B0150

Progress in the development of Nickel-less SOFCs: status of the EU project EVOLVE

Rémi Costa (1) and Asif Ansar (2)

(1) German Aerospace Center,
Institute of Technical Thermodynamics, Electrochemical Energy Technology,
Pfaffenwaldring 38-40, 70569 Stuttgart, Germany
Tel.: +49-711 6862-733
Fax: +49-711-6862-747
Contact: remi.costa@dlr.de

(2) Saan Energi AB
Ideon Innovation / Ideon Science Park
Scheelevägen 15, 223 70 Lund, Sweden

Abstract

The project EVOLVE aims at the development of new cell architecture for SOFC cell and stack, combining benefits of existing Anode Supported (high power density, lifetime) and Metal Supported cell (redox and thermal cyclability) architectures, while limiting the issue of carbon coking and sulphur poisoning by using enhanced perovskite anode materials. The core component is based on a composite anode substrate made of porous Alumina forming alloy (NiCrAl), combined with an electron conducting oxide ceramic ($La_{0,1}Sr_{0,9}TiO_{3-\alpha}$ – LST), without having pure Nickel as structural component. Two manufacturing routes were followed for the manufacturing of the electrolyte, plasma spraying or PVD avoiding thus a sintering step in air at high temperature. The first prototype have been produced through the plasma spraying route, with 100µm thick electrolyte and without anode functional layer showed a very limited peak-performance measured at 20mW/cm² at 750°C. However no significant variation has been measured and no reactivity have been detected showing thus the stability of system under SOFC operating conditions. The plasma sprayed electrolyte has been successfully replaced by a thin electrolyte produced through the PVD route approach with a thickness reduced to less than 3µm, allowing the incorporation of an anode functional layer, major improvement of cell performance is being expected..

The project has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n°303429.

Introduction

Emission of greenhouse gases (GHG) from industry, transportation and agriculture has played a major role in the recently observed global warming. In order to reduce the impact on environment, zero or near-zero emission energy systems, converting fuel efficiently into useful energy are increasingly investigated. Unprecedented rise in the fossil fuel prices has led to a growing economic concern towards the need of such energy systems. Additionally, geopolitical priority of reducing the dependence on foreign energy resources emphasizes the development of systems that may work with a variety of fuels and eventually with renewable energy resources such as hydrogen or bio-fuels.

Solid Oxide Fuel Cells (SOFCs) are one of the most attractive energy conversion devices, owing to the potential of operating at high efficiency of about 60% in standalone condition and over 80% (net) if waste heat is used for cogeneration. SOFCs do not require noble metals for catalysis in electrodes and may use a variety of fuels including hydrocarbons, CO and bio-fuels, besides hydrogen. These low-noise convertors thus offer very high potential in stationary application and combined heat and power units (CHP) for decentralized energy and in Auxiliary Power Units (APU) as well for mobile applications. Despite all the promising advantages and the unparalleled progress in its power output, SOFC faces critical challenges in term of its poor reliability, low durability and higher cost. Unless addressed meticulously, these obstacles will impede large-scale commercialization of fuel cells. Reliability and durability are adversely affected by a number of factors of which the following two can be considered as the route cause: 1) high operating temperatures (800-1000°C) of SOFC and 2) the need to use materials that provide multiple functionalities. This includes structural support, electrochemical activity, and electrical or ionic conduction, as well as at the same time compatibility with neighboring components during the manufacturing process and fuel cell operation.

Looking back to the cell architectures (Figure 1) which have been investigated in the last decades, one can point out three main cell designs: the oldest one or the first cell generation is the so called Electrolyte Supported Cell (ESC). The second cell generation that can be named as Anode Supported Cell (ASC) and finally the third architecture, called the Metal Supported Cell (MSC) have been then successively developed, targeting for each of them improved performance and reliability in comparison to the former one.

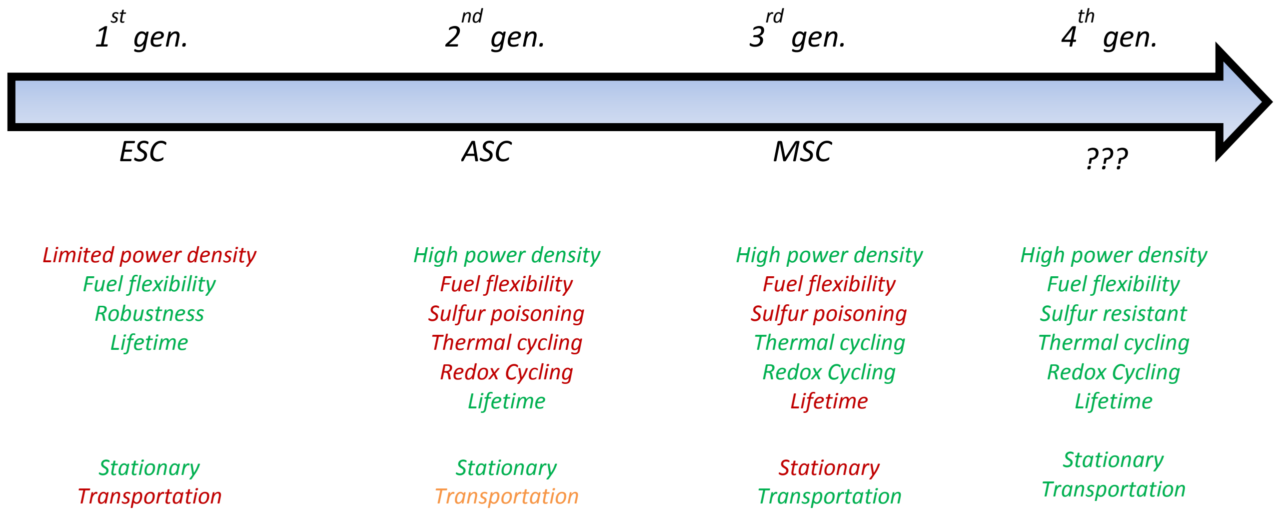

Figure 1: overview of the most common planar cell architecture, with benefit (green) and drawback (red)

Looking at the origin of the drawbacks and the benefits of different generations of product, the nature of material to be used and the architecture of the next cell generation, is still questionable.

A new design next generation cell is therefore conceived and being developed referred as EVOLVE cell. The EVOLVE cell concept aims at combining the beneficial characteristics of the previous cell generations, the so called ASC and MSC and will address further key challenge like sulfur poisoning, of these two competing technologies linked with presence of Nickel as catalyst and structural component in the nickel / zirconia standard anodic cermet [1]. The innovation of the EVOLVE cell concept remains in its anode compartment without having nickel as structural component (Figure 2). The anode compartment is based on a metal alloy forming a protective alumina layer enhancing stability during re-oxidation cycles and an electronic conducting perovskite for the current collection. This combination between a resilient metal toward oxidation and an electronic conducting ceramic oxide create and a cermet type hybrid current collector, with a mechanical stability similar to the MSCs and a microstructure similar with the one from anodic substrate of ASC.

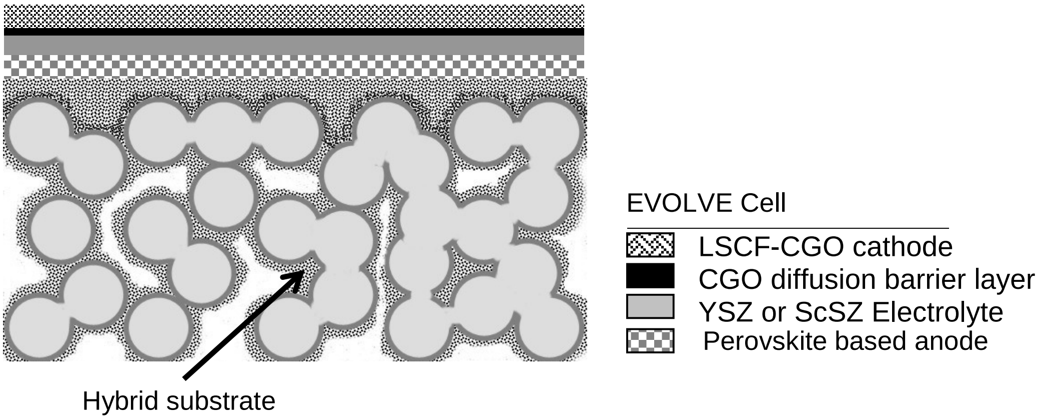

Figure 2 : sketch of the EVOLVE type cell

The major objective of this project is to demonstrate the feasibility and the benefits of such cell architecture up to industrial relevant criteria, which can be summarized as follow:

- Power density of 550 mW / cm^2 at 0,7 V at 750 °C with H_2
- Operation in H_2 or syngas with sulfur reactive species
- Improved tolerance toward thermal and redox cycles
- Upscaling (>100cm2) and integration in a 250 W stack

The consortium EVOLVE includes: the German Aerospace Center (Germany) assuming the leadership and the coordination, Alantum Europe GmbH (Germany), ARMINES (France), Ceramic Powder Technology AS (Norway), Consiglio Nazionale delle Ricerche (Italy), Institut Polytechnique de Grenoble (France), Saan Energi AB (Sweden) and Ceraco Ceramic Coating GmbH (Germany), and has been granted a financial support in 2011 by the Fuel Cells and Hydrogen Joint Understanding under the Grant Agreement n° 303429, for the development of the EVOLVE cell concept.

1. Scientific Approach

On scientific level, the project bases its development on building up a comprehensive correlation between material, processing, microstructure and electrochemical performance to have an optimized cell in terms of its performance and service life. The anode compartment of the cell will be composed of a novel generation of materials, developed

and matured over the course of recent years in different projects [2,3]. Further development of these materials is undertaken in this project. The compatibility of materials is being checked before being implemented in the fabrication of current collector and functional layers of the Evolve cell. The development of the cell is backed by advanced 2D and 3D techniques for the microstructural analysis of porous layers that is exploited with mathematical modelling. The aim of the morphological modelling of the microstructure of active layers of electrodes is to predict the influence of the various processes of fabrication of porous electrodes on their in-use performances. This allows a rational approach towards optimization of the electrochemical performances of the electrodes. The obtained estimated properties for real and simulated microstructures will be introduced in the electrochemical kinetic model for understanding the behaviour of the new perovskite material and for prediction of cell performance. The electrochemical kinetic model and its sub-parts being parameterized and validated using electrochemical measurements on symmetric cells, button cells and stackable cells as well as degradation experiments performed. This should give input to finally achieve optimized electrodes and cell design.
The strategic approach of the cell development is shown on Figure 3.

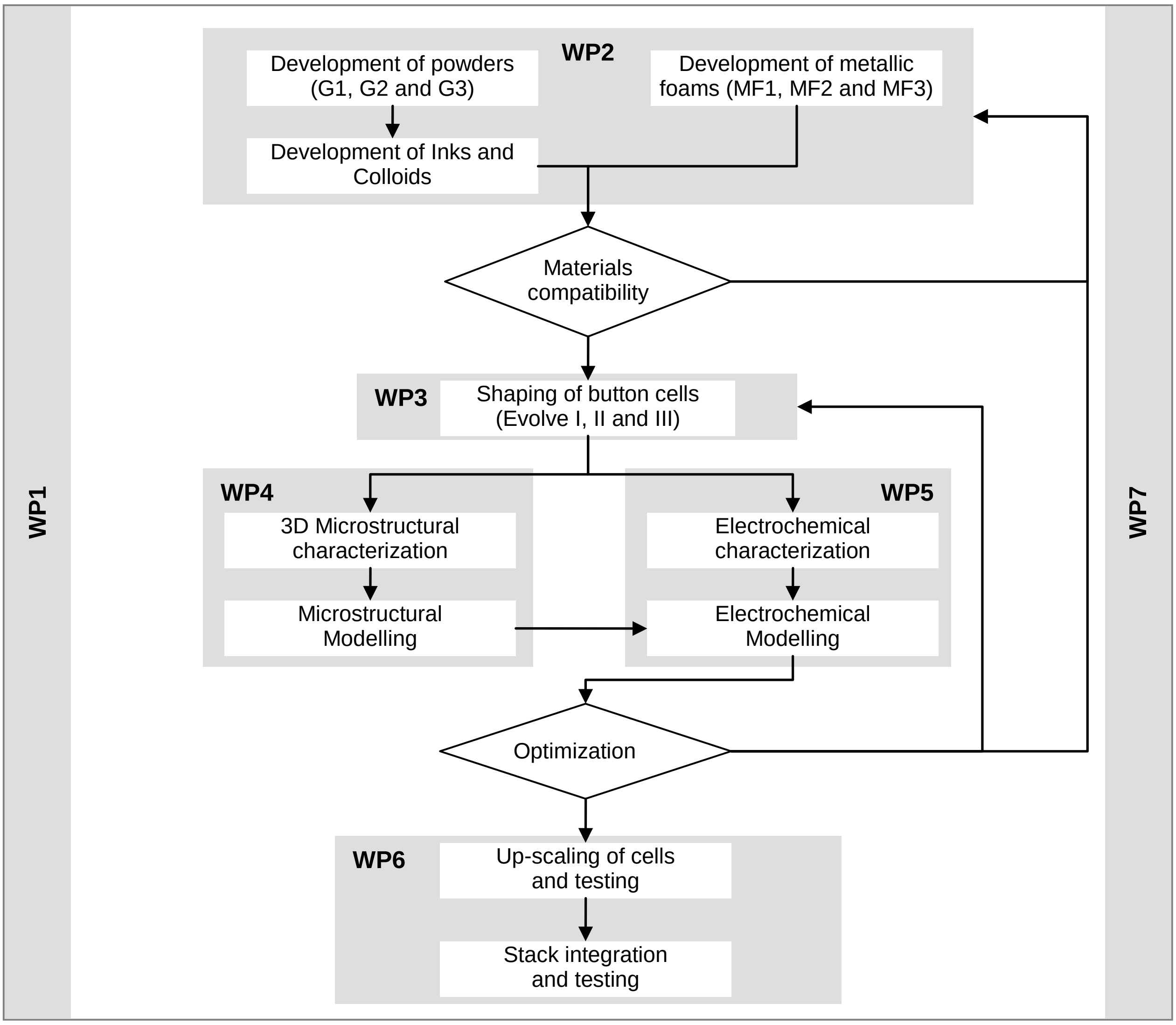

Figure 3: overview of the approach for the project with splitting into Work Package. Work Package 1 and 7 being related with management and dissemination respectively

2. Experiments/Calculations/Simulations

The materials being considered for the first development round of the EVOLVE cell are listed here after:
1: NiCrAl alloy foam with a pore size of about 450µm.
2: $La_{0,1}Sr_{0,9}TiO_{3-\alpha}$ – LST – was used as perovskite for both current collection and anodic electro–catalyst purposes alone or in combination with $Ce_{0,9}Gd_{0,1}O_{2-\alpha}$ – CGO – in a composite.
3: $La_{0,8}Sr_{0,2}MnO_{3-\alpha}$ – LSM – based or $La_{0,4}Sr_{0,6}Co_{0,2}Fe_{0,8}O_{3-\alpha}$ – LSCF – based cathode material.

The current collector was produced through dip coating approach, being used for both compatibility tests and cell building. The anode functional layer was deposited with various microstructures either on symmetrical cells for fundamental characterization and understanding of processes involved in such anode, or directly on the current collector for implementation in the full cell of ca. 45mm in diameter. The electrolyte is deposited on the current collector either by plasma spraying or by PVD. Cathode being deposited up to now by brushing for testing.

Experimental details and results linked with each specific aspect of the cell development are given in the following papers in the proceedings of the conference. References are given here after:
About material compatibility and stability under SOFC conditions: B0914, B0620.
About properties and behaviour of LST materials: B0514, B1211.
About Cell manufacturing: A1506.

3. Results

-Plasma sprayed approach:

Cross section of the prototype is shown on Figure 4. It must be pointed out a 100µm thick electrolyte necessary to reach sufficient gas tightness. Microstructure revealed a high density of contact area between the NiCrAl and the YSZ electrolyte. Indeed, it seems not possible through such route to produce a dense YSZ layer over a functional LST based anode. Under the investigated manufacturing conditions, mechanical strength of LST porous based anode seems not high enough to withstand the mechanical stress generated by the impact of molten YSZ particles. This lack of active anode layer nearby the electrolyte could be a strong limiting parameter for the electrochemical performance. The cathode was made of pure LSM which limits the active surface area to the contact points between the LSM and the YSZ electrolyte because of the lack of bulk oxygen conductivity, and is known to have limited performance at 750°C. Moreover, a 100µm thick YSZ is detrimental for the performance at 750°C due to resulting high ohmic resistance. Therefore, due to nature of materials used and taking into consideration the configuration of the different layers, the EVOLVE cell prototype remains far from being optimized for operation in such conditions. This assessment though microstructural check of the prototype is confirmed by the electrochemical testing (Figure 5). Measured OCV was 098V and can be mainly attributed to a defect in the sealing between the two atmospheres. In such condition, the peak power density was limited to ca. 20mW/cm². However one should notice the remarkable stability of the tested cell, in galvanostatic condition which did not highlighted any strong fluctuation indicating and exaggerated aging of cell components or reactivity between them in tested condition. So far, post mortem analysis did not reveal any reactivity among the different materials.

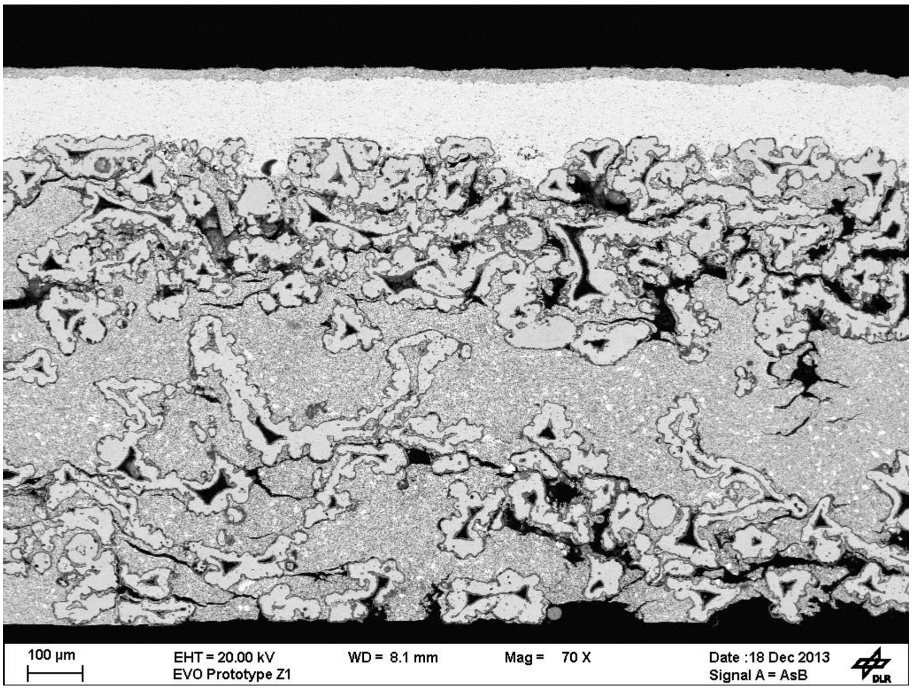

Figure 4 SEM Cross section of the first EVOLVE prototype after testing. The electrolyte appears in white uniform layer. LSM cathode is at the top and thick composite NiCrAl / LST appear in grey colors at the bottom

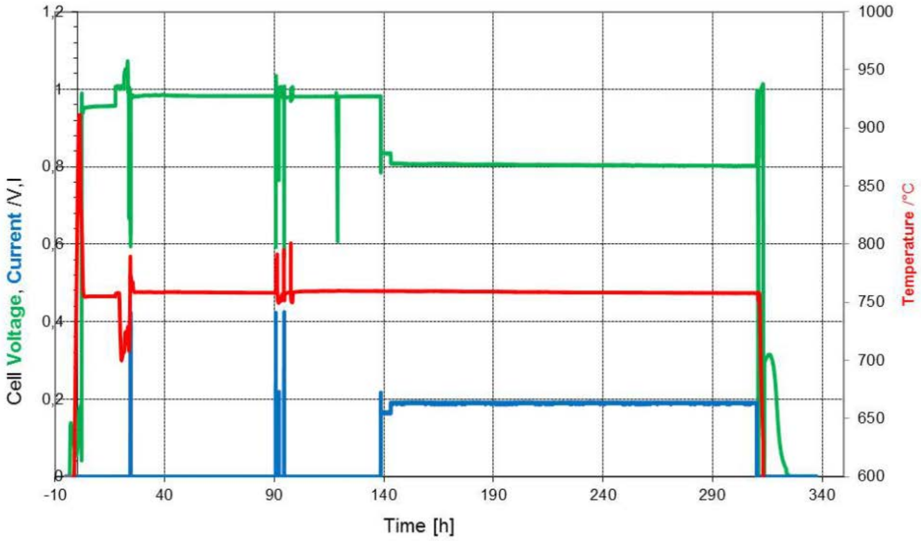

Figure 5: Voltage variation over the time as a function of the current output of the EVOLVE Cell prototype measured at 750°C in using H_2-N_2 (50:50) mixture as a fuel and Air as oxidant

Taking into consideration the obtained microstructures, the configuration of the layers and the tested parameter in correlation with the measured performance, this first prototype has demonstrated the technical feasibility of such cell architecture with such material while keeping open all possible improvement, either in term of microstructure (Anode functional layer, thin electrolyte) or in term of material (implementation of LSCF based cathode).

-PVD approach:

The PVD approach is expected to bring a disruptive improvement in the development of the EVOLVE cell by allowing the implementation of an anode functional layer while reducing drastically the electrolyte thickness down to the micron range. However the use of PVD as coating technology for the manufacturing of reliable thin electrolyte, still remain challenging and present a high technological risk [4], and requires interface and surface engineering of the underlying layers far beyond the conventional routes followed solely for electrochemical efficiency purpose.
Cross section of half-cell produced with PVD based electrolyte is shown on Figure 6. On should notice in comparison with the plasma spray route the presence of a functional anode layer and an electrolyte layer with a thickness limited to 3µm.

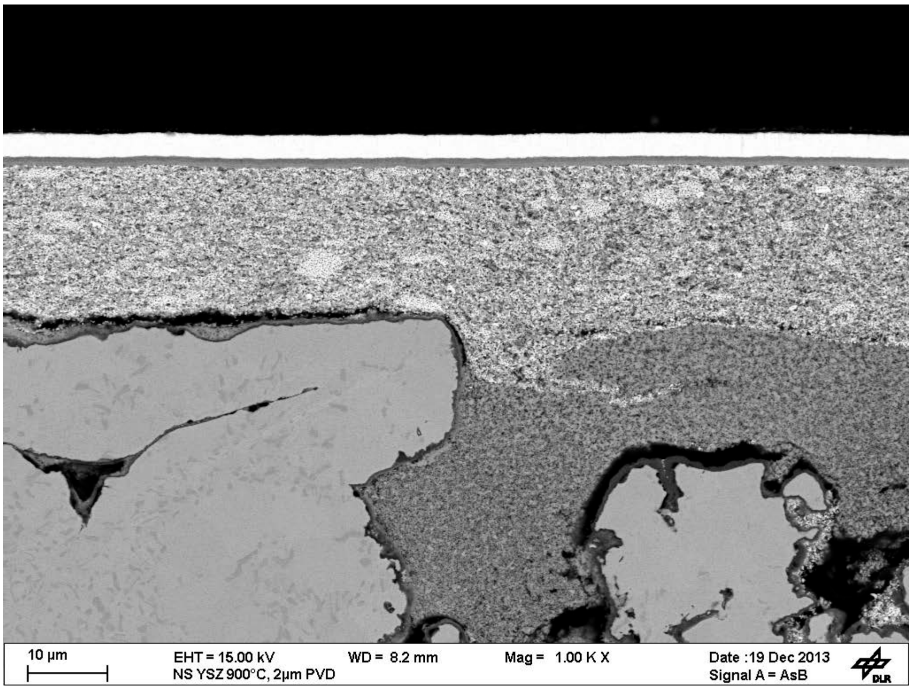

Figure 6: SEM cross section of anode electrolyte half cell produced through the PVD approach. The electrolyte bi-layer appears at the top in uniform white and uniform grey, the porous functional anode layer is about 20µm made of LST-CGO on top of the current collector (NiCrAl-LST)

Electrochemical testing of such cells are not yet available, but following the same assessment process used for the plasma spray route, one should expect significant improvement in term of cell performance.

4. Summary

The core component is based on a composite anode substrate made of porous Alumina forming alloy (NiCrAl), combined with an electron conducting oxide ceramic ($La_{0,1}Sr_{0,9}TiO_{3-\alpha}$ – LST), without having pure Nickel as structural component. Two manufacturing routes were followed for the manufacturing of the electrolyte, plasma spraying or PVD avoiding thus a sintering step in air at high temperature. The first prototype have been produced through the plasma spraying route, with 100µm thick electrolyte and without anode functional layer showed a very limited peak-performance measured at 20mW/cm² at 750°C. However no significant variation has been measured and no reactivity have been detected showing thus the stability of system under SOFC operating conditions while keeping open all possible opportunities in terms of materials and microstructures in each functional layer of the cell. The plasma sprayed electrolyte has been successfully replaced by a thin electrolyte produced through the PVD route approach with a thickness reduced to less than 3µm, allowing the incorporation of an anode functional layer, major improvement of cell performance is being expected. Next stage will be the microstructural optimization of the cell in order to maximize the cell output. All of this contributes as step forward in the development of the next generation of SOFC expected to be both sulfur tolerant and redox stable, and allowing fast transient regimes.

5. Acknowledgment

Authors acknowledge all project partners involved in the project.
The project EVOLVE has received funding from the European Union’s Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n°303429.

References

[1] H. Yokokawa, H. tu, B. Iwanschitz, A. Mai, Fundamental mechanisms limiting solid oxide fuel cell durability, J. Power Sources, 182 (2008) 400

[2] N. Christiansen, S. Primdahl, M. Wandel, S. Ramousse A. Hagen , Status of the Solid Oxide Fuel Cell Development at Topsoe Fuel Cell A/S, ECS Transactions, 57 (2013) 43

[3] P. Holtappels, J.T.S. Irvine, B. Iwanschitz, L. Theil Kuhn, L. Y. Lu, Q. Ma, J. Malzbender, A. Mai, T. Ramos, J. Rass-Hansen, B. R. Sudireddy, F. Tietz, V. Vasechko, S. Veltzé, M.C. Verbraeken, Full Ceramic Fuel Cells Based on Strontium Titanate Anodes, An Approach Towards More Robust SOFCs, ECS Transactions, 57 (2013) 1175

[4] M. Haydn, K. Ortner, T. Franco, S. Uhlenbruck, N. H. Menzler, D. Stöver, G. Bräuer, A. Venskutonis, L. S. Sigl, H.-P. Buchkremer, R. Vaßen, Multi-layer thin-film electrolytes for metal supported solid oxide fuel cells, J. Power Sources, 256 (2014) 52