

ELECTROCHEMICAL MACRO-SCALE MODEL OF A LOW TEMPERATURE SOLID OXIDE FUEL CELL WITH MIEC ELECTROLYTE

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ABSTRACT

This work presents a Macro-Scale electrochemical model of a low temperature Solid Oxide Fuel Cell (SOFC) with a MIEC electrolyte. Low temperature SOFCs potentially merge high efficiency due to relatively high temperature, presence of a solid electrolyte, and lower production costs (among others) compared to really high temperature ones. Therefore, there is great interest on them despite they have not been thoroughly studied yet. The model has been compared with a Micro-Scale one found in the literature which closely reproduces experimental data. Assuming electrochemical reactions occurring just at the electrodes/electrolyte interfaces as usually done in high temperature operation (with “classic” YSZ electrolyte) has been found not to be accurate enough, thus ionic ohmic loss in the electrodes has been accounted. The final polarization curves matching has been quite good, but solving the charge conservation equations within the electrodes would definitely enhance the model accuracy and stability.

Keywords: SOFC, low temperature, MIEC, modeling, Macro-Scale

NOMENCLATURE

Abbreviations

MIEC	Mixed Ionic and Electronic Conductor
OCV	Open Circuit Voltage
SDC	Samaria-Doped-Ceria
SOFC	Solid Oxide Fuel Cell

Symbols

A	Reference electrode area [m ²]
A_{act}	Active area within the electrode [m ²]
D	Diffusivity [m ² /s]
F	Faraday constant [C/mol]
i_0	Exchange current density [A/m ²]
j^{ely}	Electrolyte current [A/m ²]
i_{load}	Useful current density [A/m ²]
K_{eq}	Equilibrium constant [-]
L	Electrolyte thickness [m]
P	Pressure [Pa]
R	Universal gas constant [J/mol/K]
t	Thickness [m]
T	Temperature [K]
V	Voltage [V]
x	Molar fraction [-]
ϵ	Electrode porosity [-]
η	Overpotential [V]
σ	Conductivity (ionic/electronic) [S/m]
τ	Electrode tortuosity [-]

1. INTRODUCTION

Solid Oxide Fuel Cells are widely acknowledged to be a very promising technology, mainly due to their high efficiency and low emissions compared to conventional power systems. The main advantage of these kind of cells compared to others is the high efficiency and fuel flexibility, both due to high operating temperature. Nevertheless, high temperature (800-1000°C) limits SOFCs commercialization due to materials degradation, high manufacturing cost, and both time and energy consuming startup [1][2]. Therefore, nowadays efforts

are aimed at lowering their temperature in the range 500-700°C, or even below, allowing to switch to metallic construction materials, lower costs and easier operation. Nevertheless, the electrolyte would likely be a Mixed Ionic and Electronic Conductor (MIEC) material, which introduces intrinsic losses in the system due to an electronic current within the electrolyte flowing in opposite direction with respect to the ionic one.

Considering the above, it is trivial that reliable and efficient models are needed to assess the performances of these devices. This work represents an attempt of capturing the polarization behavior of a low temperature SOFC (“button cell” configuration) with SDC (Samaria-Doped-Ceria) as electrolyte using a Macro-Scale model, which does not solve charge conservation equations within the electrodes. The model is similar to the one presented by Shen et al. [3], the main differences are considering the hydrogen electrooxidation a non-reversible reaction, and the computation of ohmic losses within the electrodes. The former is necessary since the considered cell works with a not very performing anode, the latter is an attempt of overcoming the intrinsic limitations of a Macro-Scale model.

Currently, the literature generally lacks of works concerning the electrochemical modeling of low temperature SOFCs with MIEC electrolyte. Only a few works are available and most of them solve the equations needed to find the accurate ionic and electronic currents distribution within the electrodes [4][5][6]. To avoid this process, which would imply the electrodes discretization by solving the charge conservation equations along them, a Macro-Scale model has been implemented. Its main advantage is a much easier model implementation and quicker calculations, the latter feature can be relevant when solving a whole fuel cell channel. If the electrochemical model shows good matching with experimental data in several operating conditions, it could then be used to simulate a whole channel, employing an existing model used to simulate high temperature cells.

2. METHODOLOGY

The model employs a set of equations taken from the literature [3][4][7] for the calculation of electronic and ionic currents within the electrolyte, which are summarized in *table 2*. The aim is to reproduce the isothermal button cell polarization curves of reference [4], whose electrochemical model solves the charge conservation equations within the electrodes, thus it is inherently more accurate. As a matter of fact, the

reference work succeeds in reproducing experimental polarization curves.

The set of equations in *table 2* does not account any electrodes ohmic loss, as they will be discussed separately. The ionic and electronic conductivities of the electrolyte may be found in reference [4]. Ionic and electronic currents have been considered to be positive even if they have opposite direction (electrons are moved by electric potential, whereas ions are also subject to chemical forces). The term $x_{i,r}$ is the species i molar fraction at the active site, computed by considering porous diffusion from the bulk flow molar fraction ($x_{i,b}$). The porous diffusion coefficient is calculated by considering parallel Knudsen and molecular diffusion mechanisms, thus the following is its final form:

$$D_{p,i} = \frac{\epsilon}{\tau} \left[\frac{3}{4r_p} \left(\frac{\pi M M_i}{2RT} \right)^{0.5} + \frac{1}{D_{m,i}} \right]^{-1} \quad (1)$$

Where ϵ is the electrode porosity and τ is its tortuosity. These parameters may be found in the reference together with the mean pore radius r_p of the electrodes. The diffusion coefficient of a species within a mixture ($D_{m,i}$) is reported in the literature and books [8].

In *table 2*, the electronic ohmic loss within the electrolyte has an unusual form as it is the result of an integration of the ohmic loss within the electrolyte itself. The integration is necessary since the electrolyte electronic conductivity is a function of the variable oxygen partial pressure within it. The integration process can be consulted in reference [3].

Finally, the terms P'_{O_2} , $P^0_{O_2}$, $P^L_{O_2}$, P''_{O_2} are respectively oxygen partial pressures at interface anode/electrolyte within the anode, anode/electrolyte within the electrolyte, cathode/electrolyte within the electrolyte and cathode/electrolyte within the cathode. As shown in the table, $P^L_{O_2}$ is computed assuming the hydrogen oxidation reaction to be in equilibrium at the interface. Thus, the equilibrium constant of that reaction has been calculated using the integrated Van't Hoff equation (function of temperature). The following are the results obtained for temperatures within the range of interest:

T [°C]	550	575	600	625	650	675	700
$K_{eq} \times 10^{-10}$	640	221	81.2	31.5	12.8	5.49	2.45

Table 1. Hydrogen oxidation equilibrium constant

The activation losses are assumed to be concentrated at the electrode/electrolyte interfaces. To somehow account for ohmic losses within the electrodes one can assume that electrochemical reactions occur just

Sub-model	Governing equations
Energy conservation	$V_{rev,H_2} i_{O_2^-}^{ely} = V_{cell} i_{load} + i_{O_2^-}^{ely} (\eta_{ohm,O_2^-} + \eta_{act,O_2} + \eta_{act,H_2} + \eta_{conc}) + i_{el}^{ely} \eta_{ohm,el}$
Concentration loss	$\eta_{conc} = \eta_{conc,H_2} + \eta_{conc,O_2}$ $\eta_{conc,H_2} = \frac{RT}{2F} \ln\left(\frac{x_{H_2,b} x_{H_2O,r}}{x_{H_2,r} x_{H_2O,b}}\right)$ $\eta_{conc,O_2} = \frac{RT}{4F} \ln\left(\frac{x_{O_2,b}}{x_{O_2,r}}\right)$ $x_{H_2,b} = x_{H_2,b} - \frac{i_{O_2^-}^{ely} RT t_{an}}{2FP_f D_{p,H_2}}$ $x_{H_2O,r} = x_{H_2O,b} + \frac{i_{O_2^-}^{ely} RT t_{an}}{2FP_f D_{p,H_2O}}$ $x_{O_2,r} = x_{O_2,b} - \frac{i_{O_2^-}^{ely} RT t_{cat}}{4FP_a D_{p,O_2}}$
Ohmic loss	$\eta_{ohm,O_2^-} = \frac{i_{O_2^-}^{ely} L}{\sigma_{O_2^-}(T)}$ $\eta_{ohm,el} = \frac{RT}{4F} \ln\left(\frac{p_{O_2}^L}{p_{O_2}^0}\right) - \eta_{ohm,O_2^-}$ $\eta_{act,H_2} = \frac{RT}{4F} \ln\left(\frac{p_{O_2}^0}{p_{O_2}^I}\right)$ $\eta_{act,O_2} = \frac{RT}{4F} \ln\left(\frac{p_{O_2}^I}{p_{O_2}^L}\right)$ $\frac{p_{O_2}^I}{p_{ref}} = \left(\frac{x_{H_2O,r}}{x_{H_2,r} K_{eq,H_2Ox}}\right)^2$ $P^{II} = x_{O_2,r} P_a$
Activation loss	$i_{0,H_2} \left[\exp\left(\frac{F\eta_{act,H_2}}{RT}\right) - \exp\left(-\frac{F\eta_{act,H_2}}{RT}\right) \right] A_{act,an} = i_{O_2^-}^{ely} A$ $i_{0,H_2} = 23.8 T \exp\left(-\frac{73000}{RT}\right) \left(\frac{P_{H_2}}{P_{ref}}\right)^{0.47}$ $i_{0,O_2} \left[\exp\left(1.3 \frac{F\eta_{act,O_2}}{RT}\right) - \exp\left(-0.7 \frac{F\eta_{act,O_2}}{RT}\right) \right] A_{act,cat} = i_{O_2^-}^{ely} A$ $i_{0,O_2} = 2.8 \cdot 10^7 T \exp\left(-\frac{139000}{RT}\right) \left(\frac{P_{O_2}}{P_{ref}}\right)^{0.33}$
Currents	$i_{O_2^-}^{ely} = i_{load} + i_{el}^{ely}$ $i_{el}^{ely} = \frac{i_{O_2^-}^{ely}}{\sigma_{O_2^-}} \frac{\sigma_{el}^0}{1-M_0} [M_0 (P_{O_2}^0)^{-1/4} - (P_{O_2}^L)^{-1/4}]$ $M_0 = \exp\left(-\frac{F}{RT} \frac{i_{O_2^-}^{ely}}{\sigma_{O_2^-}} L\right)$

Table 2. Set of equations used to find ionic and electronic currents within the electrolyte [3][4][7]

at the electrode/electrolyte interface. In this way, the ohmic electrode loss to add in the right-hand side of the energy balance equation of table 2 would be:

$$i_{load}(\eta_{ohm,an} + \eta_{ohm,cat}) = i_{load}^2 \left(\frac{t_{an}}{\sigma_{el,an}} + \frac{t_{cat}}{\sigma_{el,cat}} \right) \quad (2)$$

Where t is the electrodes thickness and σ is their electric conductivity, which can be found in reference [4]. Nevertheless, it has been checked that this is practically equal to assuming no electrodes ohmic loss at all (high electronic conductivity of electrodes) and the risk is to achieve just a limited matching with the reference. Thus, one should somehow consider ionic ohmic loss within the electrodes to get more accurate results, since the following is an example of currents distribution through anode, electrolyte and cathode with a useful current of 1000 Am^{-2} :

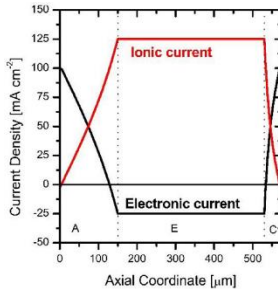


Figure 1. Example of currents distribution [4]

Therefore, one may assume that ionic and electronic currents have a linear distribution within the electrodes. Thus, the ionic current ranges from 0 to $i_{O_2^-}^{ely}$, whereas

the electronic one from i_{load} to i_{el}^{ely} . The resulting ohmic losses (4 in total) to be added in the energy balance right-hand side would be:

$$\int_0^{t_{an/cat}} \frac{i_{O_2^-}^2(x)}{\sigma_{O_2^-} an/cat} dx \quad (3)$$

$$\int_0^{t_{an/cat}} \frac{i_{el}^2(x)}{\sigma_{el,an/cat}} dx \quad (4)$$

The above integrals can be analytically calculated as functions of $i_{O_2^-}^{ely}$, i_{load} , i_{el}^{ely} , which are found with the equations in table 2. Thus no unknown variables are added to the system.

The linear currents assumption is not generally true, but now the aim is to investigate the electrodes ohmic loss impact on the polarization curves. Considered the above, several assumptions on the ohmic loss within the electrodes will be investigated in the simulations:

- i. Only electronic ohmic loss: assumption of electrochemical reactions occurring just at electrode/electrolyte interface. This is equivalent to assuming that just electric current (the useful current) flows within the electrodes, with no ionic ohmic loss.
- ii. Null anodic ionic loss: the above assumption applies just within the anode (its ionic conductivity is not really available in the reference). In the cathode the assumption of linear ionic and electronic currents has been

made, the energy loss to add in the energy balance is computed with equations (3)-(4).

- iii. Linear currents: linear electronic and ionic currents in both electrodes. The electrolyte ionic conductivity and the anode one are assumed to be equal (Ceria is present in both).

3. RESULTS AND DISCUSSION

In the following figure are shown the results of the simulation, considering a uniform temperature of 650 °C and humidified hydrogen as fuel (97% H₂ 3% H₂O, volume fractions).

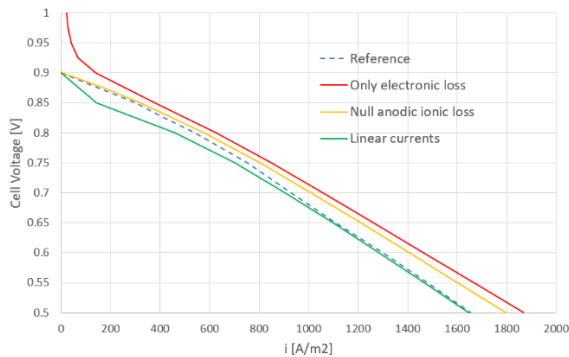


Figure 2. Comparison of assumptions on electrodes ohmic loss

From figure 2 one can see that the “red curve” model is the further from the experimental curve. Therefore, the ohmic loss assumption usually used for high temperature SOFCs simulations of electrochemical reactions occurring just at the electrode/electrolyte interface is not really accurate. Moreover, near the OCV point the red curve diverges whereas all the other curves actually get to the zero-current point at a reasonable voltage. This suggests that it is really important to evaluate the electrodes ionic ohmic losses also at the OCV point, and the “red curve” model generally underestimates losses.

In general, it seems that considering the ohmic ionic loss in both electrodes (green line) gives the best matching with the reference. Nevertheless, the correspondent curve shows some instabilities, this may be due to the assumption on the anodic ionic conductivity (or in general to the fact that it is a Macro-Scale model). Probably, the best assumption is to consider the ionic loss just in the cathode, as the relative curve does not diverge and it gets closer to the reference compared to the red one. Plus it does not show any instability as the green curve. A possible solution which may tackle the mismatch, instability and divergence problems once and for all would be to discretize the

electrodes solving the charge conservation equations, as it is done in the reference. Thus, the ionic and electronic current distributions would be known, and more accurate results may be given by the model (ohmic and activation losses would be more accurately evaluated).

The “null anodic ionic loss” case is then compared with the reference in other operating conditions to check that the model can detect temperature and fuel composition variations. The comparison is made between the reference (experimental data) and the model which considers ionic loss just within the cathode because it is thought to be the more reliable one.

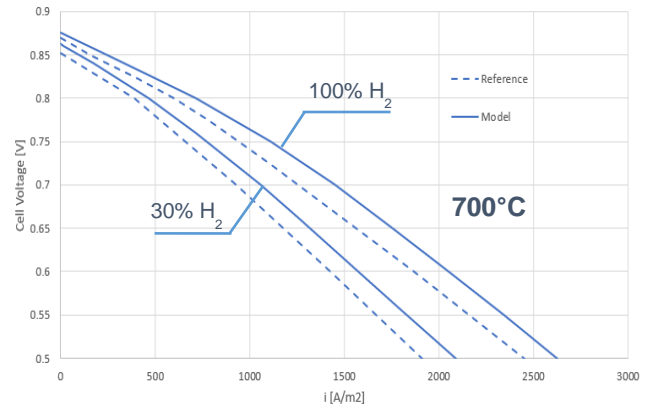


Figure 3. Composition variation influence, H₂-N₂ mixtures

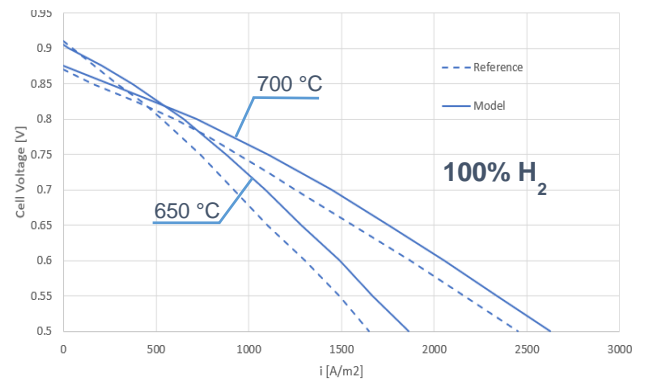


Figure 4. Temperature variation influence

The results shown in figures 3-4 prove that the model is actually capable of catching the influence of hydrogen concentration and the one of operating temperature. Despite just the “null anodic ionic loss” model results have been shown, the above conclusions hold true also for the other ohmic loss models, thus it is a general feature of the model itself.

4. CONCLUSIONS

A Macro-Scale electrochemical model for low temperature SOFCs with MIEC electrolyte has been presented and compared with a Micro-Scale one (which

matches experimental data). The model predicts temperature and composition variations fairly well, but it shows intrinsic inaccuracies (and instability, depending on electrodes ohmic loss model). Moreover, the assumption of electrochemical reactions occurring just at the interface electrode/electrolyte resulted to be not accurate enough, specially near the OCV point where it could not predict a null useful current (voltage diverges). Finally, despite the model considering ionic ohmic losses just within the cathode achieved a fairly good matching with the reference, a Micro-Scale model of the electrodes would definitely enhance the model accuracy and stability.

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