FCH-JU
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Publishable Summary

Solid oxide fuel cells (SOFCs) represent well-consolidated devices making use of hydrogen or hydrogen rich fuels to produce power and heat with very high efficiency and extremely low or zero emissions of greenhouse gases. In case of usage of biogas, a neutral carbon footprint beside the high efficiency of combined heat and power (chp) system shall be considered an excellent and win win compromise.

SOFCs are operating in stacks increasing the achievable power and allowing a handy management of gases, heat and power in a more complex plant where compressors, controllers and other needed components are introduced to obtain a complete operative system.

The state of the art materials involved in a SOFC stack are quite consolidated: (i) anode supported cells with Ni-based cermet as anode; (ii) Yttria Stabilized Zirconia (YSZ) as electrolyte; (iii) Gadolinia Doped Ceria (GDC) as diffusion barrier layer; (iv) lanthanum strontium cobaltite ferrite (LSCF) as cathode; (v) ferritic stainless steel (FSS) as structural materials and as interconnects (in this case coated with a Cr volatilization hindering product); (vi) inert highly resistive sealants, commonly ceramic-glass.

Industrial players in the field of stack manufacturing and commercialization have proprietary solutions to solve the most known issues as Cr poisoning of the cathode (e.g. usage of a Cr getter at the interface cathode/interconnects in addition to the coating), gas leakage (e.g. layered sealants and built in delta probes), reduced ohmic resistance (e.g. usage of electrode/interconnect contacting layers).

The ENDURANCE project was prepared in this context and frame with the purpose to face the still unresolved issues through innovations and improvements at all levels in order to reach and possibly outmatch the durability and reliability target demanded by the market (e.g. 50 kh of operation with a maximum of 10% of total degradation).

A fully European consortium composed by 8 research institutes and 4 industrial partners worked during three years to contribute to reach to previously described goals. Starting from state of art commercial stacks operated for several thousands hours, fundamental information about the most sensitive degradation modes and mechanisms were addressed.

With the support of a wide literature research, the experimental data were integrated in an evolved version of FMEA becoming one of the public use deliverables called Degradation Modes and Effects analysis where all degradation processes are taken into account risk ranked according to their probability (statistical frequency of the event) and harmfulness. Starting from this base thermo-mechanical, electrochemical and physical models were developed or, when already existing, refined in order to have an improved level of events and performances predictability. The main achievements in this field allowed the consortium to have and statistically prove on specific samples and excellent matching between modeled and real phenomena.

On the front of materials improvements, the activities focused on strategies meant to increase the overall durability by addressing the most critical issues recognized by DMEA: sealant, anode nickel coarsening, diffusion barrier layer between cathode and electrolyte. Two out of ten new glass-ceramic sealants were developed and validated. One of them was tested in short stacks proving an excellent resistance to thermal cycles over the long period. A strategic solution using YSZ as interlayer between FSS and sealant was successfully verified to increase the adhesion and reduce the metal ions diffusion from the metal substrate into the sealant.

Several manufacturing solutions were brilliantly applied to densify the GDC in order to improve the performances of the diffusion barrier layer (i.e. GDC impregnation, MgO as sintering aid,

applcation via Pulsed Laser Deposition). The cells resulting from this step were mounted in short and real stacks, the latter operated in reformed fuel to match real operating conditions.

A strategy of partial oxidation of the anode followed by its complete reduction has proven to be a promising counter action to reduce the risk of Ni coarsening, identified as one of the main source of anode performances degradation.

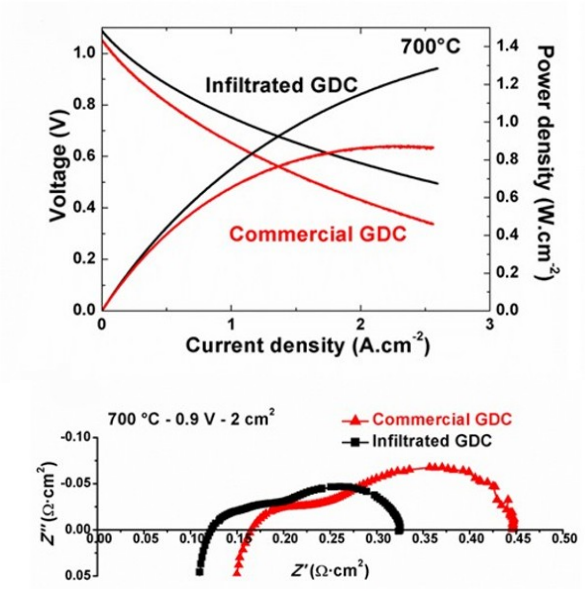
Moreover, a brand new method of interpretation of the electrochemical data applicable to both cells and complete stacks was introduced: the Differential Resistance Analysis (DRA). Such tool applied on real data and on model generated data demonstrated the possibility to detect nearly invisible deviations from the original electrochemical performances technically impossible to be observed on short tests by the usual tools. This allows to verify in a very precise and sensitive way the evolution of the cell performances even though close or below the target of 0.1% of degradation rate per 1000 hours.

The main achievements of the project are listed hereafter:

1. Enhanced understanding of degradation and failures modes: A Degradation Modes and Effects Analysis (DMEA) updated version has been compiled, based on a wide literature review.

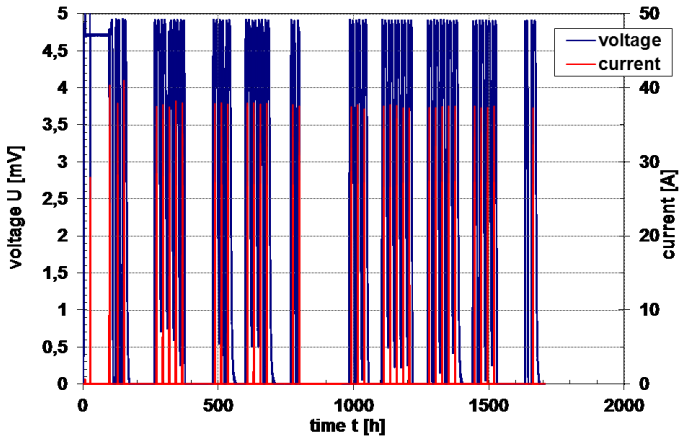
2. Improvements of materials involved in SOFC stacks:

    - Dense GDC barrier layer at the electrolyte/cathode interface were obtained, limiting the ohmic losses and preventing the formation of detrimental phases.

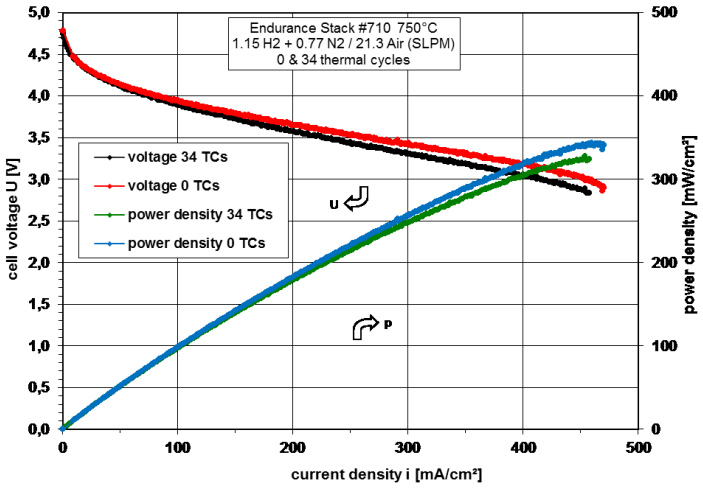
3. 

i-V curves and power densities recorded on single cells using infiltrated and commercial GDC at 700 °C (top) and the corresponding impedance diagrams recorded at 0.9 V at 700 °C (bottom).

    - Improved glass-ceramic sealant with excellent resistance to thermal cycles was implemented and validated in segmented stack tests.



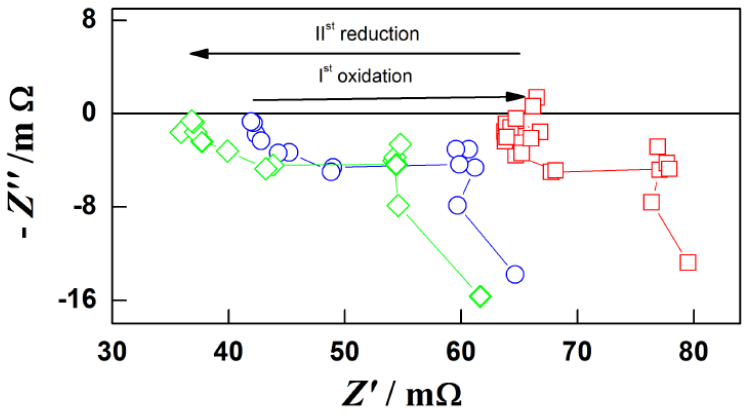
Life cycle of a stack tested applying 34 thermal cycles



Polarization curves of a stack at the start and after 34 thermal cycles

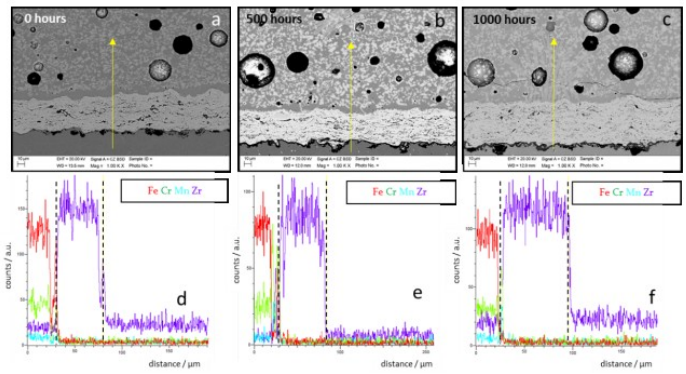
4. Several counterstrategies were developed and tested:

   - Cycles of partial reoxidation and complete reduction of anodes were proposed to control the Ni coarsening.



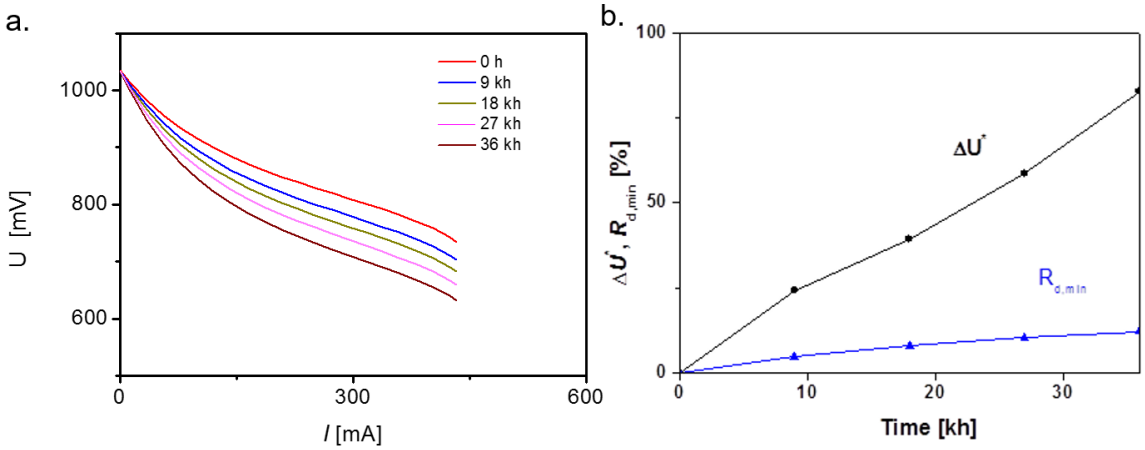
Comparison of impedance diagrams measured during reduction and reoxidation.

- Application of YSZ interlayers between interconnect and sealant to increase the adhesion and reduce the metal ions diffusion from the substrate into the sealant.



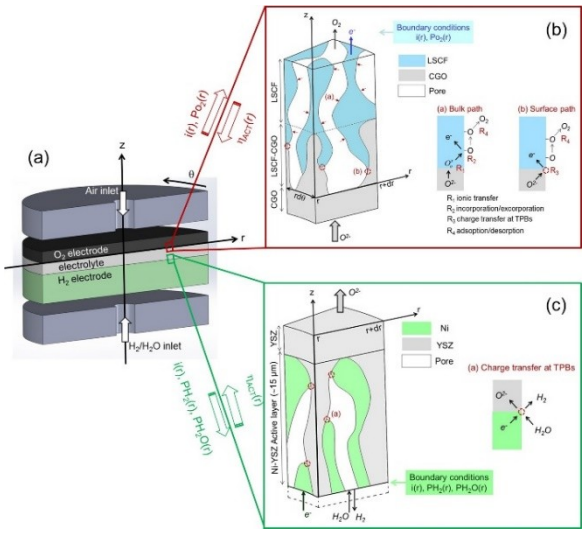
SEM-BSE images of FSS coupons combined with glass type GS-A including YSZ coating, directly after the sealing treatment (a), after 500 hours aging (b), and after 1000 hours aging (c), including the respective EDX line scans along the arrow in the images (d-f). The interfaces are indicated in the EDX scans by dashed lines.

- Development of Differential Resistance Analysis (DRA), based on simple derivative transformation of the volt-Ampere curves of cells and stacks to check, with increased sensitivity, the health state of the components at specific working points.

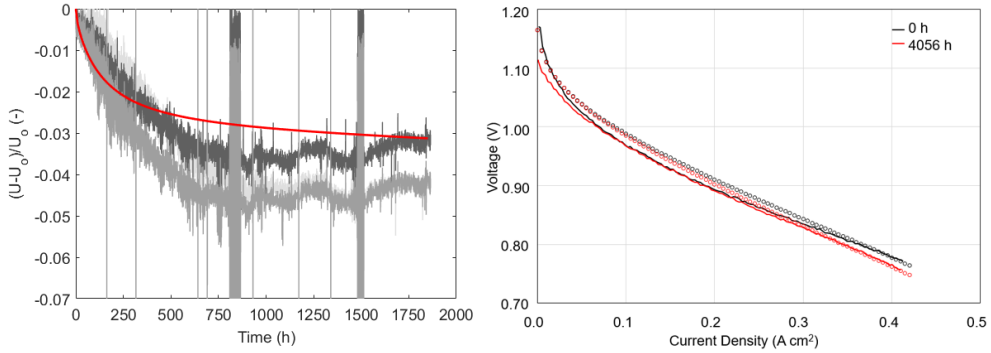


i-V characteristics (VAC) at different operation time. (b) $R_{d,min}$ and ΔU^* change in % with time.

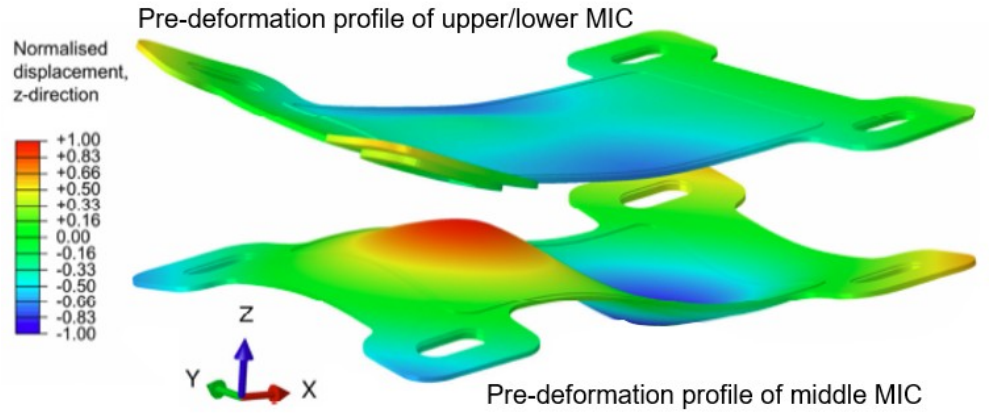
5. Refined thermomechanical and electrochemical models for improving the understanding and prediction of SOFC stack degradation based on experimental results. The model scales span from the characteristic size of the material phases in the electrodes to that of the stack and both thermo-electrochemical and thermo-mechanical aspects were investigated.



Schematic representation of the structure of the model of the SOLIDpower cell.



Left: Comparison between a 3-cell short-stack long-term tests and degradation simulations (red). Right: Comparison of experimental IV characteristics measured on the short stack test (solid lines) and model predictions (circles).

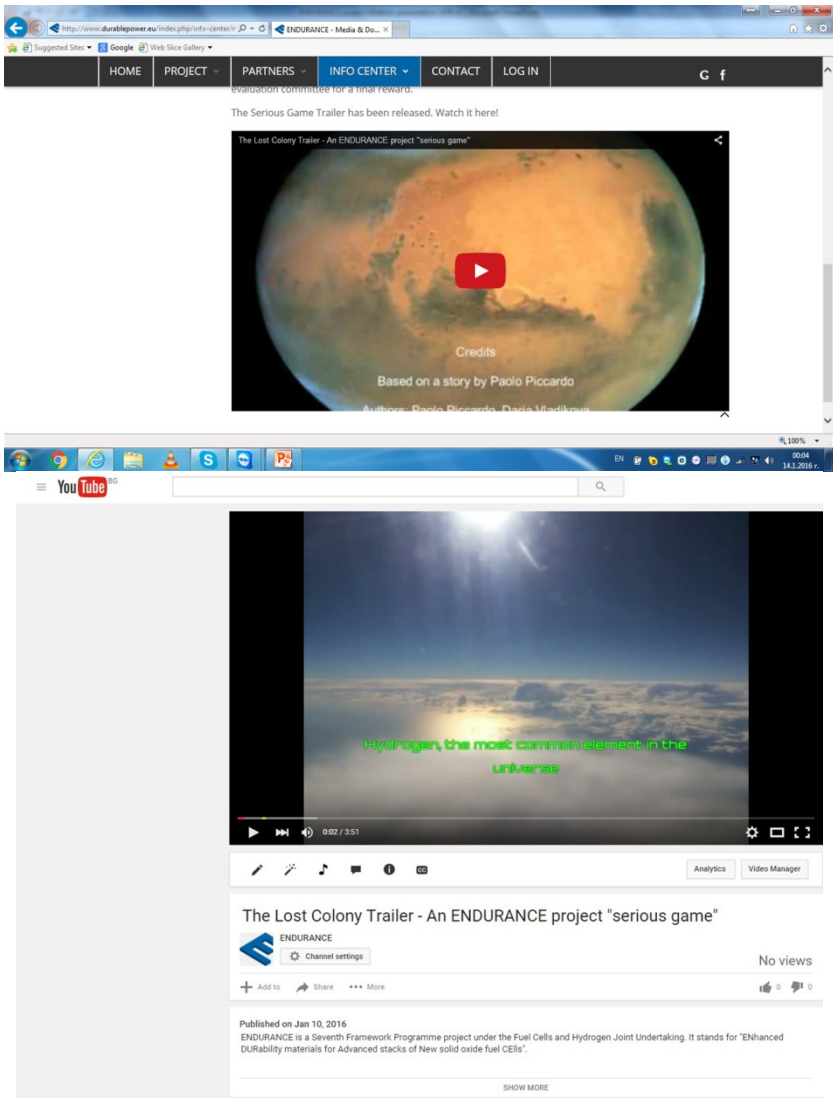


Magnified view of normalized MIC deformation implemented in the model.

6. Active dissemination:
   - Documents with high scientific value such as the updated DMEA and a handbook of test procedures and protocols were compiled with the contribution of the whole consortium and made available for public usage as eBooks downloadable from the project website.

- An international workshop on SOFC degradation and failures has been organized by the consortium involving several European projects. A collection of proceedings was made available for public usage as eBooks downloadable from the project website.
- A Serious Game in various languages has been developed. It is downloadable from website.

7.



Fragments from the Serious Game "The Lost Colony"