Parameter fitting of a reversible Solid Oxide stack model

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In this work, the fitting of five parameters of a Reversible Solid Oxide (RSO) stack model is done based on data obtained at different conditions of operation. Two types of experimental curves are used: polarization curves and sweeps. The system suffered a degradation and the analysis has permitted to study which one of the parameters was affected, indicating which part of the stack was damaged.

System description and stack model

The stack used in this work, is a 30-cell standard Solid Oxide stack produced by SOFCMAN, open cathode, composed of anode-supported cells with Ni-YSZ interconnects and sealing materials. An experimental station at Catalonia Energy Research Institute (IREC) was available to obtain the data used in this work.

The model used is a simplified version of a more complete zero-dimensional model used in previous works [1]. The model is isothermal and steady state. It has mainly two blocks: the mass flow model and the electrochemical model. The Nernst voltage and the activation, concentration and ohmic polarizations are considered. The parameters selected to be fitted can be seen in Table 1. They are part of equations 1 to 4, which correspond respectively to the exchange current densities in fuel and air sides, ohmic losses and effective diffusivity coefficient of specie *i*.

Parameter	Description	Initial Value	Units
γ_F	Phenomenological coefficient (Fuel side)	600000	A·cm-2
γ_A	Phenomenological coefficient (Air side)	415500	A·cm-2
ASR	Area-Specific Resistance	0,165	Ω·cm2
τ_F	Fuel side tortuosity	8,76	-
τ_A	Air side tortuosity	13,47	-

Table 1. Estimated parameters

$$i_{o,F} = \gamma_F \cdot \left(\frac{P_{H_2}}{P_{ref}}\right)^1 \cdot \left(\frac{P_{H_2O}}{P_{ref}}\right)^1 \cdot e^{\frac{-E_{act_F}}{RT}} \quad (1)$$

$$i_{o,A} = \gamma_A \cdot \left(\frac{P_{O_2}}{P_{ref}}\right)^{0,25} \cdot e^{\frac{-E_{act_A}}{RT}} \quad (2)$$

$$\eta_\Omega = j \cdot ASR \quad (3)$$

$$D_i^{eff} = \frac{\varepsilon_x}{\tau_x} \cdot D_{ij} \quad (4)$$

$$RMSE = \sqrt{\frac{\sum_{n=1}^{N}(\hat{v}_n - v_n)^2}{N}} \quad (5)$$

where P_x is the partial pressure of gas x in bar, P_{ref} is equal to 1 bar, E_{act} are the activation energies, R is the ideal gas constant, T the temperature, j the current density, ε_x the electrodes porosity and D_{ij} the binary diffusivity coefficient.

It must be noted that, to make the search space smaller and allow better performance of the optimization methods, $\log(\gamma_A)$ and $\log(\gamma_C)$ were used during optimization instead of γ_A and γ_C.

Methodology

The work is based on experimental data obtained in the form of polarization curves and sweeps. The polarization curves last for some hours because several minutes must be spent at each current setpoint to allow the stack to reach steady state. Ten polarization curves were performed, five in fuel cell mode and five in electrolizer mode. Different conditions of hydrogen, air and water utilizations, nitrogen and temperature were controlled. Moreover, the last curves were performed after an important degradation occurred. Current was increased step by step until the voltage was equal or smaller than 22 V, and then it was decreased until zero again. The number of steps in each polarization curve varied from 11 to 13. For the current sweeps, which only take some few minutes, all operating conditions were kept constant. The current rate of change was set to 40 A/min. Six sweeps were performed, three in fuel cell mode and three in electrolizer mode. Different conditions of hydrogen, air and water flows, nitrogen and temperature were controlled.

Particle swarm optimization (PSO), described in [3], was the global optimization method used for the parameter estimation based on the Polarization Curve data. Experimental and simulated stack voltage were compared assuming a constant temperature throughout the experiment. The real system presents a certain hysteresis during a round-trip experiment, but the model used is not able to represent this phenomenon. For this reason, only the increasing current

curves were considered in the objective function, shown in equation 5, where $RMSE$ is the Root Mean Square Error, $\hat{v}_n$ is the estimated voltage for a certain current, v_n is the experimental voltage for the same current, and N is the total number of current points of the curve. The programmed optimization algorithm initialized 30 particles (sets of 5 parameters) and distributed them in the search space, also giving them a random initial velocity. The objective function cost was analyzed, and the local and global best positions were updated. Then, the particles moved iteratively according to the PSO algorithm, updating their cost every iteration, until they converged to a global solution.

When doing the parameter fitting based on single polarization curves, each one at its operating conditions, ASR values were very dispersed. Then we changed of strategy and did the parameter fitting based on all the curves at the same time. Since ASR is the only parameter that has a linear effect on the polarization curve, it was decided to determine it first, separated from the other 4 parameters. This was done by applying the PSO algorithm to only the linear part of the polarization curve (current between 7 A and 18 A for both fuel cell and electrolizer modes) and based only on curves made at low utilization (SOFC – 40% FU, SOEC – 40% RU), to have the least impact in the polarization curve due to other losses. Then, by analyzing these selected curves, the resulting ASR value at 750ºC was found to be 0,7252 Ω·cm2. The other 4 parameters were determined using the PSO algorithm with ASR fixed at the previously determined value.

The large amount of data points in a single sweep experiment made parameter estimation with the PSO algorithm impossible. Therefore, to estimate parameters based on these curves, the Simulink Parameter Estimation tool was used. The tool allowed various sweep experiments to be analyzed at a time, achieving a single solution (set of 5 parameters) for each estimation. A pattern search method with a genetic algorithm was chosen due to its similarity to the PSO algorithm used in polarization curve analysis. Due to the largest air flow with respect to the polarization curves, the sweeps were done at a lower temperature. The effect of this change in temperature was included into the model.

Results and conclusions

When performing the parameter fitting, several conclusions have been reached. First of all, the parameters found based on data obtained in fuel cell mode and electrolizer mode were similar. Also the parameters found based on data of different curves, each one with its particular operating conditions, were similar. Therefore, all data was used at the same time to minimize the objective function. In Table 2 the different values found are indicated. When comparing parameters obtained with polarization curves and sweeps (rows one ant two) we can conclude that most of the parameter's values do not depend importantly on the type of curve used. Only the ASR changes significantly, which should be further studied. Comparing the parameters obtained before and after degradation (rows one and three) it is seen that the tortuosity of both electrodes has changed drastically. This indicates that the occurred failure damaged the electrodes properties.

Name	Temp	Deg.	γ_F	γ_A	ASR	τ_F	τ_A	Cost
6 PolCurves Before degradation ELECTR.+FC	750ºC	No	$10^{6,347}$	$10^{6,740}$	0,7252	6,799	12,085	0,554
6 sweeps Before degradation ELECTR. + FC	≈729ºC	No	10^{6}	$10^{6,5}$	1,179	7	13	0,218
4 Pol Curves After degradation ELECTR.+FC	750ºC	Sí	$10^{6,38}$	$10^{7,4}$	1,113	11	1	0,565

Table 1. Estimated parameters

References

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