

Using equivalent circuit models in understanding the performance change of metal supported SOFCs in static and dynamic conditions

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Abstract

The current paper attempts to use equivalent circuit diagrams to simulate impedance spectra of metal supported SOFCs. Measured electrical impedance spectroscopy data on full cells was fitted to an equivalent circuit with the aim to evaluate the contribution of each functional layer towards the ASR (area specific resistance) of the cell separately. Further, the suitability of equivalent circuit diagrams to predict changes in cell behaviour due to alteration in electrodes was investigated. For that purpose, two approaches were opted. First one consisted of replacing LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$) cathode with LSCF ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$) cathode whereas second comprised of redox cycling of cells provoking degradation in anodes and overall performance of the cells. Not only was the break down of the losses underlined, but also the limiting factors in the performance of metal supported cells were studied.

Introduction

Independent of the type and size of the fuel cell, it has been proven several times that microstructure and the content of impurities within the functional layers of the electrochemical cells have the most significant effect on its performance. In evaluation of the performance one of the most commonly used method is scanning the fuel cell starting from the open circuit voltage to its maximum power in steps using an electronic load and the resulting curve is named as polarisation curve. Moreover electrochemical impedance spectroscopy (EIS) is used in order to further characterize the electrode processes and complex interfaces. This method can be used as a diagnostic tool in understanding the reactivity and structure of the interface and also the mass transport limitations which actually effect the displayed performance of the system in the end [1]. Therefore in order to understand and optimize the system EIS is very useful instrument in pinpointing the limiting processes.

The vast majority of studies in understanding the discrete processes taking place at the functional layers of the fuel cells have been vastly performed on symmetrical cells or by using reference electrodes. These kinds of cells have to be produced in a special way different than the full cell which in the end results in different microstructure and cell performance. Moreover the tests with symmetric cells are usually done at open circuit condition which limits the analyses to a non-operating electrode. Therefore it can not be expected that the results of such measurements to be correlated with full cell response. That is why we intend to perform our work on full cells. Such an attempt has already been

made and presented by Barfod [2] and Hendriksen [3] on anode supported SOFCs. In this paper we intend to divide and define the losses emerging from various contributions of processes taking place in metal supported cells produced at DLR using equivalent circuit diagrams. In this analysis of experiments using equivalent circuits it is assumed that the current distribution within the bulk is frequency independent (or, in other words, the meaning of the equivalent circuit elements is invariant over the entire frequency range) [4].

In this approach the fuel cell is represented in an electrical circuit consisting of resistors, capacitors and similar elements with the assistance of commercially available software (Zahner GmbH). Afterwards the measured spectra are fitted to this equivalent circuit after several runs of the simulation. Once the plot of the measured data and the fitted curve of the circuit overlap it may be taken as a confirmation of the representability of the full cell. Although even a perfect fit might not be enough to validate the equivalent circuit model to a full extent [5], we believe that for our purpose of defining the discrete processes at the functional layers and proceed with optimization of the production properties this approach is a valid tool to start with.

Experimental

Electrochemical Testing

Electrochemical testing of two circular SOFCs, 48 mm in diameter with an effective area of 12.6 cm², was performed in a ceramic housing and connected by meshes and wires made of platinum. Following the fabrication of the cells by plasma spraying, 15 µm thick LSM or LSCF paste was screen printed onto it as connecting layer along with a fine (3600 mesh/cm²) mesh of platinum current collector. The cell was placed between the ceramic gas distribution sockets for the anode and the cathode. Coarse meshes on each side of the cell, welded with wires, served as current collector. Two additional wires were used for the voltage measurement between the electrodes. The anode gas (fuel) chamber was isolated by sealing with gold ring and glass sealant (by IKTS, Dresden). Sealing was completed by heating the system for 5 hours at 900°C, flushing the anode with 5% hydrogen in argon and air at the cathode side. Oxidizing gas was fed in similar way to the cathode. In order to have comparable results, cells were tested in similar operating conditions for about 200 hours by 200 mA/cm² loading at 800°C with a gas flow of 0.5 slm H₂ + 0.5 slm N₂ at the anode side and 2 slm air at the cathode side. The continuous loading was interrupted for measurements of i-V behaviour and impedance spectroscopy in order to define the change in the state of the cell.

Redox Cycling

After removing the electrical load from the cells, they were flushed with nitrogen in order to avoid any explosive atmosphere in the gas piping. After that oxygen was supplied to the anode side of the cell in order to oxidize the Ni at the anode electrode to Ni-O. The cells were flushed once again with nitrogen and then hydrogen was supplied to the cells for the reduction of Ni-O back to Ni. After the first, fifth, tenth, fifteenth and twentieth redox cycles, cell performance was measured together with the impedance response.

The measured impedance spectra data was fitted using the circuit representing the cells as displayed below in Figure 1. Here the RC (1-2, 6-7) elements together with the porous component (3 and 8) represent the electrodes of the fuel cell. Whereas, the third RC element (9-10) illustrates the Nernst-impedance (Gas conversion impedance) within the

cell. Besides, the serial resistance (4) and the inductive element (5) stand for the ohmic resistance within the cell and the parasitic wiring inductance resulting from the connections of the measurement equipment to the cell.

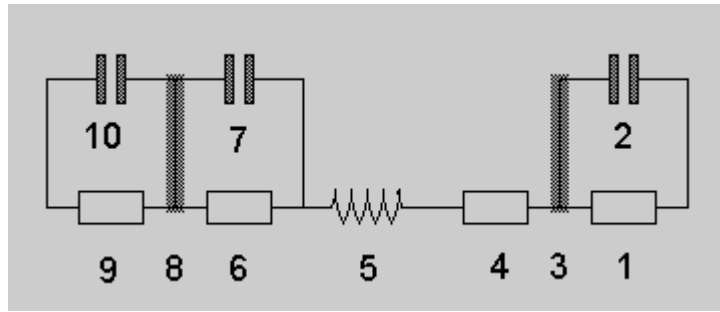


Figure 1: Equivalent circuit of the SOFC including Nernst-impedance and porous electrode model.

Results and Discussion

Electrochemical performance under fuel cell conditions

At the first evaluation step the gas tightness of the two cells was recorded. Measured gas leak through the cells at room temperature was reported to be quite similar. Gas leak rate of $3.43 \cdot 10^{-3}$ mbar.l/cm².s for LSM and $3.91 \cdot 10^{-3}$ mbar.l/cm².s for LSCF at 100 mbar pressure difference were recorded. As it was expected, the measured open circuit voltages at the same operating conditions were quite close, see Figure 2. This can be attributed to the comparability of the gas tightness of both electrolytes.

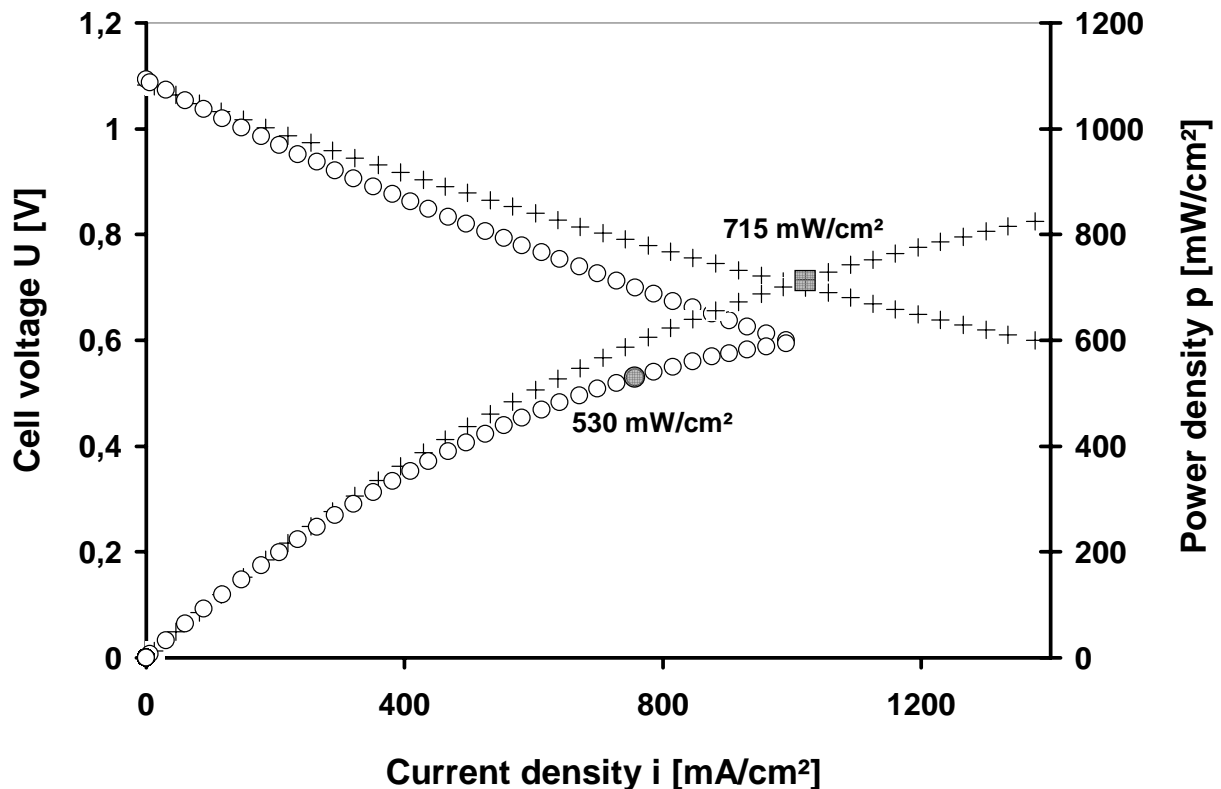


Figure 2: Polarisation curve comparison of the two cells with LSCF and LSM cathode respectively. The measurement was performed at 800°C with a gas supply of 1.0 slm H₂ and 2.0 slm of air.

As it was proven that the cells are comparable, they were mounted in a SOFC test rig to be tested. Due to its relatively high electronic and ionic conductivity, the cell with LSCF cathode exhibited 715 mW/cm² at 0.7 V at 800°C, while supplied with hydrogen and oxygen. This was 35 % higher in power density than the cell with LSM cathode.

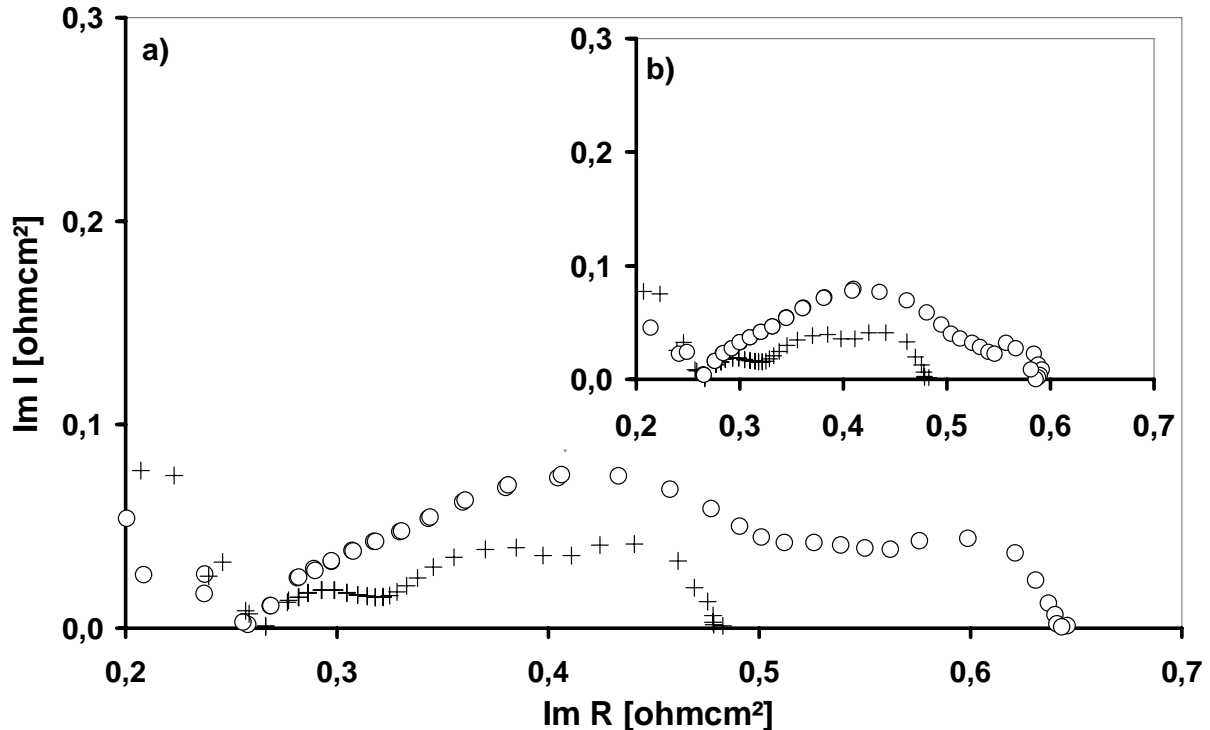


Figure 3: Electrochemical impedance spectra recorded right after each polarization curve displayed in Figure 2 (a) unloaded and (b) loaded at 200 mA/cm² with the same operating conditions with LSM (O) and LSCM (+) cathodes

The major difference in the cell performances can be better understood when examining the related impedance measurements in unloaded and loaded conditions. As seen in Figure 3 when unloaded, during which the activation polarization prevails in the total cell resistance, the measured resistance of LSM cathode is 33 % higher than with LSCF, whereas, at loaded conditions, the resistance of LSM cell is only 21 % higher than LSCF. This can be attributed to the higher activation energy necessary for the reactions to take place when the cathode material is LSM.

The cell impedance was measured at 800°C with a gas supply of 1.0 slm H₂ and 2.0 slm of air while increasing the current density of the cell by 50 mA/cm² steps until 800 mA/cm² and 900 mA/cm² loading. After fitting the measured data to the described circuit displayed in Figure 1, it was found out that a clearly separated contribution of the related cell components was possible to be displayed. As the very difference between the two cells was that they had two different cathode materials it was relatively easy to differentiate the contribution of each electrode. In Figure 4 above the splitted impedances from different functional layers at different current densities can be seen in detail.

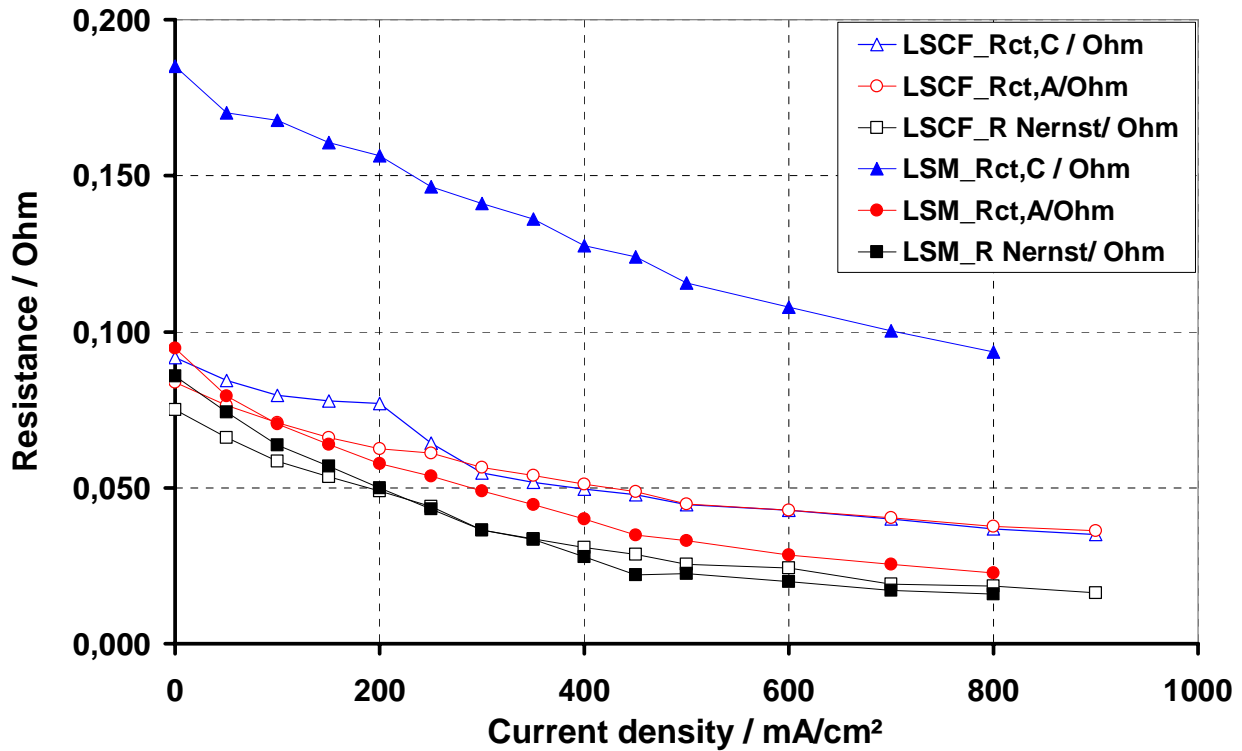


Figure 4: Contribution of the anode, cathode and Nernst impedances along the current density obtained by fitting the measured impedance spectra to the circuit as displayed in Fig. 1. All measurements were performed at 800°C with a gas supply of 1.0 slm hydrogen and 2.0 slm of air.

In the table below the improvement achieved by the development of the cell with the LSCF cathode has been calculated. The average improvement of 60 % was recorded in the measurements.

Table 1: Cathode contribution to the total cell impedance at each loading

Current density /mA/cm²	Cathode Impedance / Ohm*cm²		Improvement / %	Current density /mA/cm²	Cathode Impedance / Ohm*cm²		Improvement / %
	LSM	LSCF			LSM	LSCF	
0	0.185	0.084	54.732	350	0.136	0.054	60.397
50	0.170	0.076	55.115	400	0.128	0.051	59.901
100	0.168	0.071	57.813	450	0.124	0.049	60.689
150	0.161	0.066	58.905	500	0.116	0.045	61.257
200	0.156	0.063	59.976	600	0.108	0.043	60.289
250	0.146	0.061	58.258	700	0.100	0.040	59.667
300	0.141	0.056	59.955	800	0.094	0.038	59.825

After 200 hours of static operation the cells were exposed to 20 reduction and oxidation cycles as explained before. The open circuit voltage decreased only slightly during the cycles for both cells. The cell with an LSM cathode could perform the same power even after the 15th cycle although it was much lower than power exhibited by LSCF cell. On the other hand LSCF showed a drastic decrease in its performance already after 5th cycle. This proves on one hand the different response of cells with different materials.

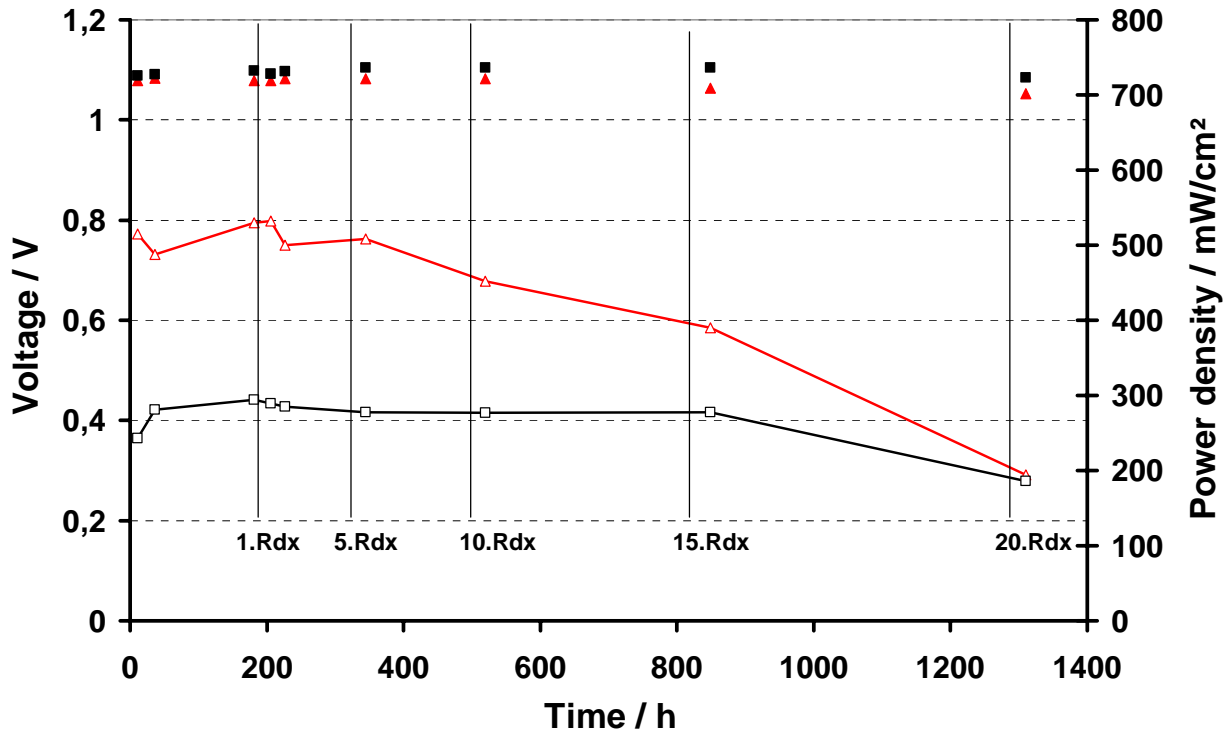


Figure 4: Effect of 20 reduction-oxidation (Rdx) cycles on open cell voltage and power density at 800°C with a gas supply of 1.0 slm hydrogen and 2.0 slm of air.

Conclusion

The performance of the metal supported fully plasma sprayed SOFCs which has been improved by 35 % at 800°C by changing the perovskite-type cathode material from LSM to LSCF. This has been achieved by adapting the plasma spraying parameters in the manufacturing process. Using an equivalent circuit and fitting the measured electrochemical impedance spectra at different operating times and conditions of the cell it was made possible to split the discrete contributions of the functional layers. The contribution of the improvement in the cathode layer was found to be around 60 % decrease of its polarisation resistance which in turn resulted in the increase of the performance.

References

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