

Recent Progress in Intermediate Temperature SOFCs (ITSOFCs) Development at DLR

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Abstract

Metal-supported ITSOFCs having NiO or NiO+YDC 15 anode, yttria stabilized ceria electrolyte (YDC 15) and LSCF or LSCF+CGO composite cathodes were fabricated via plasma spraying for operation in the temperature range of 600-700°C. Highest performance was recorded with NiO+YDC 15 / YDC 15 / LSCF+CGO cells. In the next step it is planned to optimize fabrication parameters in order to attain crack free and thinner electrolytes and more porous composite cathode which will lead to double cell performance.

Keywords: Intermediate Temperature Solid Oxide Fuel Cell (ITSOFC), metal supported fuel cell, ceria-based electrolyte, YDC 15, plasma spraying, Ideal-Cell, Electrochemical impedance spectroscopy

1. Introduction

Yttria stabilized zirconia (YSZ) exhibit high oxygen-ion mobility and negligible electronic conduction within the temperature range of 700-1000°C, due to its high oxygen vacancy concentration. Addition to its excellent thermal and mechanical stability, YSZ is also chemically stable in both oxidizing and reducing atmospheres. All above mentioned features and its availability and cost was the main reason of YSZ to be integrated in pre-commercial SOFC systems. Plasma spraying technology has been extensively used for the fabrication of SOFCs by many groups including Siemens Westinghouse since several decades. A full review on this technology and its high temperature application was published in a review by Henne [1]. Today it is widely accepted that in order to achieve commercialization in SOFCs, long term stability can be realized mainly by minimizing materials degradation by using alternative electrode and electrolyte materials which perform comparably high power densities even operating at lower temperatures (600-700°C).

In this regard ceria-based electrolytes are considered to be a strong candidate not only due to their higher oxygen-ion conductivities even at lower temperatures (450-750°C) but also their higher thermal expansion coefficient $12.5 \times 10^{-6} \text{ K}^{-1}$ (app. 20% higher than YSZ) which is more compatible with metallic components and cathode materials such as LSCF (TEC: $14 \times 10^{-6} \text{ K}^{-1}$). It was also reported that the surface exchange coefficient of bare YDC 10 is significantly higher than YSZ even when contacted with a porous Pt electrode. This shows that YDC surface is catalytically active for the dissociative adsorption of oxygen molecule. Due to the fact that LSCF exhibit relatively high oxygen self diffusion (D^*) and surface exchange coefficient (k) electrode resistances associated with YDC 15 and LSCF

is expected to be extremely low compared to YSZ and LSCF couple. Moreover LSCF appears to be chemically stable in contact with ceria-based electrolytes[2, 3].

The Ideal-Cell concept [4] is an innovative dual membrane ceramic fuel cell design aims at a reduced operating temperature and water free electrodes reaction in order to realize long term stability. Basically a proton conducting and an oxide ion conducting ceramic fuel cells are combined with a porous dual membrane consisting of both electrolyte materials at their junction, where water forms at intermediate high temperatures of 600-700°C. In the Ideal-Cell project funded by EU 7th framework Program, ceria-based electrolyte was selected for the oxygen compartment. In addition to tape casting, screen printing, wet powder spraying and sintering technologies, plasma spraying is also considered as an alternative method for functional layers fabrication of the dual cell, in order to investigate the readiness for an industrial application of the innovative concept. Therefore, development of an ITSOFC cell and operation of a short stack at 600-700°C was scheduled as a subtask for DLR as an intermediate step towards a fully plasma sprayed dual cell. This paper presents the latest results of this subtask.

2. Experimental

Full ITSOFC cells were fabricated by plasma spraying onto porous metallic ITM substrates (Plansee, Austria) having 48 mm diameter and 1 mm thickness. Only agglomerated NiO anode was applied as the anode functional layer of the 1. generation cells. Whereas agglomerated YDC15+NiO powder was fed into the plasma in order to achieve a homogenous and porous cermet anode with a better TEC match with its electrolyte in the 2.generation cells. Besides in order to reduce the roughness of the resulting anode layer, an additional anode–electrolyte interlayer was realized by spraying YDC15 and agglomerated YDC15 + NiO powder simultaneously. Electrolyte layer was achieved in both cases by dry plasma spraying of fused and crushed powders from Saint Gobain (France) onto the anode, which resulted in different microstructures and room temperature gas leak rates which are discussed in the results section. Finally agglomerated LSCF powder and submicronic particles of LSCF or LSCF+GDC10 in ethanol suspension was plasma sprayed onto the finished full cells. In order to improve the current collection on the cathode side, a fine platinum mesh (3600 mesh/cm²) was attached onto the cathode using a contacting paste of LSCF.

Right after the deposition of the electrolyte layer, gas leak rate was measured by recording the rate of pressure change when the sample is placed under pressure difference on both sides at room temperature. Measured gas leak indicates how dense the plasma sprayed electrolyte is.

All of the cells were tested in ceramic housing with platinum current collectors and leads. The gas supply to the cells was achieved by a radial distribution on both sides. The cells were sealed only on the anode side using gold ring and high temperature glass sealant paste from IKTS (Dresden, Germany). Heating up was achieved in 3K/min only up to 900°C with a dwell time of 1 h in order to avoid and chemical and structural changes in the cathode.

Electrochemical impedance spectra were recorded using an electrochemical workstation IM6 by Zahner (Germany) in OCV and loaded modes in a frequency range from 100 mHz up to 1 MHz with an applied ac amplitude of 10 mV.

3. Results and Discussion

In this paper the development of ITSOFCs will be presented in two generation steps. In table 1 detailed information on materials, mass gain and resulting gas leak rate information is given. An anodic interlayer corresponding to half of the mass of anode was applied to all four cells in the 2. generation step in order to achieve a smoother surface. The aim of this was to achieve a flat, dense and gas tight electrolyte layer with a homogeneous thickness covering the anode layer beneath. Moreover, in the 2. generation the heat transfer from the plasma to particle was increased by adding H₂ as plasma forming gases in addition to Ar and He, which enhanced melting of the individual particles. As a result better melted particles which have lower viscosity filled the globular porosity and denser electrolyte layer (Fig. 2.f) in a single pass of the plasma torch was achieved with higher deposition efficiency in comparison to 1. generation electrolyte (Fig. 2.e) fabricated with 16 passes. On the other hand as the particles attain a higher temperature, the quenching rates become more severe enhancing the thermally generated stresses. This may not only increase the micro-cracking but may cause macro-cracking if the thermally generated stresses exceed yield strength of the coating. This may be one of the explanations of the macro-cracks along the thickness of the 2. generation electrolyte (Fig. 2.b). A relatively homogeneous thickness in the range of 60-100 μm electrolyte with the interlayer (Fig. 2.b) was achieved in the 2. generation step, whereas it was changing between 30 to 60 μm in the 1. generation (Fig. 2.a) cells. As a consequence the measured leak rate was more than double the value of the 1. generation cells. This was also translated in the measured OCV values which were 30 and 22 mV less at 600 and 650°C respectively.

Table 1. Materials, mass gain and leak rate values for the first and second generation cells

Cell Name	Anode		Electrolyte		Cathode		Leak Rate x 10 ⁻³ mbar.l/cm ² .s
	Mat.	Mass /g	Mat.	Mass /g	Mat.	Mass /g	
1. gen-7	NiO	592.6	Y D C	379.6	LSCF (dry)	228.9	5.83
1. gen-8		596.6		420.0		192.1	5.28
1. gen-10		571.7		389.7		216.0	4.76
2. gen-1	YDC15+ NiO and YDC15	703.8	1 5	459.1	LSCF (sps)	142.1	11.70
2. gen-2		736.6		471.5	LSCF+GDC10 (sps)	110.6	12.35
2. gen-4		716.0		452.0	LSCF (sps)	131.7	12.40
2. gen-6		717.0		467.3	LSCF+GDC10 (sps)	111.7	10.50

Performance of the cells were evaluated by recording the voltage response while increasing the dc current in 2.4 mA/s steps up to only 550 mV in 50% H₂ in N₂ and air, therefore the maximum power density was not recorded. Observed improvement in power density was 4 % and 24 % at 600°C and 650°C, respectively (Fig. 1). The calculated (as described by FP6 FCTESQA) area

specific resistances (ASR) at 800 mV were reduced from 0.84 to 0.64 $\Omega\cdot\text{cm}^2$ at 650°C and 1.8 to 1.1 $\Omega\cdot\text{cm}^2$ at 600°C.

Recorded power density values are expected to be even higher when the 2. generation electrolyte is fabricated crack free which causes drastic decrease in the measured OCV values. In such a case the estimated power density values for 2. generation cell at 550 mV loading is calculated to be 200 and 136 mW/cm^2 at 650 and 600°C respectively. Further improvement for such cells could be the decrease of electrolyte thickness by half which would correspond to power density values of 420 and 280 mW/cm^2 .

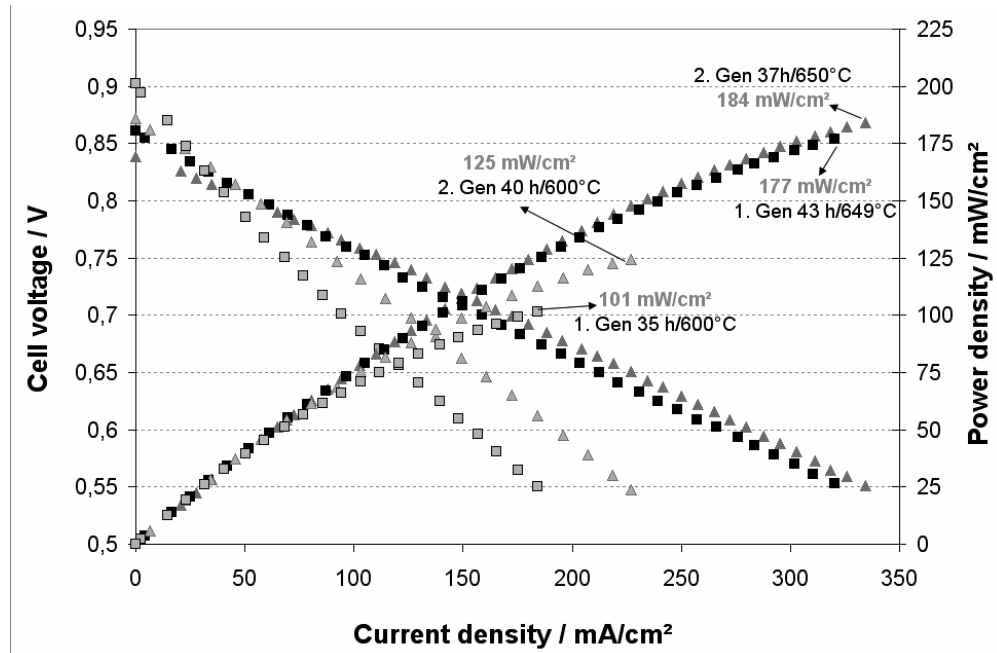


Fig 1. Gas leakrate, electrolyte and anode mass gain of the 2. generation ITSOFC cells.

In Figure 2.a and b, polished cross sectional view of full cells representing both 1. (all pictures on the left) and 2. (all pictures on the right) generation cells are presented. Both cells were contacted with an additional current collection layer of LSCF paste which is the first layer seen on top. Below is the cathode functional layer which can be better seen in c) dry powder plasma sprayed and d) LSCF and GDC suspension plasma sprayed. It can be easily seen that relatively better distributed porosity is achieved in suspension plasma sprayed sample. Moreover the GDC (30%) particles (white) are well distributed in the LSCF (70%) skeleton (darker). In an other paper [5] we reported that homogeneously distributed fine porosity with conserved connectivity within the composite cathode exhibit highest performance. Finally Ni (white) map within the operated anodes prove that the distribution should also be achieved more homogeneously.

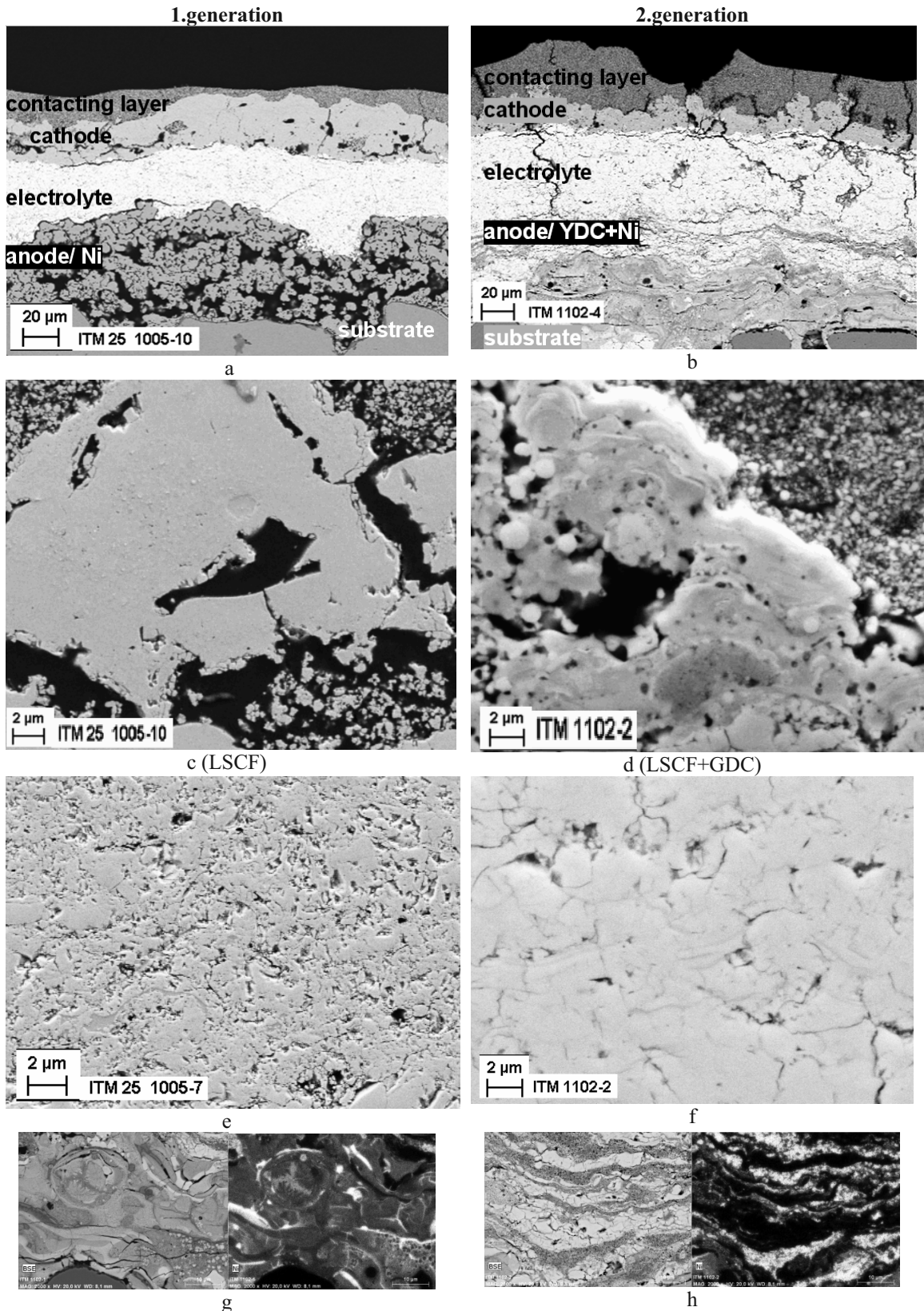


Fig. 2. Micrograph of plasma sprayed YDC 15 electrolyte of an a) 1. generation 2. generation 1 as sprayed b) operated full cell ITSOFC.

At high temperatures (Fig.3.a) an additional LF arc appears which can be attributed to the polarization caused by the gas phase diffusion within the porous

electrode[6]. This additional arc corresponds to 80% and 25% of the total polarization resistance for 1. and 2. generation cells at 818 and 813°C respectively. This proves the improved gas diffusion in the 2. generation electrodes. Furthermore improved electrode resistance was also measured at 600°C.

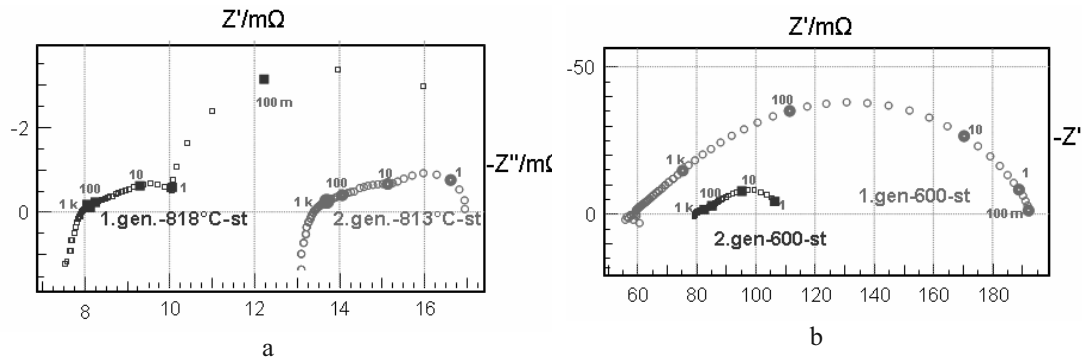


Fig. 3. Complex plane impedance diagrams of both generation cells a) at 813°C and b) at 600°C in comparison.

By recording the impedance spectra at different operating temperatures an Arrhenius diagram of the measured ohmic conductivity of 1. and 2. generation cells were plotted in comparison to cold pressed and sintered pellets and literature data for YDC 10 and YSZ. Plasma sprayed layers together with cold pressed and sintered pellets exhibited similar conductivity values as reported in literature.

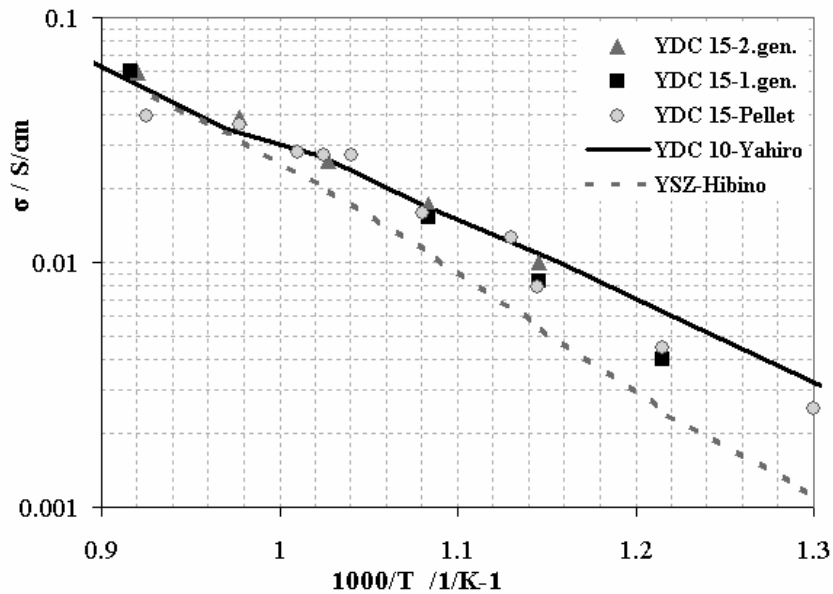


Fig. 4. Arrhenius plot of measured ohmic conductivity for 1. and 2. gen. cells, cold pressed sintered YDC 15 pellet in comparison to literature[7, 8].

4. Conclusions

In this paper the development of ITSOFCs were presented in two generation steps. Dry powder sprayed ceria-based electrolytes and suspension plasma sprayed LSCF+CGO composite cathodes have shown the highest performance. In our further work it is planned to attain crack free and thinner electrolytes by optimizing the fabrication parameters. In this case it was estimated that recorded power density values of 184 and 125 mW/cm² can be potentially increased to 420 and 280 mW/cm² at 650 and 600°C respectively.

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References

- [1] R. Henne, Solid oxide fuel cells: A challenge for plasma deposition processes, *Journal of Thermal Spray Technology* 16 (3) (2007) 381.
- [2] B. Steele, Interfacial reactions associated with ceramic ion transport membranes, *Solid State Ionics* 75 (1995) 157.
- [3] D. Marinha, et al., Performance of (La,Sr)(Co,Fe)O_{3-x} double-layer cathode films for intermediate temperature solid oxide fuel cell. *Journal of Power Sources*, 196 (11) (2011) 5084.
- [4] A. Thorel, et al., IDEAL-Cell, a High Temperature Innovative Dual mEmbrAne Fuel-Cell. *ECS Transactions* 25 (2) (2009) 753.
- [5] D. Soysal, Z. Ilhan, A. Ansar, R. Costa, Novel processing approach to nanostructured composite cathodes for SOFC applications, in *Advances and Innovations in SOFS – from materials to systems*, 2011, Katarino, Bulgaria.
- [6] N. Grunbaum, et al., Rate limiting steps of the porous La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3- δ} electrode material, *Solid State Ionics* 180 (28-31) (2009) 1448.
- [7] T. Hibino, et al., Proton Conduction at the Surface of Y-Doped BaCeO₃, *The Journal of Physical Chemistry B* 105 (46) (2001) 11399.
- [8] Y. Hidenori, et al., High Temperature Fuel Cell with Ceria-Yttria Solid Electrolyte. 1988, ECS. p. 2077.