Multiphysics modelling and Electrochemical Impedance Spectroscopy as a tool for predicting Solid Oxide Fuel Cells performance and rational cell design

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Highlights

- 1. Diffusion is a limiting phenomenon at high cell utilization
- 2. EIS is a powerful tool to identify limiting phenomena
- 3. A decrease of cathode thickness ensure a better electrode utilization

1. Introduction

Solid oxide fuel cells offer a clear and efficient alternative to conventional power generation based on fossil fuels combustion. However, their commercialization is still challenging because of different forms of polarization, mainly related to the slow oxygen reduction reaction (ORR) rate [1]. In this study a 2D axial symmetric isothermal multiphysics model for a button LSCF-CGO|CGO|Ni-YSZ fuel cell, operating at intermediate temperature, has been developed, to predict the cell's performance via polarization curves, and to obtain electrochemical impedance spectra under cell voltage perturbation. Particularly, electrochemical impedance spectroscopy is a powerful technique helping the identification and separation of individual processes occurring at the electrodes [2]. Sensitivity analysis have been performed to predict the effect of operating conditions and material properties on the cell's performance, guiding toward a rational design of electrodes dimension and textural properties. This model has been calibrated on experimental data provided by the Department of Chemical Science of the University of Padua.

2. Methods

The model has been developed with Comsol Multiphysics®, capable of solving simultaneously algebraic and differential equations describing the fuel cell, such as conservation equation, momentum balance, species mass balance and charges balances, accounting for the electronic transfer reactions occurring at the two electrodes.

Polarization curves are the results of steady state simulations, varying the potential applied to the cell, whereas Nyquist plots are obtained applying a sinusoidal voltage perturbation as input and measuring the response of the system in a wide range of frequencies (10^6 - 10^{-2} Hz).

Model assumptions are listed as follows:

- The reactant gas mixtures are approximated as ideal gases, thus gas mixture physical properties such as specific viscosity, density, etc., can be easily estimated according to the mixed gas composition.
- Since the button cell is relatively small, the temperature variation across the cell is assumed to be small, thus an isothermal model is used, and the physical properties are evaluated at the average cell temperature.
- The reaction active sites are uniformly distributed in the electrode. The two conducting phases, electronic conducting phase and ionic conducting phase, are considered to be continuous and homogeneous. Since the material properties of both electronic conductor and ionic conductor are only represented by model parameters, the model itself could be assumed to be not material specific.

3. Results and discussion

Figure 1 shows the results of the base case simulation, representing the fuel cell tested at Department of Chemical Science of the University of Padua. The model is proved to be capable of describing all forms of polarization, particularly concentration overvoltage becomes progressively more relevant when the overvoltage increases. This hypothesis is enforced by the Nyquist plot, where the arc on the extreme left, representing slow phenomena such as gas diffusion in the porous electrodes, becomes larger as the overvoltage increases, demonstrating that the cell becomes limited by diffusion phenomena.

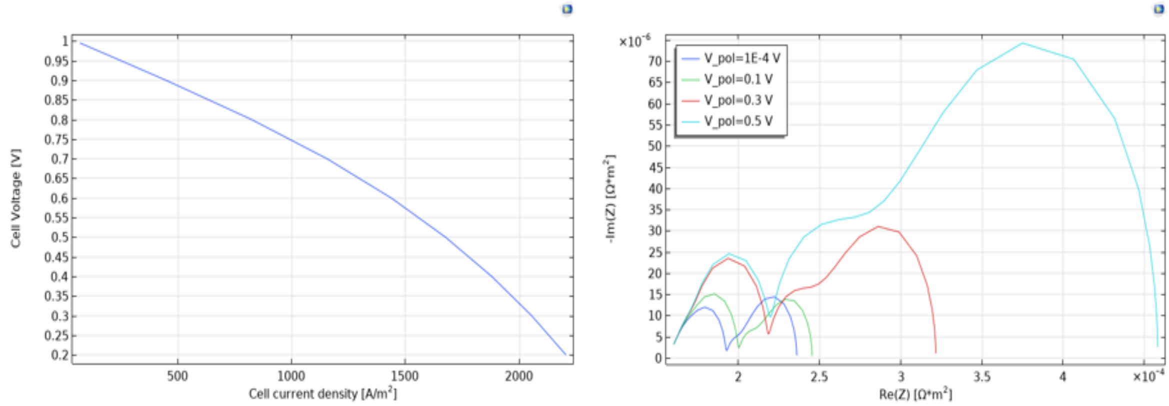

Figure 1*:* Polarization Curve (left), Nyquist plot at different cell voltage (right)

Since the oxygen reduction reaction (ORR) is known to be the limiting process in solid oxide fuel cells [3], sensitivity analyses have been done on cathode properties. Particularly, cathode porosity is proved to be the most relevant textural property and its increase improve the gas diffusion within the electrode, shifting the concentration polarization at higher overvoltage and enhancing the cell's performance, being the current density equal to 1570 A/m^2 for ε_c=0.2 and 1760 A/m^2 for ε_c=0.3 (fixed the cell voltage at 0.5V). Another relevant parameter has proved to be the cathode thickness, particularly a thinner cathode ensures a larger oxygen concentration in the electrode, enhancing the ORR kinetics and consequently the current generation, from 2.6·10^7 A/m^3 at h_c=40μm to 4.1·10^7 A/m^3 at h_c=30μm, fixed the cell voltage at 0.5V. Therefore, the cell current density at different cathode thickness is almost constant, showing only a slight increase of 3% in cell current density, but a thinner cathode leads to a better electrode utilization and lowers the manufacturing costs. Other sensitivity analyses have been performed on operating conditions, such as reactant flowrates and air-to-fuel ratio, demonstrating how an increase in air inlet flowrate results in a larger current density. However, this effect is negligible, if compared to those of cathode thickness and porosity.

4. Conclusions

The model is capable of representing the fuel cell developed and tested at the Department of Chemical science and can be used to identify, through EIS, limiting phenomena lowering the cell performance. Moreover, it suggests modification in terms of cell design and material structure to achieve a better cell utilization. Particularly, for the simulated cell, an increase of cathode porosity, obtained with a larger quantity of pore former during electrode manufacturing, and a decrease of cathode thickness leads to larger current density.

References

[1] Banerjee, A., and O. Deutschmann. "Elementary kinetics of the oxygen reduction reaction on LSM-YSZ composite cathodes." *Journal of catalysis* 346 (2017): 30-49.

[2] Torben Jacobsen, Peter Vang Hendriksen, Søren Koch, Diffusion and conversion impedance in solid oxide fuel cells, Electrochimica Acta, Volume 53, Issue 25, 2008, Pages 7500-7508, ISSN 0013-4686, https://doi.org/10.1016/j.electacta.2008.02.019.

[3] Mefford, J. Tyler, et al. "Interpreting Tafel behavior of consecutive electrochemical reactions through combined thermodynamic and steady state microkinetic approaches." Energy & Environmental Science 13.2 (2020): 622-634.

Keywords

IT-SOFC; multiphysics modelling; cathode properties; electrochemical impedance spectroscopy