MIECs) have been published in the literature, employing a different degree of simplifying assumptions [26–34]. Some of these models have been implemented for the simulation of chemical, electrical and electrochemical potential profiles across the YSZ or Ce_{0.9}Gd_{0.1}O_{1.95-8} (CGO10) layer of a SOC at open circuit voltage (OCV) or under polarization, taking into consideration electrode activation losses [33–38] and in some cases also gas conversion and concentration contributions in the fuel electrode [35,36].

(La_{1-x}Sr_x)_{1-y}MnO₃₋₈ (LSM) that was traditionally used for the O₂ electrode has in modern SOCs been replaced by more active electrocatalysts such as (La_{1-x}Sr_x)_{1-y}CoO₃₋₈ (LSC) or (La_{1-x}Sr_x)_{1-y}Co_{1-z}Fe_zO₃₋₈ (LSCF). To inhibit formation of SrZrO₃ upon reaction of LSC or LSCF with YSZ, an interlayer of acceptor doped ceria is introduced. A dense YSZ layer is still needed to suppress electronic leak currents [38]. This has led to a few publications where chemical and electrochemical potential profiles are modeled within bi-layer electrolyte SOFCs [29–40]. This effort is extended here to a two dimensional bi-layer electrolyte SOC model including activation, concentration and conversion contributions to both electrodes, using the analytical solutions proposed by Jacobsen et al. [33,34], for the transport within the electrolyte layers. An extensive parametric study is then undertaken and selected results that help promote understanding of SOEC performance and durability are presented. The developed model is further used to simulate long-term durability experiments, establish chemical and electrochemical potential profiles during different stages of operation, and thereby help rationalize the observed trends appearing in post-test microstructural and chemical characterization.

2. Theoretical considerations

2.1. Model description

A schematic of the developed two dimensional model used to simulate the performance of and electrochemical potential profiles in a bi-layer electrolyte SOC is shown in Fig. 1. The various layers are shown along with their corresponding resistances and their dependence on operating and cell construction parameters.

Mass transport (R_{conc}) through the porous support structure and the O₂ electrode has been described using the dusty gas model with viscous flow [35,41] and the Bosanquet approximation [42], respectively. Gas conversion (R_{conv}) in the fuel and O₂ compartments is accounted for by implementing the mass balance in each segment (k) along the gas flow [35] in a plug flow co-flow configuration. The expressions used for the electrochemical polarization resistances (R_{elc}) of the two electrodes, as well as the transport properties (σ_{ion} , D_e and D_h) and electronic defect properties (c_e , c_h , K_{eh}) of YSZ and CGO10 are listed in Table 1. D_e^{CGO10} and D_h^{CGO10} are deduced from the electron and hole partial conductivities [43] and their concentrations, which are estimated from the oxygen vacancy dependent equilibrium enthalpy and entropy change for the reaction $O_O^{\times} \leftrightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g)$ [44] and the equilibrium enthalpy and entropy change for the reaction $O_O^{\times} + 2h^{\bullet} \leftrightarrow V_O^{\bullet\bullet} + \frac{1}{2}O_2(g)$ [43]. R_{elc} values for Ni-YSZ and LSM-YSZ electrodes (routinely produced in-house) have been derived from the analysis of a series of electrochemical impedance spectroscopy

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