

Thermal Cycling Stability of Electrolyte Supported Cells

A. Glauche^a, T. Betz^a, S. Mosch^b, N. Trofimenko^b and M. Kusnezoff^b

^a Kerafol GmbH, Eschenbach i.d. Opf. 92676, Germany

^b Fraunhofer Institute for Ceramic Technologies and Systems, Dresden 01277, Germany

The electrolyte supported cells with low area specific resistance (ASR < 0.34 Ωcm²) have been tested for thermal stability in ceramic housing. It has been shown that the cells with optimized anode microstructure have no measurable resistance change in the range of mistake of used method after ten thermal cycles. The small fluctuation of contact resistance between anode and current collector has been observed due to direct influence on the bonds between anode and current collector during cycling experiments.

Introduction

The robustness of SOFC systems against thermal cycling and accident events such as load throw-off, abrupt cooling down and anode oxidation because of the interrupt of fuel supply lead to requirements in respect to the thermal and redox cyclability of the stacks.

Ageing of cell properties during operation is generally not desired. The main degradation effects during the long-term operation and redox cycling take place in the anode. The reasons for the degradation of the anode in contaminant free fuel are:

- (i) Ni-agglomeration
- (ii) Mechanical stresses induced by thermal, load and redox cycles.

The Ni-agglomeration during operation and redox cycling generally can not be avoided. The agglomeration rate can be reduced to acceptable level by using ZrO₂/NiO composites.

It has been demonstrated that the long-term degradation at high current densities can be reliably solved for electrolyte supported cells operating at 850°C (1). The goal of the carried work was to optimize the electrode (microstructure) to sustain the thermal cycling.

Experimental

The lanthanum strontium manganite (La_{0.75}Sr_{0.2}MnO_{3-x}, uLSM), Y₂O₃ stabilized ZrO₂ (YSZ), Sc₂O₃ stabilized ZrO₂ (ScSZ) and NiO powders used in this work were supplied by different manufacturers, according to given specifications for the stoichiometry, crystalline phase, specific surface and particle size distributions.

The cathode pastes based on the uLSM/ScSZ composite were fabricated by a method which is described elsewhere in detail (1, 2).

The pastes based on the NiO-YSZ cermet powder were prepared by mixing with organic binder, organic solvent and surface active additives.

For screen printing dense 10Sc1CeSZ tapes (50x50x0.150mm³) were used as substrate material. All electrochemical experiments were carried out on cells with symmetrically screen-printed cathode and anode having lateral dimensions of 40x40 mm². For each experiment the cells are manufactured under similar conditions.

The cathode layer (45 μm) is composed of lanthanum strontium manganite (La_{0.75}Sr_{0.2}MnO_{3-x}, uLSM) and ScSZ.

The anode layer is electrochemically active cermet anode. The anode and cathode are sintered in co-firing at 1300°C.

The morphology of the studied electrodes is observed using field emission scanning electron microscopy.

All electrochemical experiments were carried out using the testing bench for MEA characterization at Fraunhofer IKTS, Dresden. The apparatus consists of a custom-built ceramic housing integrated in a furnace operated by a temperature controller enabling the temperature-time profile management up to 1100°C. Pt and Ni meshes were used as contact material for cathode and anode respectively.

The SOFC cells were characterized by impedance spectroscopy under current load at temperatures of 850-950°C in air:hydrogen/steam dual atmosphere using impedance analyzer IM6 (Zahner, Germany). The frequency was varied between 10 mHz and 100 kHz, the excitation AC voltage was fixed at 10 mV. The contributions of anode, cathode and electrolyte in the overall resistance are extracted from impedance spectra using Thales® Software (Zahner, Germany) and adequate equivalent circuit by deconvolution of impedance spectra.

Thermal cycling test

The cell is first heated up to 950°C in nitrogen and then reduced. The air flow of 60 nl/h and hydrogen:steam flow of 40 nl/h are fed to the cell resulting in the open circuit voltage of 892 mV at 950°C. The current-voltage characteristics are measured at 950°C and 900°C to validate the cell performance. Afterwards the cell is cooled down to operation temperature of 850°C and the current density of 650 mA/cm². Before thermal cycling treatment the cell has been operated for 200h at 650 mA/cm² to pass the activation phase reported (3). The thermal cycling between 850°C and 500°C is made with 2 K/min in ceramic (Al₂O₃) housing. The conditions for 10 thermal cycles are summarized in Table I.

TABLE I. Experimental conditions for 10 thermal cycles.

Step	Duration
Cooling down to 500°C	2 K/min
Hold at 500°C	3,5 h
Heating up to 850°C	2 K/min
Hold at 850°C	3,5 h
Operation at 850°C @ 650 mA/cm ²	12 h

After each thermal cycle the cell has been operated for 12h at 650mA/cm² before the current-voltage characteristic with 0,2A/min up to 10,4 A and impedance spectra have been measured. The ASR of the cell has been corrected to fuel utilization and calculated using following equations:

$$\hat{U}_{Nernst} = U_{Nernst,0} + \frac{R \cdot T}{2F} \left(\ln \frac{\dot{n}_{H_2,0} - 0,5 \cdot \frac{I}{2F}}{\dot{n}_{H_2O,0} + 0,5 \cdot \frac{I}{2F}} + 0,5 \left(\ln \frac{\dot{n}_{O_2,0} - 0,25 \cdot \frac{I}{2F}}{\dot{n}_{Luft,0} - 0,25 \cdot \frac{I}{2F}} \right) \right) \quad [1]$$

with I - current, T - temperature, R – universal gas constant, F – Faraday constant, $U_{Nernst,0}$ – open circuit voltage without current flow, $\dot{n}_{H_2,0} = X_{H_2,0} \dot{n}_{fuel,0}$ - hydrogen flow rate, $\dot{n}_{H_2O,0} = X_{H_2O,0} \dot{n}_{fuel,0}$ - steam flow rate, $\dot{n}_{O_2,0} = X_{O_2,0} \dot{n}_{Luft,0}$ - oxygen flow rate.

and

$$ASR_{korr} = \frac{\hat{U}_{Nernst} - U_{Cell}}{I / A_{Electrode}} \quad [2]$$

The relative error of ASR value calculated from current-voltage characteristic is $\pm 2,7 \%$.

Results and Discussion

The optimization of the anode has been made to provide the intact and stable anode microstructure. The ASR at 850°C of cells manufactured using optimized technology of paste preparation, screen printing and sintering are shown in Table II. The thermal cycling stability of one cell has been tested.

TABLE II. Reproducibility of ASR by different MEA lots.

MEA	temperature [°C]	j [mA/cm ²]	R _{zelle} [Ωcm ²]
579	851	725	0.286
584	851	741	0.28
603	851	700	0.297
640	851	750	0.277
687	850	747	0.278
703	851	684	0.303
549	850	715	0.292
146	853	696	0.292
145	854	723	0.289
104	850	728	0.285
693	851	650	0.317
694	851	679	0.306
697	854	667	0.308
705	854	680	0.303
641	853	699	0.302
642	855	732	0.289
678	854	716	0.291
691	853	711	0.293
695	853	727	0.284
707	856	652	0.319

Thermal cycling test

The results of thermal cycling of the cell in ceramic housing are shown in Fig. 1. It was found that the temperature of the cell in the housing can not be exactly reproduced from cycle to cycle. The temperature varies also during current-voltage characteristics measurement because of heat production at high power densities. This leads to the scattering of measured ASR values. The clear correlation of low ASR values to higher operation temperatures is observed.

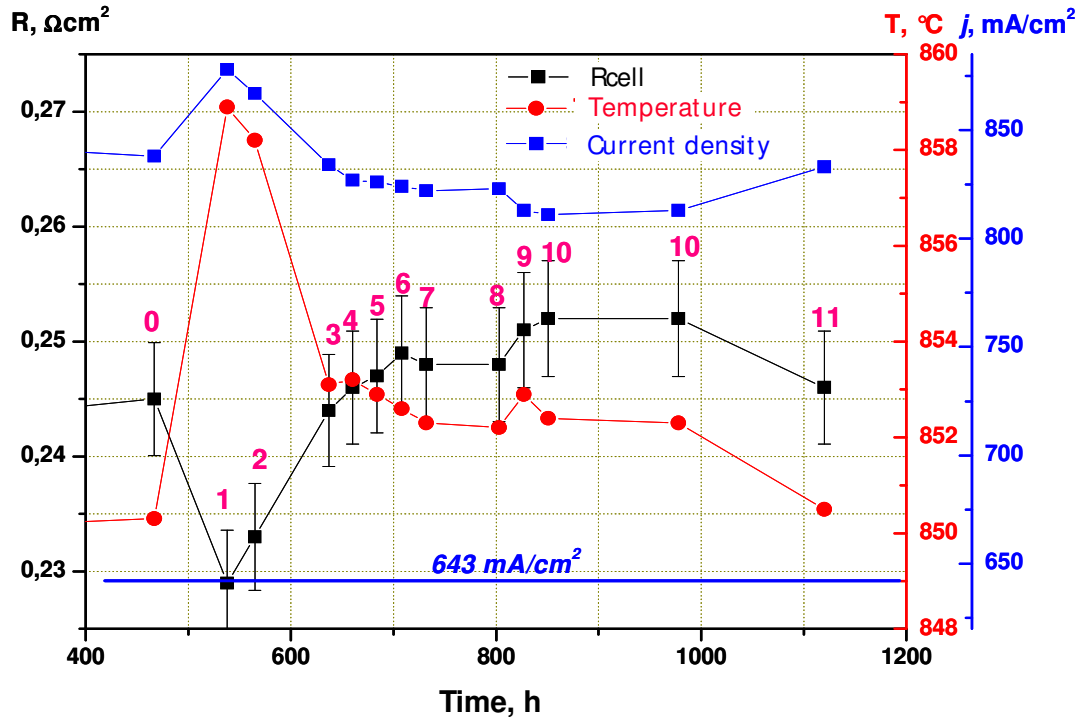


Figure 1. MEA stability during thermal cycling.

The results of impedance measurements (Fig. 2) show that the change of ASR values is mainly caused by change of high frequency part of impedance spectra (= R_{ohm}). The absolute value of observed change in high frequency part of impedance is 1.25 mΩ and can be attributed to the change of the electrolyte or contact resistance. Due to reliable contact on the cathode side only anode contact can be affected by cycling. To clear whether the contact or electrolyte resistance has an impact on ASR degradation the cell is cooled down to room temperature and initialized. It has been seen that after activation procedure the cell reaches the starting ASR value. It means that the contact resistance between anode and nickel current collector is mainly affected by thermal cycles and not the resistance of the cell itself. The reason for this is the presence of mechanical stresses between the nickel current collector and the cell during the thermal cycling in ceramic housing. These stresses lead to the break of bonds between MEA anode and the nickel current collector. The healing of the contacts during/after cell reduction and activation at operating temperature takes place very slowly and probably depends on the annealing temperature. Annealing at higher temperature helps to achieve initial contacting area on the anode side more rapidly.

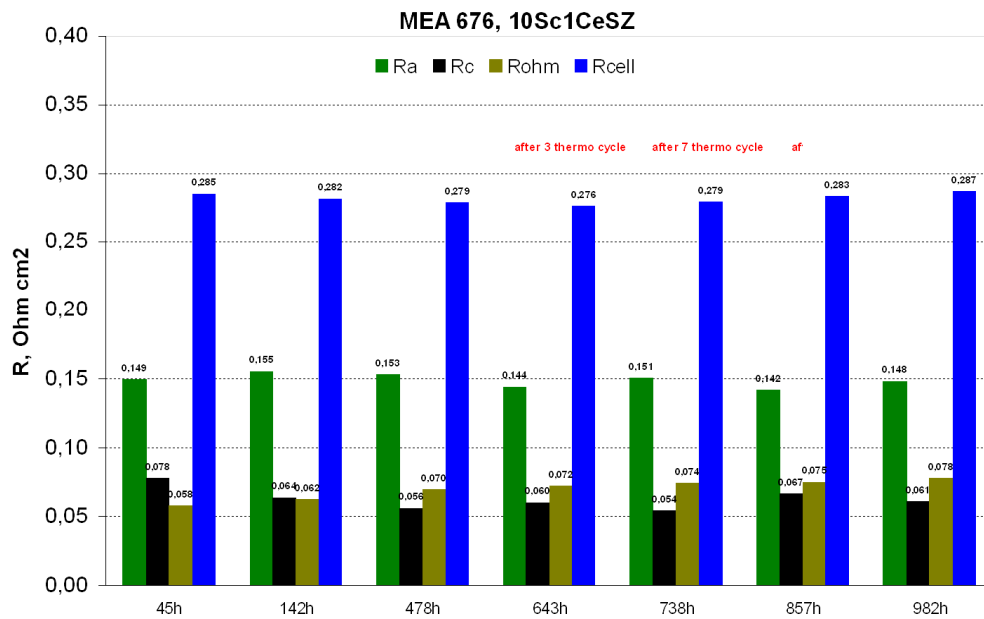


Figure 2. Constituents of ASR obtained by deconvolution of impedance spectra.

Conclusions

The thermal cycling stability of electrolyte supported cells can be achieved by optimizing the anode and has been demonstrated on the newly developed cells. No regular change of cell resistance was observed after thermal cycles. During measurement of the current-voltage characteristics the increase of cell temperature due to self heating at high current densities is observed. The measured ASR values correlate with cell temperature showing lower values at higher effective temperatures. The critical issue for thermal cycling in stack environment is the reproducible contacting of the anode to the current collector which should be addressed by proper choice of materials and supported by stack design.

Acknowledgments

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References

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