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More accurate macro-models of solid oxide fuel cells through electrochemical and microstructural parameter estimation – Part II: Parameter estimation

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HIGHLIGHTS

- Theoretical-experimental approach to appraise modelling parameters.
- Tortuosity in the electrodes estimated using the Modified Stefan–Maxwell model.
- Reaction orders of H_2, H_2O and O_2 estimated from a linearized Butler–Volmer.
- Cell performance is mainly driven by charge transfer phenomena in the cathode.

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ABSTRACT

This paper presents a systematic synergetic approach between experimental measurements, equivalent circuit modelling (described in Part I) and macro-scale modelling theory which has proved to be instrumental for the estimation of microstructural and electrochemical features of a Ni-YSZ|YSZ|$Pr_2NiO_{4+\delta}$ – GDC solid oxide fuel cell (SOFC). The aforementioned parameters have been used to generate a more accurate CFD macro-model which has been validated against the experimental results (presented in Part III).

1. Introduction

After decades of research and development, the first generation of SOFC technology-based combined heat and power (CHP) devices are finally leaving the production line towards demonstration plants and early-market consumers. Alas, these systems cannot yet fully compete with traditional power generation technologies in terms of robustness, reliability and cost-effectiveness, thus a profound and systematic research of basic materials and elements is still needed in order to improve the lifetime span, targeting a second generation which should be able to withstand more than forty thousand hours of continuous operation with a low performance degradation rate (<0.1%/kh) [1,2].

Since the mid 1990's with the advent of the first fuel cell models (as an example and naming the most influential ones: Achenbach et al. [3], Virkar et al. [4] and Yakabe et al. [5]) until nowadays, little has changed in the interaction between experimental and modelling fields, being often too disjoined and not operating in full awareness of each other. A vast number of articles found in

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literature deal with modelling the immediate performance of SOFCs when varying one or more operating parameters such as temperature, gas composition and cell potential [6], nevertheless, most of these works employ microstructural and electrochemical modelling parameters (i.e. porosity, tortuosity, exchange current density, *etc* …) from other works rather than from experimental data obtained for the specific type of cell being modelled, detracting to some extent from the soundness of the model and hence from the validity of the results. It is crucial to generate a model which encompasses realistic data from the SOFC being studied in order to not only get a robust model which can predict reasonably well the immediate performance of the cell, but most importantly to go one step beyond the state-of-the-art and start predicting the effects of degradation phenomena in the concerned type of cell. Attending to the above mentioned requests, it seems undisputable how the use of novel analysis tools and techniques is the fundamental pillar on which the future models must rest.

The work reported in this article is a compendium of how to employ the experimental results obtained from a specifically designed experimental campaign (fully described in Part I) to estimate the microstructural and electrochemical parameters driving the operation of the SOFC button cell in order to employ them in a CFD macro-model (fully described in Part III).

2. Parameter estimation

2.1. Experimental results

Estimation of the modelling parameters is done via a symbiotic approach encompassing experimental results with theoretical and semi-empirical mathematical equations. The experimental results have been presented in the second part of this work alongside the description of the thorough experimental campaign which foresaw the operation of the SOFC single cell under a number of different conditions by varying one at a time: temperature, hydrogen partial pressure in the anode, steam partial pressure in the anode and oxygen partial pressure in the cathode. For each of the conditions an electrochemical impedance spectroscopy (EIS) measurement was carried out and then fitted by means of the equivalent circuit model (ECM) depicted in Fig. 1 (see Part I for an extensive explanation on how this ECM was obtained). Each of the electrical elements of the ECM represent a precise physicochemical process occurring in the SOFC, thus it is possible to quantitatively associate a resistance value to a particular process and monitor how this modifies according to the operating conditions.

2.2. Assumptions and considerations

The test station configuration, the relatively small active area of the button cell and the high volumetric flow rates of the gases used enable to take into consideration a number of assumptions that render simpler the procedure of obtaining the modelling parameters with small information loss or deviance. These assumptions and considerations are hereby listed:

- *One-dimensional domain*: on the one hand gas concentrations along the fuel and air channels are uniform because of the high molar flows being employed, thus, even when not operating under OCV conditions the fuel and air utilizations are rather low. On the other hand, the current density is uniform over the entire electrode attending to the aforementioned gas distributions.
- *Stationary conditions*: the testing procedures foresaw sufficient stabilization time when gas flows, temperature or current density were modified.
- *Isobaric conditions*: the pressure drop in the porous electrodes is negligible. The pressure in the system is considered to be the atmospheric one (P = 101325 Pa).
- *Isothermal conditions*: it has been experimentally demonstrated how the temperature of the button cell remains in a range of ±2 °C during the polarization curve even when operating at very high current densities.
- *Reactions occur only in the electrode/electrolyte interface*: even if this does not adjust to reality for cermet-type anodes and composite cathodes, this assumption is widely extended in the modelling field as the anode's and cathode's active layers are very thin when compared with the gas diffusion layer, thus they are often considered as interfaces rather than as volumes [6,7].
- *Species transport is driven only by diffusion*: velocity of the fluid inside the electrode can be neglected.
- *Negligible performance degradation*: cell performance is always evaluated before and after the electrochemical tests in order to quantify the degradation induced by these. A high degradation value would invalidate the whole procedure violating the principle of univocal state of the test specimen.

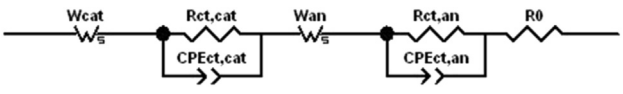

Fig. 1. Equivalent Circuit Model (ECM) of the PRN cell.

2.3. Microstructural parameter identification

2.3.1. Porosity and particle radii

The description of the methodologies employed in order to measure or estimate the anode porosity, and the particle radii in anode and cathode is present in the second part of this work (More accurate macro-models of SOFCs through electrochemical and microstructural parameter estimation – Part I: Experimentation). However, the values of three microstructural parameters have been hypothesized due to the difficulties in obtaining them experimentally, these are: cathode porosity, and the volume fraction of the electronic and ionic phases in both electrodes. For the first parameter (ε_{cat}) a value of 35% has been employed whilst for the last two a volume fraction of 50% was established.

2.3.2. Tortuosity

It is very difficult to determine the actual paths that molecules travel because the paths in porous materials are very complicated [8]. In this work the tortuosity has been estimated indirectly by means of the concentration overpotential resistances, which are governed by the species concentration in the TPB.

The steady-state species transport partial differential equation (PDE) is expressed by means of Eq. (1) when transport by convection is neglected and it is assumed that the electrochemical reaction occurs in the electrode/electrolyte interface.

$$\nabla \vec{J}_k = 0 \tag{1}$$

where $\vec{J}_k$ is the diffusive flux.

The modified Stefan–Maxwell model (MSMM) has been employed to describe the multicomponent species transport in anode and cathode, namely: