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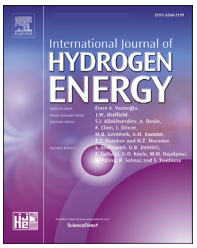

A three dimensional multiphysics model of a solid oxide electrochemical cell: A tool for understanding degradation

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ABSTRACT

Mitigating degradation is essential for extending the lifetime of solid oxide electrochemical cells (SOCs). The conditions leading to degradation, e.g. overpotentials, gas partial pressures, thermal gradients are hard, if not impossible, to retrieve experimentally. Thus, to deconvolute the response from cell testing, modeling can be applied to understand the degradation phenomena in greater detail. Modeling of SOCs is well developed. For computational efficiency, the electrodes are often represented with a mathematical abstraction of zero thickness layer. In this work, further attention is given to the local conditions in the through-thickness of the electrodes, by rigidly integrating classical electrochemistry into a three dimensional multiphysics model of an SOC. Hereby, local conditions (e.g. overpotential) vary through the electrode, and with the coupling to the different transport phenomena occurring (mass, current, momentum and species), this becomes available in three dimensions, throughout a cell. To investigate the validity of the model, a high number of experiments are conducted at different operating conditions, i.e. in both fuel cell and electrolysis mode of operation with H_2/H_2O as feedstock varying parameters such as temperature, gas flows and gas compositions.

Introduction

Solid oxide electrochemical cells (SOCs) are devices that can be operated reversibly as electrolysis cells (SOECs) to produce hydrogen (H_2), carbon monoxide (CO) or syngas (CO and H_2 simultaneously) using electrical energy, or as fuel cells (SOFCs) to produce electrical energy using the same fuels. The performance and durability of SOCs depends on the cell geometry, the materials selected, the cell manufacturing process, particle sizes, porosity, tortuosity and operating parameters such as temperature, pressure, gas flow rates, cell voltage, gas composition, etc. In order to accelerate the

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commercialization of the technology, the durability of SOCs or knowledge about operation must be improved as degradation issues hinder the long-term operation of the cells, making cost of replacement a significant parameter.

Optimizing performance by modeling of SOFCs resulted in substantial amounts of achievements over the past twenty years [1–16]. The focus has been on developing models able to predict macroscopic variations of temperature, stress and current density as function of position and time for different cell configurations and operating conditions to achieve an overall idea on how to operate SOFCs.

For computational reasons, the majority of the SOEC models reported until now, considerably less than for SOFC mode, are based on one dimensional (1D) mathematical models or 1D/2D multiphysics simulations on a unit cell or a stack of planar SOECs, where parametric studies are performed, see e.g. [17–33]. For example, Lay-Grindler et al. [32] developed and used a 1D in-house micro-model to quantify the role of the microstructure in the electrode performance.

To describe the spatial variations across a SOEC various 2D models have been developed. Grondin et al. [24] conducted a simulation of a circular SOEC taking into account charge, mass and heat transfer. Jin and Xue [25] used a similar model but also investigated the position of possible delaminations at the electrode/electrolyte interface. Ni [17,18] also developed multiphysics models for a 2D planar cell operating in co-flow configuration for both H_2O electrolysis and co-electrolysis of H_2O and CO_2. Laurencin et al. [26] further introduced the Dusty gas model (DGM) for a more accurate description of the resistance due to gas diffusion in the porous cathodes. They further enhanced the computational efficiency of the in-house code by an analytical integration of the DGM. The effects of the cell polarizations, geometry and operation parameters as well as the radiative heat losses were studied for an SOEC stack. To describe degradation mechanisms, Chatzichristodoulou et al. [34] developed a 2D SOC model with a single or bi-layered electrolyte, including activation, concentration and conversion contributions to both electrodes, and mixed ionic and electronic transport within the electrolyte layers. This model was used for a sensitivity analysis showing detailed potential distributions in the electrolyte and at the electrolyte/electrode interfaces as a starting point for discussing degradation mechanisms.

The first three dimensional (3D) model was reported by Hawkes et al. [27] and O'Brien et al. [28–30]. Hawkes et al. presented 3D multiphysics cell stack models, operating in cross-flows configuration, including all the transport conservation equations as well as the electrochemical reactions developed with the commercial computational fluid dynamics (CFD) code Ansys Fluent with a modified SOFC add-on module to account for the electrolysis mode. Boëdec et al. [31] developed a new 3D SOC stack, model with Ansys Fluent, to evaluate the contact resistance under operation, as it appears to be a critical issue for the stack performance. Ansys Fluent, as with other commercial codes, presents some limitations. In these 3D models the electrodes were thus described as zero thickness layers, in which the local conditions cannot be resolved (such as the overpotential through the thickness of the electrode).

The degradation of SOCs is in many cases directly related to the local overpotential at the reactive sites due to a too high or too low oxygen activity, e.g., formation of O_2 bubbles in the electrolyte, delamination of the electrolyte/air electrode interface, Si poisoning of the fuel electrode, Zr nanoparticles on Ni grains at the fuel electrode, etc [34–36]. Thus, to be able to deconvolute the degradation occurring in SOC tests, the models must be able to capture the variations of the overpotential and thus also spatial distribution of local gas composition in all directions, especially in the through thickness direction of the electrodes. This has been addressed to some extent by Grondin et al. [24]. They conclude that to deduct the electrode reaction kinetic parameters, further experimental work is needed.

The number of parameters and variables involved in modeling the multiphysics of SOCs is high, and some of them are interplaying through strongly coupled physical phenomena. To deconvolute the measured response, a significant number of experiments with systematic variation of operational conditions are therefore needed. Many researchers have compared their models to experimental data. For example did Ni [19] validate his model by comparing two current density versus voltage (i-V) curves against data from literature for two different temperatures and fuel compositions. Cai et al. [23] also validated their model against literature data and pointed out the difficulty of obtaining relevant data for validation. Jin et al. [25] compared two i-V curves for the same fuel composition at two different temperatures and pointed out the need of using several parameters to adjust the numerical model to the experimental data. Boëdec et al. [31] used one i-V curve for validation. Geisler et al. [9] made a considerable effort to match their model with experimental data investigating the effect of gas-composition, temperature and the effect of using a current collector with ribs. Despite the mentioned examples of validation, this is a critical point for the SOC model establishment, and something which should be carried out to a greater extend.

In this work, we address modeling of the local conditions in the SOC electrodes (e.g. overpotentials, gas compositions, and thermal gradients), as this is essential to understand their degradation in greater detail. This is done by integrating classical electrochemical description of the electrodes into a 3D multiphysics model of a planar SOC. The model thus describes the spatial variation of gas compositions (in channels and porous electrodes), electric potential, ionic potential, overpotentials, temperature and couplings through local electrochemical reactions. To investigate the validity of the model it has been compared to experimental data from a SOC operated at different temperatures, with different flows and gas compositions. In this work, a H_2/H_2O mixture has been used as feedstock and compared to experiments conducted both in fuel cell and electrolysis mode of operation. Furthermore, the effect of the thermal boundary conditions (adiabatic/in cell testing house/perfect insulation) on the model output was investigated to understand the necessity of modeling the thermal boundary conditions in detail. The model is in ongoing studies used to study different SOC degradation phenomena, e.g. carbon deposition in electrolysis using CO_2 as a feedstock.