

Modelling of Solid Oxide Electrolyzer and hydrogen leak estimation

A. Cifuentes¹, A. Husar¹, V. Roda¹, M. Morales², L. Bernadet², M. Torrell², M. Serra^{1*}

¹Institut de Robòtica i Informàtica Industrial (CSIC-UPC), C. Llorens i Artigas 4-6, 08028 Barcelona, Spain

²Institut de Recerca en Energia de Catalunya, Jardins de les Dones de Negre 1, 08930 Sant Adrià de Besòs, Spain

(*) Corresponding author: maserra@iri.upc.edu

Keywords: Dynamic modelling, Solid Oxide Electrolyzer, Hydrogen leak estimation

1. Introduction

Solid Oxide Electrolyzers (SOEC) are electrochemical devices that produce hydrogen from water using the energy of an electric power source. SOEC operate at high temperatures (around 800°C) and have efficiencies around 53% [1]. One of the most interesting scenarios of SOEC use is the storage of energy in hydrogen form when renewable power sources do not match the load. Because of this, it is important to study the dynamic behavior of SOEC systems in order to know their ability to adapt to changing power profiles. Different works describe SOEC models in the literature, as reviewed in [2], but time dependent models are scarce [3] and very few of the models are experimentally validated. This work presents a dynamic model of a SOEC implemented in MATLAB Simulink and its match with experimental data.

One important issue in SOEC stacks is hydrogen leak, which aggravates with ageing and is mostly caused by the high operating temperatures. The analysis of the experimental data of this work suggested hydrogen leak. Based on the SOEC thermal model, a methodology to quantify the flow of hydrogen that is leaked out is proposed and applied to the experimental system.

2. Experimental

2.1 Experimental setup

The SOEC system studied is a 700W open oxygen electrode and fuel electrode supported stack by SOFCMAN. It has 30 cells and an active area of 65 cm². The stack is installed into an insulation oven with temperature control in the Institut de Recerca en Energia de Catalunya (IREC) laboratories.

2.2 Experimental curves

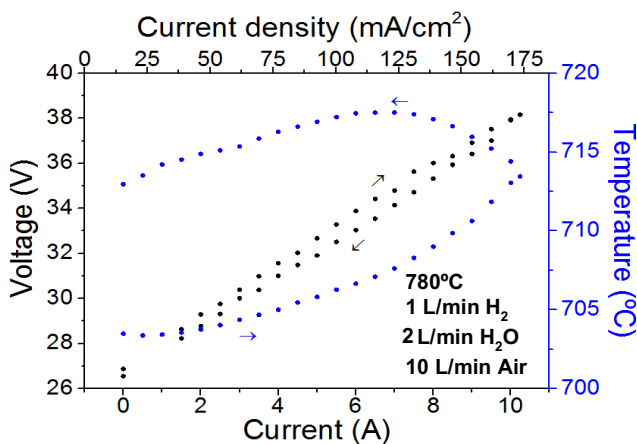


Figure 1. Polarisation curve of SOEC at 780°C

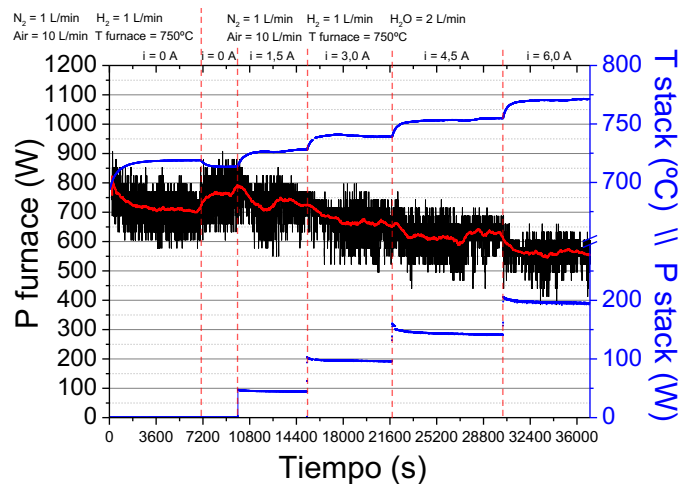


Figure 2. Polarisation curve of SOEC at T=750°C

Fig. 1 shows polarisation curves at 750 and 780°C respectively. In Fig. 1, temperature has a non-expected behavior which is the increase of temperature with current in the endothermic zone (low currents). The hypothesis is that this behavior is caused by an hydrogen leak.

3. Model description

The SOEC model is divided in three parts: fluid dynamics, electrochemistry and heat transfer.

3.1 Fluid Dynamics

A mass balance equation is done over any volume unit and Darcy's law is applied to these volumes:

$$\dot{m} = k\Delta P \quad \text{eq. 1}$$

where \dot{m} is the mass flow inside the volume, and ΔP is the pressure difference between the outlet pressure and the pressure inside the volume.

3.2 Electrochemistry

To obtain the voltage of the stack, the voltage of each cell is calculated first with the following equation:

$$V_{cell} = V_{nerst} + V_{act} + V_{ohm} + V_{con} \quad \text{eq. 2}$$

where V_{nerst} can be calculated as follows:

$$V_{nerst} = \frac{\Delta G}{nF} + \frac{R_g T}{nF} \ln \left(\frac{P_{H_2} \sqrt{P_{O_2}}}{P_{H_2O}} \right) \quad \text{eq. 3}$$

and where ΔG is the free energy of Gibbs increase, n is the number of electron moles transferred in the reaction, R_g is the universal gas constant, T is the temperature of the cell, F is the Faraday constant and P_{H_2} , P_{O_2} , P_{H_2O} are the partial pressures of hydrogen, oxygen and steam respectively.

The activity voltage loss is:

$$V_{act} = \sum_i \frac{R_g T}{nF} \sinh^{-1} \left(\frac{J}{2\gamma_{ie} \left(\frac{E_{act,i}}{R_g T} \right)} \right) \quad \text{eq. 4}$$

where J is the current density applied to the cell.

The ohmic voltage loss can be calculated as the current density multiplied by the ohmic resistance k_Ω as follows:

$$V_{ohm} = J \cdot k_\Omega \quad \text{eq. 5}$$

Finally, the concentration voltage loss is divided into the anode and cathode side contributions:

$$V_{con} = \frac{R_g T}{nF} \ln \left(\frac{\left(1 + \frac{JR_g T \delta_c}{2FD_{H_2O}^{eff} P_{H_2}} \right)}{\left(1 - \frac{JR_g T \delta_c}{2FD_{H_2O}^{eff} P_{H_2O}} \right)} \right) + \frac{R_g T}{nF} \ln \left(\sqrt{1 + \frac{JR_g T \delta_a}{4FD_{O_2}^{eff} P_{O_2}}} \right) \quad \text{eq. 6}$$

where $D_{H_2O}^{eff}$ and $D_{O_2}^{eff}$ are the effective steam and oxygen diffusion respectively, δ_c is the cathode thickness, and δ_a is the anode thickness.

3.3 Heat transfer

An energy balance equation has been done over the SOEC. To calculate the temperature of the stack, the first thermodynamic principle is applied:

$$T_{stack} = \int \frac{1}{M_{stack} \cdot k_{stack}} \cdot (\dot{Q}_{reaction} + \dot{Q}_{gas} + \dot{Q}_{losses} + P_{furnace}) dt \quad \text{eq. 7}$$

where M_{stack} is the mass of the stack and k_{stack} is the thermal conductivity of the stack. $\dot{Q}_{reaction}$ is the heat of the electrochemistry reaction corresponding to the electrical power injected to the system; \dot{Q}_{gas} is the convective heat due to the circulating gases inside the stack; \dot{Q}_{losses} is the heat lost through the oven walls; and finally, $P_{furnace}$ is the furnace electrical power, which is the heat injected into the stack.

3.4 Hydrogen leakage estimation

One of the main problems of a SOEC system is hydrogen leak. Being the SOEC nominal operating temperature higher than that of hydrogen autoignition, if there is a hydrogen leak, this hydrogen combusts and becomes a new source of heat. The heat of the combusted hydrogen is assumed:

$$\dot{Q}_{heat H_2} = \dot{m}_{H_2} LHV_{H_2}$$

where \dot{m}_{H_2} is the mass flow of the hydrogen leaked out and LHV_{H_2} is the hydrogen Lower Heating Value. To implement the hydrogen leak in the model, it is assumed that the partial pressure of hydrogen in the catalyst layer is not changed due to the leak and therefore, the voltage is not affected.

4. Model validation

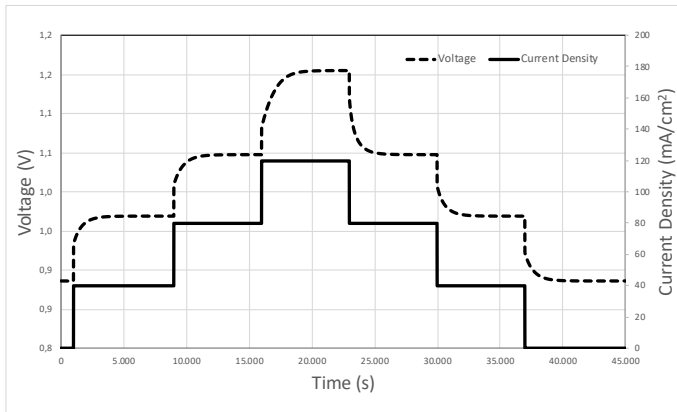


Figure 3. Dynamic polarisation curve from model

5. Results and Discussion

Since the thermal model has been adapted to consider the heat produced by hydrogen combustion, it has been possible to estimate the flow of hydrogen leaked out. The proposed strategy is to compute the stack temperature with the model and compare the measured temperature with the modelled one. Despite the thermal model has not been validated, each one of the heats of equation 7 is determined or validated separately: $\dot{Q}_{reaction}$ and $P_{furnace}$ are known, \dot{Q}_{gas} is computed assuming that outlet gases are at stack temperature and the losses through the oven walls are obtained with a dedicated experiment. An estimation of the hydrogen leak is done, as indicated in Figure 4.

Figure 3 shows the simulated dynamic evolution of voltage caused by different current steps. Operating conditions are the same as in Fig. 1: the same inlet flows and an operating temperature of 708 °C. The correspondence with the experimental voltage in value and time validates the electrochemical and fluid dynamic models. On the contrary, it has not been possible to validate the thermal model completely as temperature behavior is found to be greatly affected by the environment.

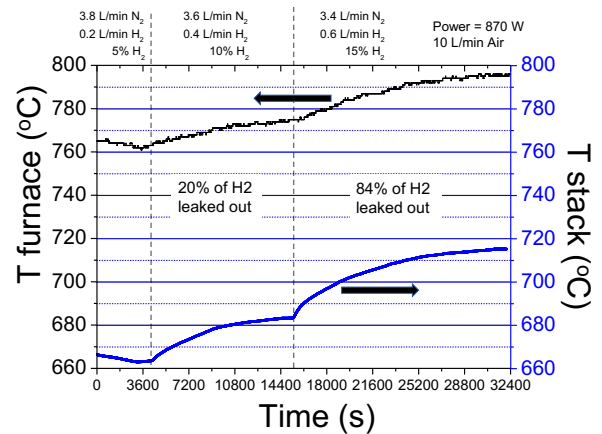


Figure 4. Experimental test for H₂ leak estimation

6. Conclusions

This work presents a SOEC fluid dynamic and electrochemical model experimentally validated. The different heat sources have been determined separately. Complementary, the work explains and applies a methodology to estimate the hydrogen leaks, based on the model.

Acknowledgements

This work was done with the support of ACCIÓ (Operational Program FEDER Catalunya 2014-2020) through the COSIN project (ref. COMRDI15-1-0037-06), the Spanish national project MICAPEM (ref. DPI2015- 69286-C3-2-R, MINECO/FEDER) and the Spanish State Research Agency through the María de Maeztu Seal of Excellence to the Institut de Robòtica i Informàtica Industrial (MDM-2016-0656).

References

- [1] A. A. AlZahrani, I. Dincer, Thermodynamic and electrochemical analyses of a solid oxide electrolyzer for hydrogen production, *International Journal of Hydrogen Energy*, 42 (2017) 21404-21413.
- [2] J. P. Stempien, Q. Sun, S. H. Chan, Solid Oxide Electrolyzer Cell Modeling: A Review, *Journal of Power Technologies* 93 (2013) 216–246.
- [3] J. Udagawa, P. Aguiar, N. P. Brandon, Hydrogen production through steam electrolysis: model-based dynamic behaviour of a cathode-supported intermediate temperature solid oxide electrolysis cell, *Journal of Power Sources*, 180 (2008) 46–55.