

Long-term Stability of Electrolyte Supported Cells

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The electrolyte supported cells with low area specific resistance (ASR < 0.34 Ωcm^2) have been tested for long-term stability in ceramic housing. It has been shown that the cells with optimized anode microstructure have degradation < 0.1 % / 1000h.

Introduction

A stable operation at high current densities (>300 mA/cm²) is a crucial issue for the application of MEAs in the stacks and systems. The inhomogeneous current distribution over the single cell in the stack, especially during self sustaining thermal operation, results in high local current densities, which can lead to accelerated cell degradation.

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 long-term stability test at high current densities.

Experimental

The lanthanum strontium manganite ($\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_{3-x}$, uLSM), Y_2O_3 stabilized ZrO_2 (YSZ), Sc_2O_3 stabilized ZrO_2 (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 ($50 \times 50 \times 0.150 \text{ mm}^3$) were used as substrate material. All electrochemical experiments were carried out on cells with symmetrically screen-printed cathode and anode having lateral dimensions of $40 \times 40 \text{ mm}^2$. For each experiment the cells are manufactured under similar conditions.

The cathode layer ($45 \mu\text{m}$) is composed of lanthanum strontium manganite ($\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_{3-x}$, 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 $850\text{--}950^\circ\text{C}$ 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.

Long-term stability test

The durability test is performed with current density of 650 mA/cm^2 in ceramic housing over 3.000 h in air / hydrogen:steam mixture (1:1). 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/cm^2 with corresponding fuel utilization of 21% is adjusted. During the long-term operation the load throw-offs, thermal cycles and redox cycles can occur and become part of the experiment. The measurement of the degradation is the change of the cell voltage at 650 mA/cm^2 during overall operation of the cell calculated from a linear fit of written voltage-time dependence. The accuracy of measurement of cell voltage during operation is $\pm 1 \text{ mV}$. The impedance of the cell is measured at the start and the end of the experiment as well as during current throw-off phases.

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 I. The long-term stability of one cell has been tested.

TABLE I. Reproducibility of ASR by different MEA lots.

MEA	temperature [°C]	j [mA/cm ²]	R _{cell} [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

Long-term stability test

The voltage change during the long-term stability test at 650 mA/cm² is shown in Fig. 1. The degradation rate calculated from linear fit of voltage-time dependence is 0.02%/1000h. The results of the analysis of impedance spectra before and after long-term operation are shown in Fig. 2. The ASR values obtained by impedance spectroscopy slightly differ from the values calculated from current-voltage curves. This effect has been discussed by X. Zhou et al. (4) and is partially caused by non-linearity of current-voltage characteristics (impedance spectra is a derivative of I-V-curve in operation point contrary to the ASR value calculated from whole range of current change). The decrease of the cathode polarization resistance due to formation of nanopores at the cathode/electrolyte interface (3) and slight increase of high frequency impedance which is a sum of electrolyte and contact resistance are observed. Decrease of the anode polarization resistance after thermal cycle and repeated reduction procedure after safety alarm has been observed.

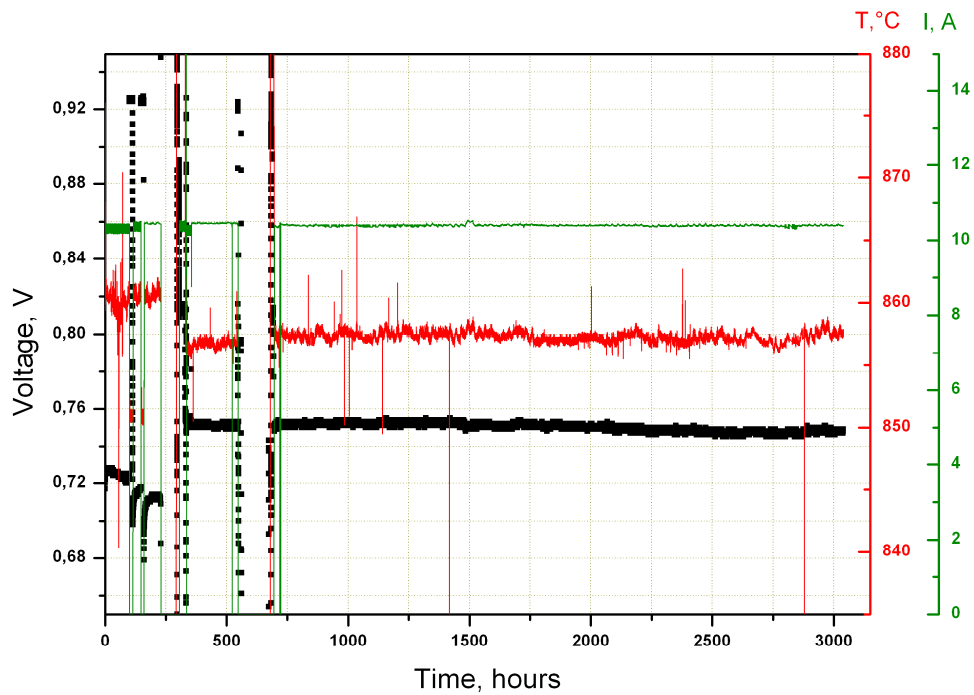


Figure 1. MEA stability during durability test.

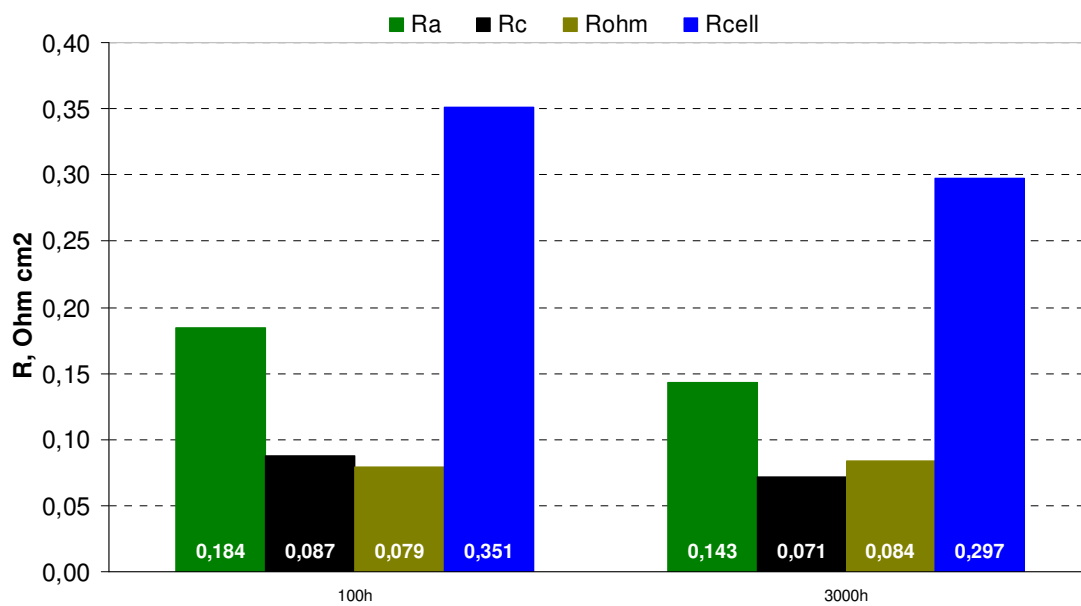


Figure 2. Constituents of ASR obtained by deconvolution of impedance spectra: Rohm – high frequency resistance, Rc – cathode resistance, Ra – anode resistance, Rcell – overall cell resistance.

Conclusions

The long-term stability of electrolyte supported cells can be achieved by optimizing the anode and has been demonstrated on the newly developed cells. The degradation rate obtained after 3.000h of operation is lower than 0.1% / 1000h.

Acknowledgments

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