



Scientific Summary



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Name, title and organization of the scientific representative of the project's coordinator:




Prof. Symeon Bebelis
Foundation for Research and Technology Hellas-Institute of Chemical Engineering & High Temperature Chemical Processes

Tel: 0030 2610 969 511 or 0030 2610 965 265 or 0030 2610 965 240

Fax: 0030 2610 965 223

E-mail: simeon@chemeng.upatras.gr

Project website address: <http://robanode.iceht.forth.gr/>

Beneficiary Number	Beneficiary name	Beneficiary logo	Country	Contact Persons
1 (CO)	Foundation for Research and Technology Hellas-Institute of Chemical Engineering Sciences (FORTH/ICE-HT)		Greece	1) Prof. Symeon Bebelis, E-mail: simeon@chemeng.upatras.gr 2) Dr. Stylianos Neophytides, E-mail: neoph@iceht.forth.gr 3). Prof. Costas G. Vayenas E-mail: cgvayenas@upatras.gr 4) Dr. Dimitris K. Niakolas, E-mail: niakolas@iceht.forth.gr
2	Technische Universität Clausthal (TUC)		Germany	Dr. Georgia Sourkouni, E-mail: Georgia.sourkouni-argirusi@tu-clausthal.de
3	National Technical University of Athens (NTUA)		Greece	Prof. Christos Argirusi, E-mail: argirusi@central.ntua.gr

4	Ecole Polytechnique Federale de Lausanne (EPFL)	 ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE	Switzerland	Dr. Jan van Herle, E-mail: jan.vanherle@epfl.ch
5	Agencia Estatal Consejo Superior de Investigaciones Cientificas (CSIC)		Spain	1) Prof. Jose Ramon Jurado, E-mail: rrjurado@icv.csic.es 2) Dr. Eva Chinarro, E-mail: martin@icv.csic.es 3) Dr. Berta Moreno, E-mail: berta@icv.csic.es
6	Centre National de la Recherche Scientifique (CNRS)		France	Dr. Spyros Zafeiratos, E-mail : spiros.zafeiratos@unistra.fr
7	Materials Industrial Research & Technology Center (MIRTEC S.A.)		Greece	1) Dr. Dia Andreouli, E-mail: d.andreouli@ebetam.gr 2) Prof. Vassilis Stathopoulos, E-mail: vasta@teihal.gr
8	Saint-Gobain Centre de Recherches et d` Etudes Europeén (Saint Gobain C.R.E.E.)		France	Dr. Nathalie Petigny, E-mail: Nathalie.Petigny@saint-gobain.com

One of the main obstacles for commercialization of Solid Oxide Fuel Cells (SOFCs) is insufficient durability, which is largely due to degradation of the anode electrode. Anode degradation in hydrogen fuelled SOFCs corresponds mainly to micro-structural changes due to thermal and/or electrochemical sintering and oxidation/reduction of the anode, due to interruption of the fuel supply. Anode degradation in SOFCs using natural gas or other hydrocarbon fuels is additionally due to carbon deposition and sulphur poisoning, which result in severe decrease of both the electrocatalytic activity of the anode and its catalytic activity for internal reforming or direct oxidation of the fuel. The **key objective of ROBANODE** is the development of an integrated strategy for understanding the mechanism of anode degradation in SOFCs. This is envisaged through a combination of theoretical modeling with experiments over an extended range of operating conditions, using a large number of modified state-of-the-art (SoA) Ni-based cermet anodes.

The main targets accomplished and conclusions drawn by the end of ROBANODE can be summarized as follows:

NiO/GDC cermet powders for preparation of anodes and assembling of corresponding fuel cells were synthesized and characterized, focusing mainly on high specific surface area (SSA) **NiO/Gd_{0.1}Ce_{0.9}O₂ (65/35 wt%) cermets prepared via combustion synthesis**. Materials for use as adhesion (buffer) layers between the anode and the electrolyte were also additionally prepared (**Gd_{0.1}Ce_{0.9}O₂** and **Gd_{0.4}Ce_{0.6}O₂**).

Modified anode powders for study of degradation due to carbon deposition and sulphur poisoning were prepared. The performed work concerned preparation of Cu-, Ag-, Au-, Mo-, Re and ternary Au – Mo – NiO/GDC, Au – Re – NiO/GDC cermet powders. Specifically, commercially available NiO/GDC cermet powder was modified with Au and/or Mo, using deposition – precipitation (D.P.) and deposition – coprecipitation (D.CP.) methods, resulting in new binary and ternary composites with different structure properties and carbon tolerance under conditions of catalytic methane dissociation and steam reforming. These preparation methods, which were for the first time applied to state-of-the-art NiO/GDC cermets, permitted modification of the structure/composition of a commercial powder and lead to cermets exhibiting improved catalytic performance as it concerns the reactions of CH₄ steam reforming and CH₄ catalytic dissociation. The sono-chemical method was also successfully used for molybdenum oxide preparation and corresponding modification of Ni-based cermet powder, either via decoration of the NiO/GDC cermet powder with initially prepared molybdenum oxide or via co-sonication of molybdenum, rhenium and tungsten oxide precursors with the NiO/GDC cermet

powder. NiO/YSZ cermet powders were also used in the frame of ROBANODE, but they were mainly treated as reference anodes without any further modification.

Half and full anode-supported cells (ASCs) and full electrolyte-supported cells (ESCs) were prepared, using the aforementioned modified NiO/GDC and NiO/YSZ powders for the anode electrodes and were tested under H₂ or CH₄ steam reforming conditions, as described below. Specifically, circular electrolyte-supported (approx. 300 μm thick 8YSZ electrolyte) cells of 25 mm diameter with deposited electrodes of 1.76 cm² geometric surface area were fabricated in order to be used for kinetic and electrochemical measurements (including, measurement of rates and selectivity as a function of current) for investigation of the anodes performance under H₂ and CH₄ steam reforming conditions. Standard Saint Gobain anode-supported button cells (20mm dia. anode support) were also prepared, in order to perform a second series of electrochemical measurements under similar H₂ and CH₄ steam reforming conditions.

Comparison between the electrolyte-supported and anode-supported cells that comprised the modified NiO/GDC anode functional layers (AFLs) was performed, resulting in interesting conclusions. In particular, for the ASCs the sintering behaviour of the AFLs, modified with additives, was found to be completely different than that of the non-modified powders. Thus, different temperature adjustment was required in order to achieve sufficient tightness of the half cell. Tightness specifications were not similar to standard ASCs, since the anode functional layer was more porous for Au-Mo-NiO-GDC and NiO-GDC, therefore leading to higher values of leak rate. Nevertheless, some of the fabricated ASCs exhibited leak rate values conforming to the standard required tightness and these were sent for testing to EPFL. Moreover, the location of the additives on anodes in ASCs fabricated by Saint Gobain was investigated using the microprobe technique. The results indicated that the Au percentage on the anode surface was not the same as that in the initial powder, especially in the cases where higher sintering temperatures were applied. In addition, molybdenum was also difficult to be detected. This behaviour is directly attributed to the high (approx. 1430 °C) sintering temperature that was applied for the preparation of the ASCs from Saint Gobain. In combination with additional characterizations which are described below, it was concluded that during the high temperature sintering process, where the powders are in the oxidized form, Au suffers from sintering, while molybdenum is prone to sublimation. However, after the anodes are sintered and reduced then both Au and Mo become stable due to the formation of solid solution with nickel. Therefore, the Au and/or Mo modification of the NiO/GDC is definitely applicable on Electrolyte Supported Cells, where lower sintering temperatures can be applied. In the case of Anode Supported Cells further investigation is needed in order to adjust the sintering temperature at levels where the modifiers are not severely damaged.

The prepared Ni-based powders were characterized by a number of techniques, mainly XRD, SEM/EDS, TEM and XPS, in particular as it concerns the state of the modifiers. The characterization included study of the prepared anode powders with XPS and of anode electrodes with *in situ* ambient pressure X-ray photoelectron and near edge X-ray absorption fine structure spectroscopies (APPEs and NEXAFS, respectively), under working catalytic conditions. It was found that the binary Au – NiO/GDC (D.P.) cermet powder contained fine dispersed Au nano-particles (see **Figure 1**), the binary Mo – NiO/GDC cermet powder contained molybdenum oxide (MoO_x) species on the surface of the sample, whereas the ternary Au – Mo – NiO/GDC (D.CP.) as-prepared cermet powders contained both fine dispersed Au nano-particles and MoO_x surface species.

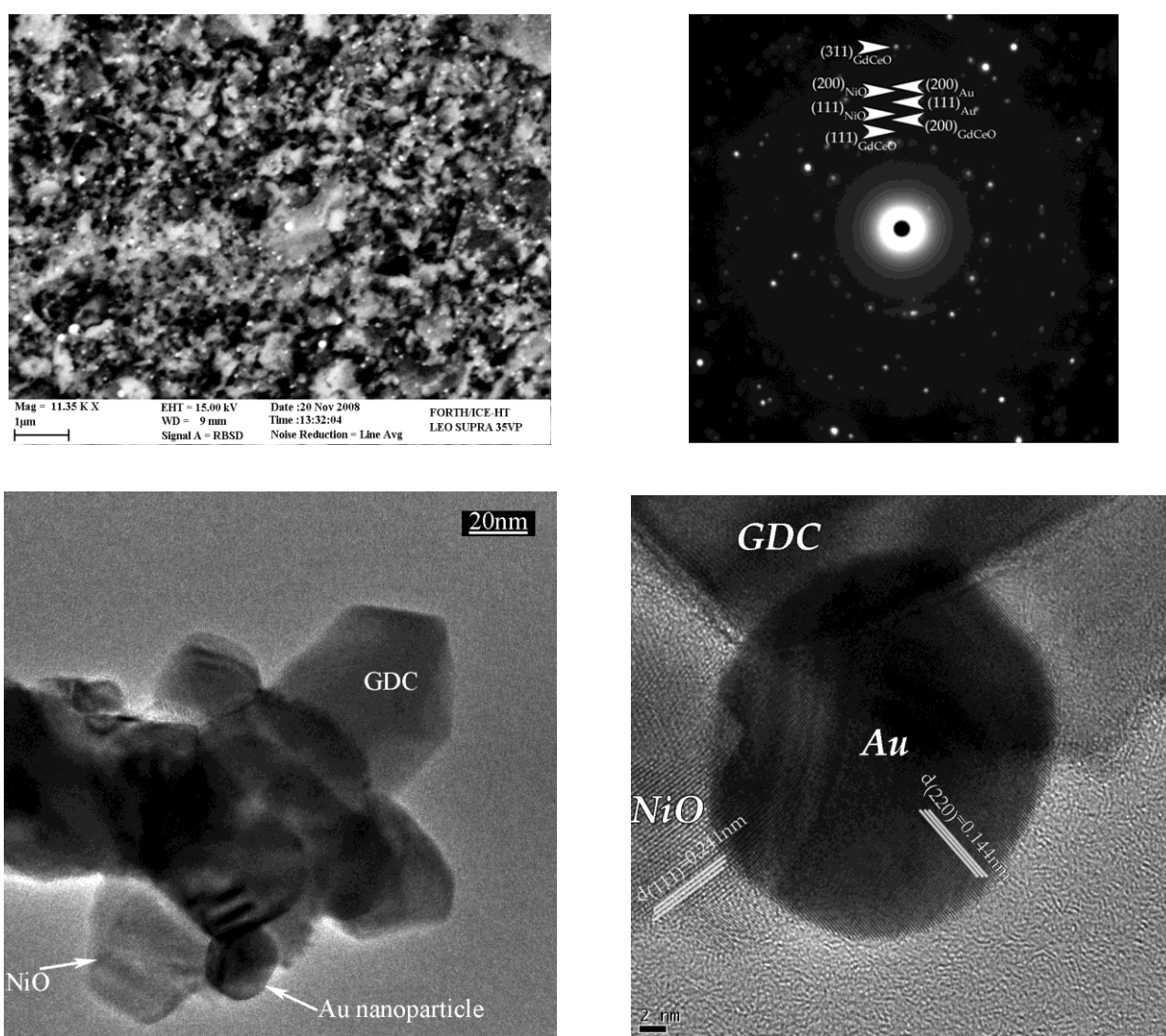


Figure 1: (a) SEM – BSE compositional image, (b) Selected Area Electron Diffraction patterns, (c) Low Magnification (LM) micrographs and (d) HRTEM images of 10 wt.% Au-NiO/GDC powder prepared using the (D.P.) method. The d-spacing of the (220) planes of Au and the d-spacing of the (111) planes of NiO are indicated respectively by white lines [1].

The most interesting structural findings were observed in the reduced form of the prepared powders, where a bimetallic Ni – Au solid solution is formed in the Au – modified sample and a bimetallic Ni – Mo solid solution in the Mo – modified sample. In the reduced form of the ternary composite material, a novel ternary Ni – Au – Mo solid solution seems to be formed (see **Figure 2** and **Figure 3**) [1].

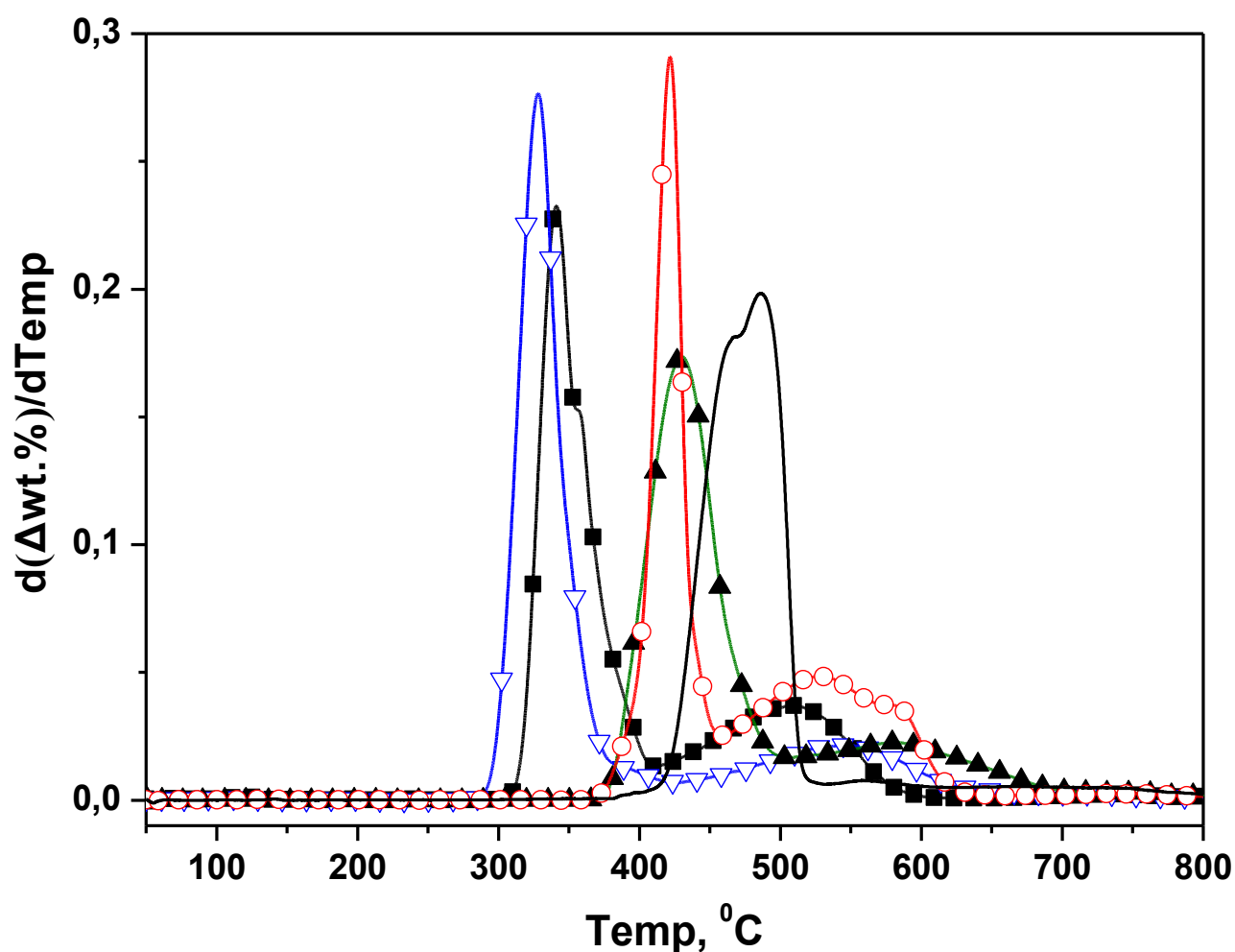


Figure 2: H_2 – TPR of blank (-■-) Ni/GDC and of (Au and/or Mo) modified powders prepared via deposition-precipitation and deposition-coprecipitation: (-▽-) 3 wt.% Au-Ni/GDC (D.P.), (-○-) 10 wt.% Mo-Ni/GDC (D.P.), (-▲-) 3 wt.% Au – 10 wt.% Mo-Ni/GDC (D.CP.) and (-●-) 3 wt.% Au – 30 wt.% Mo-Ni/GDC (D.CP.). All samples were tested under 10 vol.% H_2/Ar , increasing the temperature from 50 to 800 °C at a rate of 5 °C min^{-1} and the loading of each sample was approximately 23 mg [1].

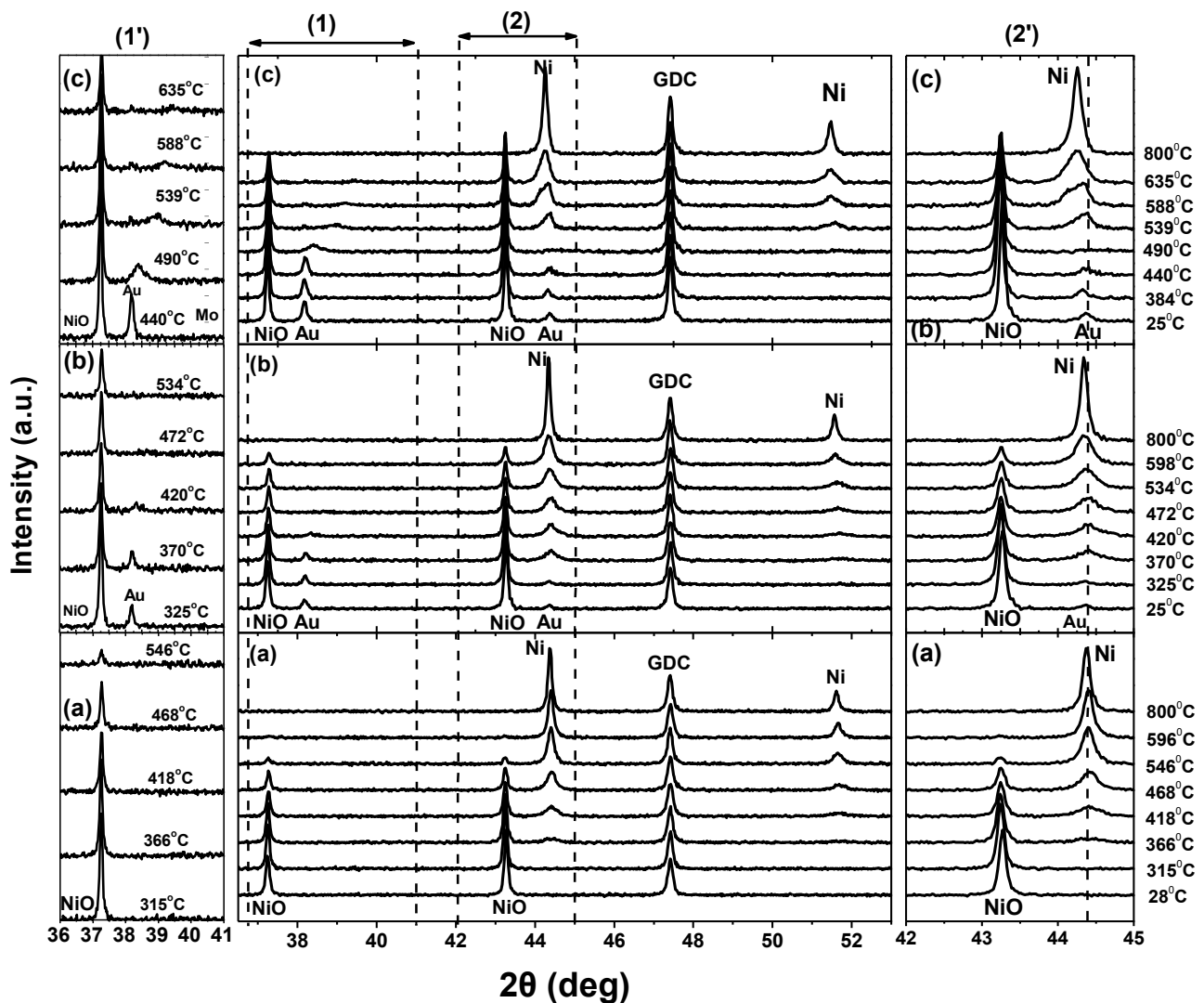


Figure 3: XRD – TPR patterns of (a) blank Ni/GDC, (b) 3 wt.% Au-Ni/GDC (D.P.) and (c) 3 wt.% Au – 30 wt.% Mo-Ni/GDC (D.CP.). During the XRD analysis all samples were in situ reduced under 2 vol% H₂/N₂, while the temperature increased from 50 to 800 °C at a rate of 5 °C min⁻¹. The frames (1') and (2') depict the magnification of the dotted (1) and (2) areas. The labeled XRD peaks correspond to Au (JCPDS 04-0784), NiO (JCPDS 44-1159), GDC (JCPDS 46-0508) and Ni (JCPDS 04-0850) [1].

In addition, SEM/EDS characterization revealed that molybdenum oxide preparation via the sono-chemical method was successful and reached the literature standards. As mentioned above, modification of the commercial Ni/GDC cermet powder using the sono-chemical method was performed either via initial Mo₂O₅·xH₂O preparation, followed by decoration of the NiO/GDC cermet powder or via co-sonication of molybdenum oxide precursor material with NiO/GDC cermet powder. The SEM/EDS characterization revealed that the first modification route had 25% yield, while the second one 12% yield. In general, both techniques were applied for less than 90 min, as it is proposed

in literature. It is believed that attempting decorations for longer times, up to 3 h, will yield higher decoration levels.

Regarding the physicochemical and structural properties of the modified NiO/GDC cermets, the most interesting findings concern the reduced form of the prepared powders, as already mentioned above. Furthermore, the fundamental characteristics of an operating Ni/GDC anode were described and the optimal surface state for maximum cell current was established, corresponding, under the conditions examined, to a mixture of zero-valence Ni and Ce^{3+} species in a Ni/Ce surface atomic ratio close to 0.4 (see **Figure 4**) [2].

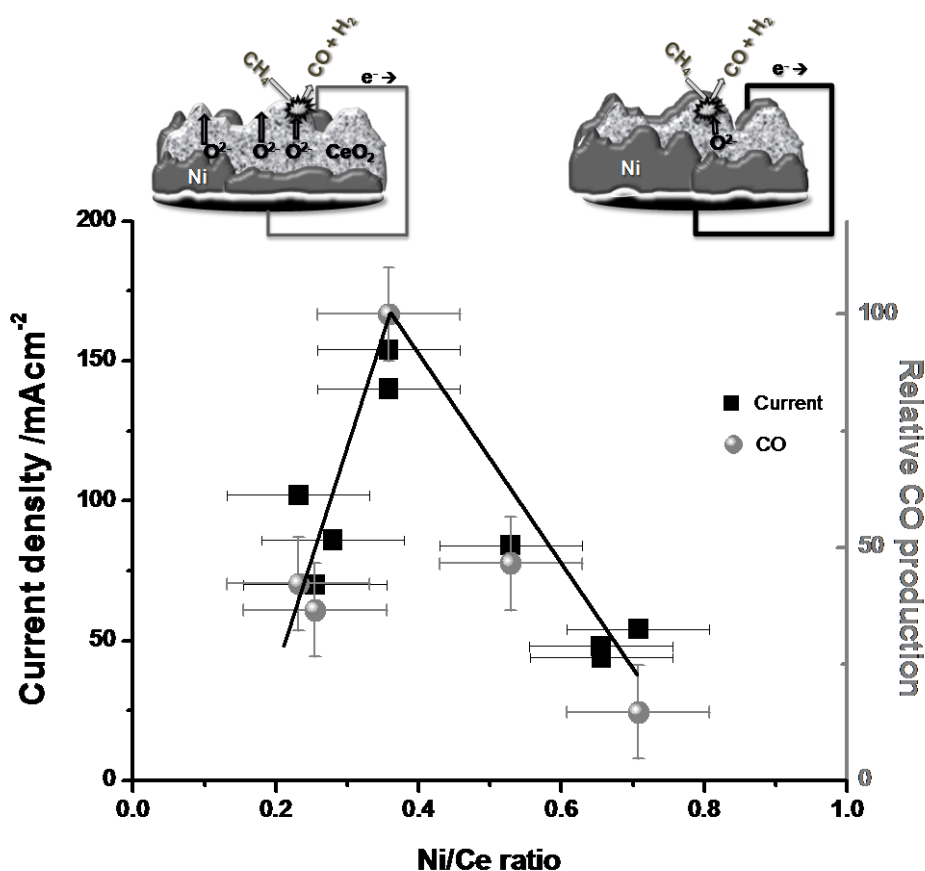


Figure 4: Current and CO production as a function of surface composition; The current flowing at the SOFC (left y-axis) and the relative carbon monoxide production (right y-axis) as a function of the Ni/Ce ratio measured by *in situ* APPEs. Measurements are performed on samples with identical nominal composition, but subjected to different pretreatments in the cell prior to the measurements. In all cases ceria and nickel exist exclusively in the Ce^{3+} and Ni^0 oxidation states. The error bars represent estimated uncertainty based on the photoelectron peak area and mass spectrometry signal calculations. Lines serve as guides to the eye. *Conditions:* anodic polarization (+1 V), atmosphere: 0.1 mbar CH_4 , temperature: 700° C. The schematic shows the proposed surface arrangement in the case of a low (left) and a high (right) Ni/Ce ratio [2].

Density Functional Theory (DFT) modeling gave insight into the function of Ce^{3+} ions and unravelled the multistep electrochemistry of Ni/ceria anodes. NiO and CeO_2 oxides were associated with lower cell currents, implying the occurrence of additional deactivation mechanisms of SOFCs besides the well-established carbon deposition and sulphur poisoning. Modification of the sample conditions (temperature, gas environment, etc.) has a direct effect on its surface state (see **Figure 5**) highlighting the importance of tracking the surface composition with *in situ* methods. This work [2], performed in the frame of ROBANODE, is a clear step forward towards rational design of active anodes for SOFCs.

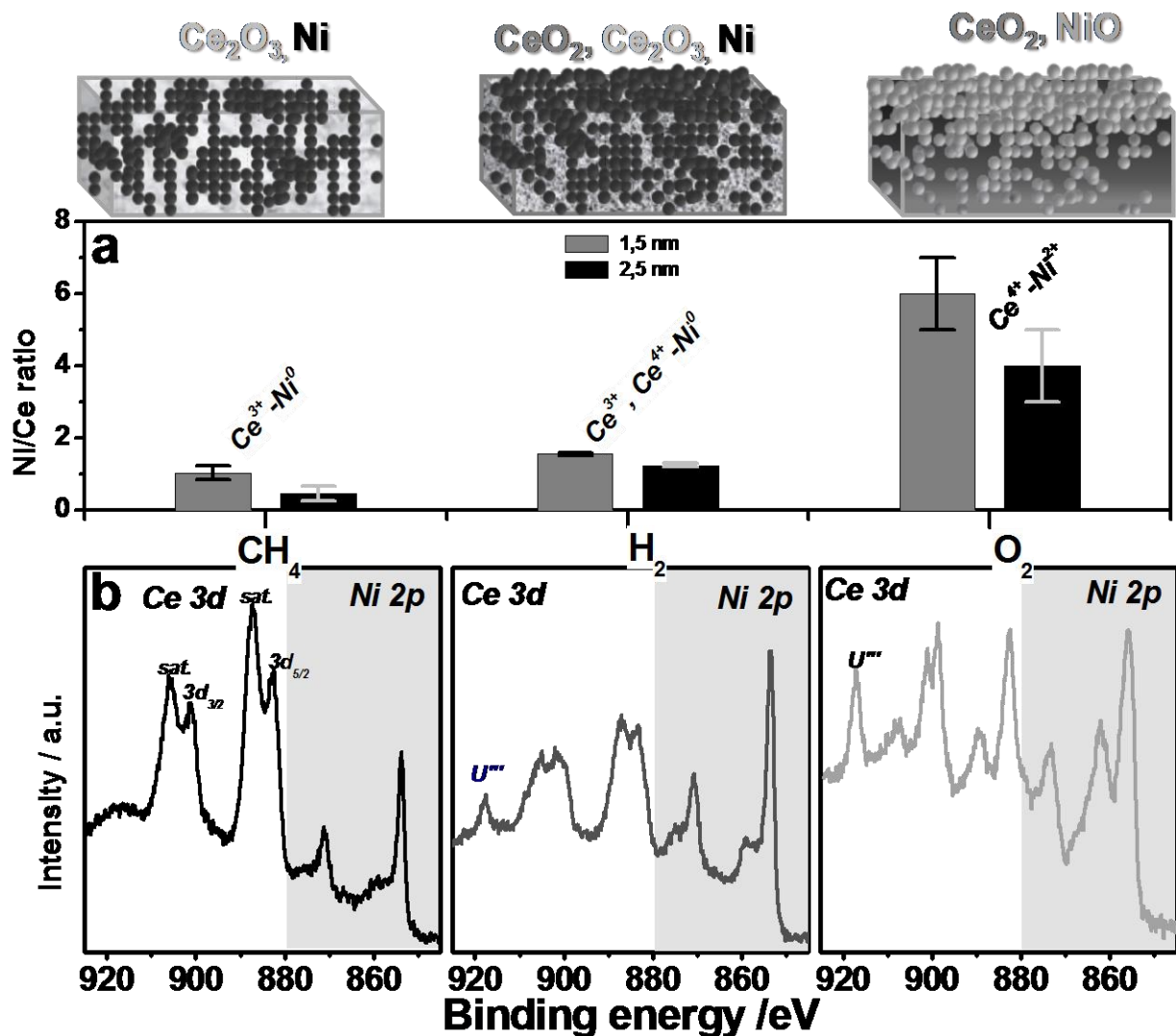


Figure 5: The Ni and Ce APPES spectra and composition ratios in different gas atmospheres and at OCP. a) Ni/Ce composition ratios *vs.* nickel and cerium surface chemical state, measured at two different photon energies at 700°C and at OCP. The error bars indicate uncertainties determined on the basis of 5 replicate measurements on different samples b) the Ce 3d and Ni 2p APPES spectra ($h\nu=1350$ eV) in different gas atmospheres. A schematic representation of the surface state is given at the *top* [2].

Another noteworthy remark came out from *in-situ* PES and NEXAFS measurements in H₂O(g) ambience, in order to elucidate the mechanism of steam electrolysis in cells that comprised NiO/GDC, as cathodes. The study was performed at two temperatures (500 and 700 °C), and under different cathodic potentials (up to max. -1.5 V). The effect of the surface oxidation state on the currents measured under cathodic polarization (pumping of O²⁻ away from the surface, inciting the water electrolysis reaction to occur) was investigated. In summary, the results showed that when cathodic potentials are applied in the solid oxide electrode assembly, comprising NiO/GDC as cathode, electrolysis of H₂O occurs in the gas phase with parallel production of gases and current (maximum 20 mA). The oxidation state and the segregation of the cathode materials upon polarization were evaluated by means of APPEES and NEXAFS spectroscopy. Kinetic experiments indicate that upon cathodic polarization only the oxidation state of nickel changes, due to reduction from the gas phase produced H₂. What is remarkable is that the existence of Ni/NiO mixtures does not inhibit the process; on the contrary, larger current values are measured for Ni/NiO mixtures compared to metallic Ni. In other words Ni/NiO mixtures can act beneficially on the electrolysis process. The partial pressure of H₂ that is produced during electrolysis is crucial for this kind of experiments; H₂ catalyses the reduction of NiO to Ni and sustains metallic Ni on the surface. An equilibrium between the gas phase induced oxidation of Ni and the reduction due to the produced hydrogen is achieved after two hours. The opposite effect (i.e. oxidation of Ni, surface segregation of NiO) is observed during subsequent anodic polarization. The O²⁻ ions do not seem to interact with nickel: they neither facilitate the oxidation of Ni (anodic polarization) nor the reduction of NiO (cathodic polarization). Concerning surface cerium, its oxidation state is not affected by the applied bias; part (25-28%) of cerium remains constantly at the Ce³⁺ state during cathodic polarization at both temperatures tested. However, the role of Ce³⁺ ions is most probably important to the process, since they seem to have some catalytic action (the electrolysis is not totally inhibited when NiO exists on the surface) whereas they presumably serve as charge carrier in the process of O²⁻ ions pumping.

The modified anode powders were also tested concerning their carbon tolerance for the reactions of methane decomposition and steam reforming, using *in-situ* thermogravimetric analysis (TGA) combined with mass spectrometry (see indicatively **Figure 6**) [1]. These tests revealed that the presence of Au has a more significant positive effect compared to Mo as it concerns inhibiting carbon deposition, under severe carbon forming conditions in the reaction of CH₄ steam reforming and catalytic dissociation. In the ternary cermet powder Mo seems to act synergistically with Au and Ni, as indicated by the exhibited enhanced carbon tolerance compared to the individual carbon tolerances of Au-Ni/GDC and Mo-Ni/GDC cermet powders. Specifically, in the methane steam reforming tests carried out isothermally at 750 °C the measured CH₄ conversion for Ni/GDC, 10wt.% Mo-Ni/GDC,

3wt.% Au-Ni/GDC and 3wt.% Au – 10wt.% Mo-Ni/GDC was approximately equal to 44%, 37%, 38% and 32%, while the specific rate of carbon deposition was equal to 1.2, 1.3, 0.5 and 0.3 mmol s⁻¹ m⁻², respectively.

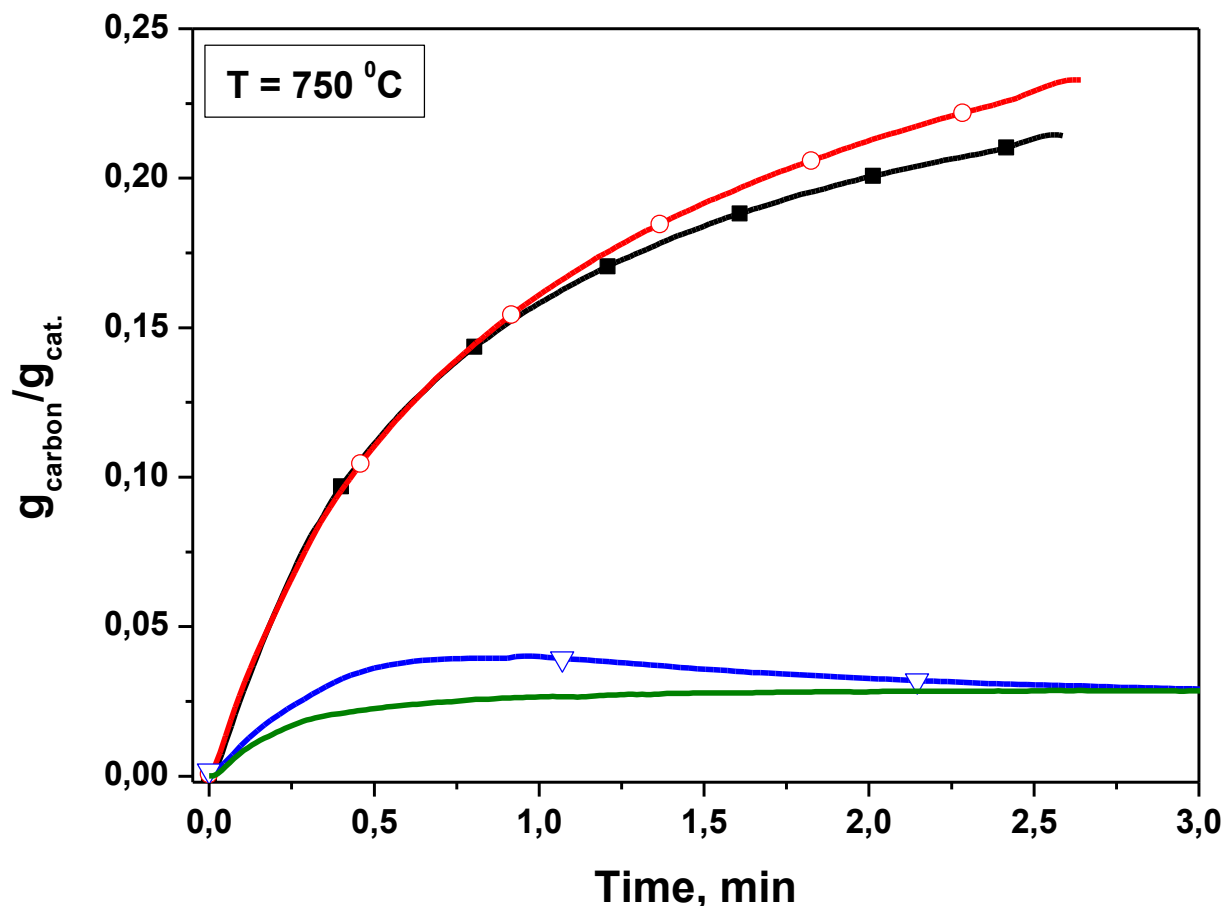


Figure 6: TG analysis of blank (-■-) Ni/GDC and on (Au and/or Mo) modified powders prepared via deposition-precipitation and deposition-coprecipitation: (-○-) 10 wt.% Mo-Ni/GDC (D.P.), (-▽-) 3 wt.% Au-Ni/GDC (D.P.) and (-) 3 wt.% Au – 10 wt.% Mo-Ni/GDC (D.CP.). The measurements were carried out isothermally at 750 °C under CH₄ steam reforming conditions with 20 vol% CH₄/Ar, 10 vol% H₂O in Ar (CH₄/H₂O = 2:1) at the total flow rate of 130 cc min⁻¹ [1].

In brief, among the studied catalysts-cermetes the 3wt.% Au-Ni/GDC sample showed the best combination of results in terms of structural-physicochemical properties, carbon tolerance and selectivity to the desirable products (H₂ and CO). The interaction between Ni and Au through the formation of the proposed Ni – Au solid solution causes presumably a weakening of the Ni – O bond strength and an enhancement of the NiO reducibility. The latter seems to induce a positive effect on the carbon tolerance of the sample and the selectivity to H₂ and CO in the CH₄ steam reforming reaction. Molybdenum doping by itself has a negative effect on carbon tolerance. As it concerns the

effect of addition of both gold and molybdenum, for the studied loadings, the corresponding ternary sample exhibited improved carbon tolerance indicating a noteworthy synergistic interaction between Ni, Au and Mo, whereas it appeared less active for H₂ and CO production and much more selective for the Water Gas Shift (WGS) reaction. The origin of the observed synergy between Ni, Au and Mo is not entirely clear. Considering the results of structural and catalytic characterization it can be suggested that molybdenum addition in the ternary sample, for nominal loadings 10 wt.% of Mo and higher, strengthens the Ni – O bond to an extent that proves to affect negatively the catalytic performance for the CH₄ steam reforming reaction, though it significantly inhibits the kinetics of carbon deposition. An important aspect raised from this synergistic interaction between Au, Mo and Ni is that molybdenum can substitute gold to some extent without significant change in the performance, enabling in this way the possible decrease of the latter precious metal, which would possibly result in a cheaper electrocatalyst for CH₄ fuelled solid oxide fuel cells.

As it concerns internal steam reforming in SOFCs, an important issue arises from the promotion of the competitive catalytic cracking of hydrocarbons on Ni-based cermet electrodes, which results in degradation due to carbon deposition and in significant overpotential losses. Consequently, the key goal in optimizing internal steam reforming in SOFCs is to minimize the rate of carbon deposition and to achieve appreciable rates of hydrogen and carbon monoxide production, while maintaining high electric conductivity and high electrocatalytic activity. Nevertheless, the results suggest that a certain decrease in catalytic activity might unavoidably accompany controlling the carbon formation and deposition process. The studied materials have the potential to be used as anodes in CH₄ fuelled SOFCs that operate in the so-called intermediate temperature region (600 – 800 °C), where carbon deposition is thermodynamically favored thus making the anode electrode much more prone to degradation. A very recently published study concerning the aforementioned synergy between Ni, Au and Mo in modified NiO/GDC cermets [1] alongside with earlier published work reporting the promising behavior of a CH₄ fuelled SOFC that comprised Au-modified NiO/GDC anode [3] could be used as guide for the future modification of Ni-based anodes. However, there are still many parameters that need to be investigated, in order to further elucidate the reaction processes and kinetics alongside with long-term electrocatalytic SOFC experiments.

Regarding modification with rhenium, the main conclusion is that rhenium-modified Ni/GDC cermets seem not to be proper anodes for SOFCs under internal CH₄ steam reforming conditions. Although ReO_x-NiO/GDC exhibited higher catalytic activity than NiO/GDC for the CH₄ steam reforming reaction in the temperature region 500 – 800°C, there was enhanced carbon deposition and concomitant degradation of electrocatalytic activity. Moreover, ReO_x sublimates at the high temperature, where the anodes need to be sintered for the preparation of the cells. In conclusion, the

efficiency of Re-modified NiO/GDC cermets as improved catalysts/electrocatalysts for SOFC anodes needs to be further studied.

Overall, the aforementioned results of the testing and characterization revealed that the modification of state-of-the-art NiO/GDC cermets with Au and/or Au-Mo is a promising and commercially applicable way to tune its catalytic properties for development of new efficient and carbon tolerant SOFC anodes, , without abandoning the advantages of nickel (low cost, material compatibility).

In a next step, anode degradation under fuel cell operation was investigated, applying the gained knowledge from the materials and cells preparation. Taking into account that anode degradation is directly reflected on its electrochemical characteristics, part of the investigations included the determination as a function of time of the polarization and impedance characteristics of fuel cells with modified Ni-based anodes over a wide range of operating conditions, in order to obtain information about the underlying degradation processes. Moreover, the investigation comprised experiments on both ESCs and ASCs.

Specifically, unmodified (standard) NiO/YSZ anode-supported cells from Saint-Gobain were tested in EPFL under dry and wet hydrogen, as well as under internal reforming (IR) conditions, with steam-to carbon (S/C) ratio ranging from 0.5 to 2, at 800°C and for approximately 2000 hours. The results showed a small amount of degradation, due to contributions of the cathode process (disappears before 1000 h), the anode contact (suppressed when replacing Ni foam for Ni anode paste), and 3 anode processes appearing at ca. 10 Hz, 100-200 Hz and 1-2 kHz. Part of the anode degradation under IR conditions is solely due to the high concentration of steam, as verified by comparative testing in wet hydrogen. The 10 Hz process may be attributed to diffusion through the anode support which could be blocked by carbon deposits under low steam-to carbon (S/C) ratio in the feed; regeneration is possible after switching to (especially wet) H₂ fuel (re-gasification). The 100-200 Hz process may be attributed to adsorption at active sites in the anode functional layer, and is similarly affected by high steam concentration and carbon deposits (plugging); partial regeneration is only possible, after switching the feed to (dry) H₂. The 1-2 kHz process may be attributed to charge transfer at the anode and is irreversibly affected, especially for the lower S/C ratios (1.25, 0.58).

Modified anode-supported cells from Saint-Gobain were also tested in EPFL. In these cells NiO/GDC instead of NiO/YSZ was used as anode functional layer whereas Au was used as modifier. The tested cells showed an inferior performance compared to that of the (NiO/YSZ-based) cells prepared with the standard anode fabrication process, most probably due to the fact that fabrication of cells comprising modified anode powders was not optimized yet. Only little degradation was observed over 100 h of operation under internal reforming conditions with a very low S/C-ratio, equal to 0.58, in the feed. A process located around 2 kHz, most probably corresponding to anode charge transfer, was

evident in the impedance spectra, which did not change appreciably with time. However, due to air supply failure, this observation concerns only a short duration test. The Au-impregnated Ni-CGO anode active layer showed only a slightly lower performance compared to the Au-free anode. Also, it exhibited a slight degradation both in dry H₂ and under internal reforming conditions but the test was run for only 900 h, while the target was testing for more than 1500 hours. However, the degradation seemed independent of carbon deposition, as it continued in dry H₂, and is again related to the anode process at 2 kHz. There was also a performance decrease in OCV due to seal leakage (cracks in cell edge). Yet after 900 h (700 h under IR at low S/C), the Area Specific Resistance (ASR) of the cell in H₂ remained stable. Considering the yet non-optimized nature of such a modified anode functional layer in ASCs, the latter result can be considered interesting and promising.

Circular planar electrolyte-supported (approx. 300 μm thick 8YSZ electrolyte) cells of 25 mm diameter and 1.76 cm² anode electrode geometric surface area were also used for assessment of the electrocatalytic and catalytic performance of Au-, Mo, and Au – Mo- Ni/GDC modified anode functional layers, including measurement of rates and selectivity (where applicable) as a function of current. The performance of the modified Ni/GDC cermet anodes was assessed both as it concerns the reaction of electrochemical H₂ (100 vol%) oxidation and the CH₄ steam reforming reaction at different temperatures (700 – 900 °C) and for CH₄/H₂O ratios ranging from 2 to 0.25. The first apparent observation was that modification of the Ni/GDC anode had a negative effect on the electrocatalytic activity for electrochemical oxidation of H₂. The situation was different under methane steam reforming conditions where the tested Au-Ni/GDC anodes appeared at low S/C ratios (<1) more active for electrochemical partial oxidation than for steam reforming of methane and quite carbon tolerant. Special tests were carried out for achieving adequate current collection from the cell anode and for avoiding any imponderable parameters that could obscure the assessment of the anode performance and the related effect of anode modification.

One of the most interesting findings that came out from the above electrocatalytic measurements on electrolyte-supported cells (ESCs) is that direct partial electrochemical oxidation of CH₄ at low S/C is the essential difference in the performance of Au-Ni/GDC anode compared to that of Au-Ni/YSZ, under similar conditions. In the case of Au-Ni/GDC, CO electrochemical oxidation under low S/C=0.25 does not apparently occur. This possibly shows that besides direct electrochemical oxidation of CO to CO₂, there is also partial contribution of the W.G.S. reaction. Meanwhile, in the case of Ni/GDC the presence of Au and its interaction with Ni seems to retard CH₄ dissociation into carbon species thus improving the carbon tolerance of the catalyst. The latter remark has been already confirmed [3] from the appreciable long-term stability of a Solid Oxide Fuel Cell that comprised a Au-modified anode, compared to another cell that comprised blank Ni/GDC as anode functional layer.

Specifically, the Au-modification process allowed for the tested cell a carbon tolerant operation at $T = 850\text{ }^{\circ}\text{C}$ under fuel rich internal steam reforming of methane, with a stable power density of $0.41\text{ W}/\text{cm}^2$ at 810 mV for over 200 h (see indicatively **Figure 7**).

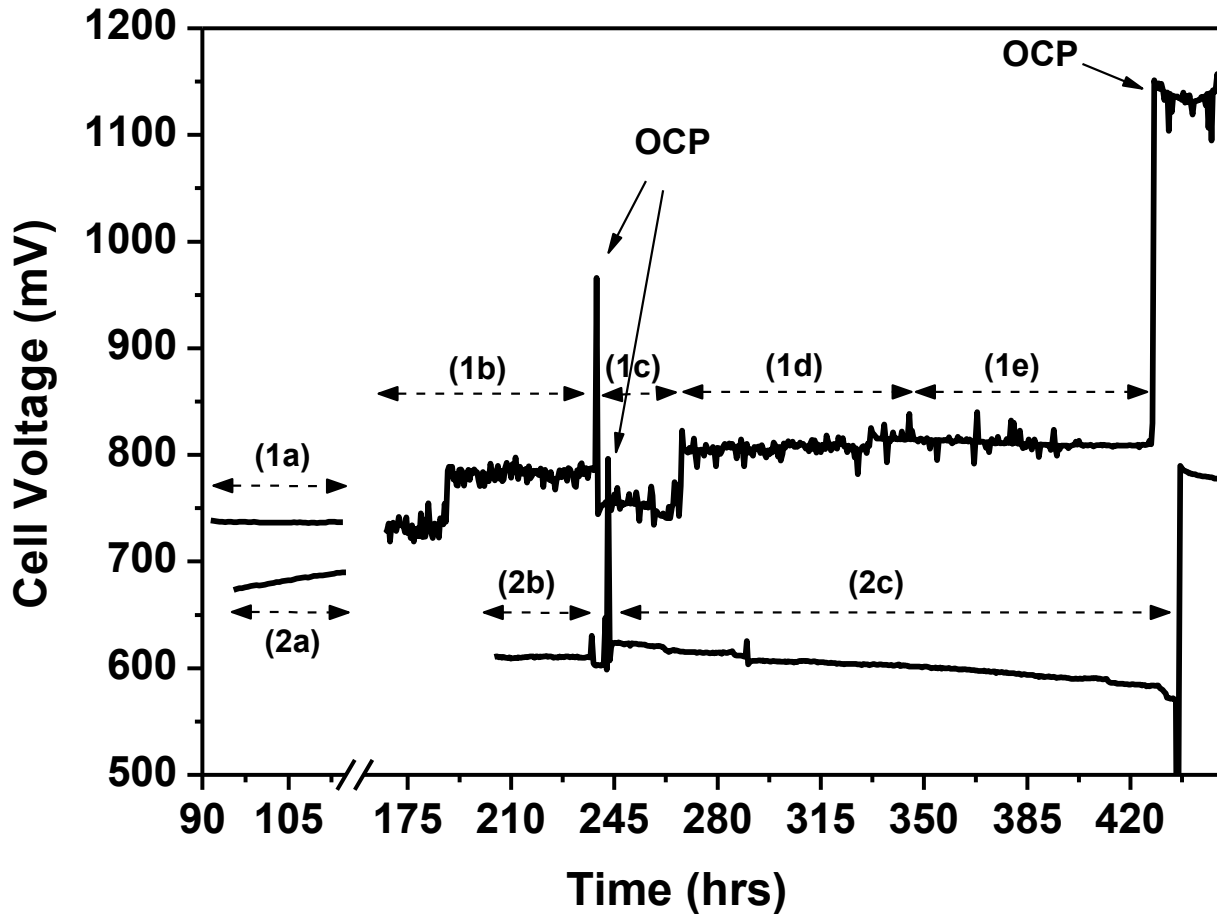


Figure 7: Stability test diagram of two cells comprising 1.5 at% Au-Ni/GDC and Ni/GDC as anodes at $T=850\text{ }^{\circ}\text{C}$ and 500 mAcm^{-2} . Label 1 corresponds to the performance of the cell with the Au-modified anode and label 2 to the blank cell. Conditions: **(1a)** $\text{H}_2\text{-3\%H}_2\text{O}$, $F_{\text{anode}}=520\text{ ccmin}^{-1}$, **(1b)** Steam/Carbon $\approx 3/2$: $P_{\text{H}_2\text{O}}=60.2\text{ kPa}$, $P_{\text{CH}_4}=41.2\text{ kPa}$, $F_{\text{anode}}=224\text{ ccmin}^{-1}$, **(1c)** reformat feed: 77 vol.% H_2 , 8 vol.% CO and 15 vol.% H_2O , $F_{\text{anode}}=374\text{ ccmin}^{-1}$, **(1d)** Steam/Carbon $\approx 1/2$: $P_{\text{H}_2\text{O}}=33.0\text{ kPa}$, $P_{\text{CH}_4}=68.3\text{ kPa}$, $F_{\text{anode}}=135\text{ ccmin}^{-1}$, **(1e)** dry CH_4 feed, $F_{\text{anode}}=90\text{ ccmin}^{-1}$. **(2a)** $\text{H}_2\text{-3\%H}_2\text{O}$ $F_{\text{anode}}=856\text{ ccmin}^{-1}$, **(2b)** Steam/Carbon $\approx 3/2$: $P_{\text{H}_2\text{O}}=60.1\text{ kPa}$, $P_{\text{CH}_4}=41.2\text{ kPa}$, $F_{\text{anode}}=509\text{ ccmin}^{-1}$ and **(2c)** Steam/Carbon $\approx 1/2$: $P_{\text{H}_2\text{O}}=33.2\text{ kPa}$, $P_{\text{CH}_4}=68.1\text{ kPa}$, $F_{\text{anode}}=308\text{ ccmin}^{-1}$ [3].

The performance of the abovementioned modified anodes in ESCs was also assessed under methane steam reforming conditions and in the presence of H_2S . In brief, it was observed that Ni/GDC remained stable in the presence of 10 ppm H_2S , but only in the case where pure H_2 was used as anode

feed. In the case where $S/C = 2$ or 0.13 , the performance of Ni/GDC anode was severely deteriorated, whereas the Au-Mo-modified anode exhibited the best performance.

Regarding the behavior of the ternary Ni-Au-Mo/GDC samples, the experience that was gained lead the strategy to decrease of the molybdenum content to a nominal loading of approximately 3 wt.% (in the total mass of the catalyst before reduction). These compositions have been investigated as anodes in SOFCs under internal CH_4 steam reforming conditions in the presence of H_2S . The results of the stability tests for the ternary 3 wt% Au-3wt%Mo-NiO/GDC anodes, concerning H_2S poisoning, were quite promising. This additionally indicates that the observed and discussed synergy between Au, Mo and Ni has a positive impact on anode performance for CH_4 , H_2O and H_2S anode feeds. Moreover, anodes with higher loadings of Au (e.g. 10 wt.% Au) could prove to have a positive effect in decreasing carbon deposition, which can limit the drawback of cost increase. However, there are still many parameters that need to be investigated, in order to further elucidate the reaction mechanism and kinetics, alongside with long-term electrocatalytic experiments.

A method for investigation of the Ni anode reduction and oxidation kinetics was devised. Re-oxidation irreversibility of anode supports was investigated in depth and great progress in its understanding was achieved, using advanced microscopy techniques (FIB-SEM, E-TEM). Based on this information, a redox robust anode microstructure could be designed. Furthermore, studies regarding micro-structural changes on Ni-based cermets, such as nickel coarsening in the anode, revealed that these changes slowly decrease the triple phase boundary (TPB) length and lower the efficiency of the fuel cell. The first step to resolve this issue is to understand and model the mechanism that leads to coarsening and anode degradation.

Research on degradation in Ni-YSZ cermet anodes has been slow as no easy microscopy method exists to observe and analyze their microstructure. Some optical microscopy techniques have been used, but inference layers are required to lower the high light backscatter coefficient of nickel and the achieved resolution (200 nm) remains insufficient. SEM images taken in backscattered electron (BSE) mode show only negligible contrasts between YSZ and Ni, because their backscatter coefficients are quite close at normal accelerating voltages. A contrast can be obtained via high-voltage SEM, but the phases are over- or under-estimated due to the increased interaction volume. Until now, the successful method was a Low Voltage Scanning Electron Microscopy (LV-SEM) technique that involved the lateral secondary electron detector, high working distances and fast scan rates. While this is a possible solution, better systems are needed to avoid surface charging, while allowing secondary electrons to escape the sample. In the framework of ROBANOde, a new method was used to obtain high resolution SEM images of Ni-YSZ cermet anodes with useful contrasts. By using a LV-SEM in ultra high-resolution conditions with an immersion lens, low working distances and a through-the-lens

detector in BSE mode, even small details like nano-porosities in the nickel phase could be easily observed. This technique was applied to study samples from an anode-supported solid oxide fuel cell, fabricated by Saint-Gobain. The anodes to be tested were placed in an oven at 800 °C under Ar/H₂ (dry) or H₂O/H₂ (wet) and samples were removed after, 24, 48, 96, 192 and 384 hours. The most remarkable changes in the anode active layer were observed during the NiO reduction process towards the formation of metallic Ni, which lead to both micro- and nano-porosities and to nickel coarsening. Still, more advanced image processing software must be utilized in the future to investigate these changes in detail.

One of the primary targets of ROBANOde was to develop a detailed study of the mechanism of the anode degradation processes, through identification of similarities/differences in the degradation behavior of unmodified and modified (via different methods and modifiers) state-of-the-art Ni-based cermet anodes, assisted by detailed characterization of the anode materials (as-prepared and used). An important point of the proposed strategy was development of a theoretical model for description of the performance and degradation of the anode, with non-adjustable parameters, accepting as input values of parameters that have been experimentally determined.

There has been a progressive evolution in the development of the mathematical model, according to the scheduled work-plan. There was continuous input of experimental data to the model, which mainly concerned electrocatalytic and kinetic investigations under methane steam reforming conditions using both state of the art Ni-based (Ni/GDC) and modified Ni-based cermets prepared in the frame of the project (specifically, Au-Ni/GDC and Au-Mo-Ni/GDC). These data were mainly used for validation of the developed model regarding description of the catalytic performance of the anode under open circuit conditions. They were also used in further development of the model for description of the catalytic/electrocatalytic performance of the anode under closed circuit conditions. In brief, the open-circuit kinetic data were obtained with a Ni/GDC and a 3wt.% Au-Ni/GDC anode, respectively, at different temperatures (800 – 900°C) and different methane (P_{CH_4} =0.5 – 16.5 kPa) and water ($P_{\text{H}_2\text{O}}$ =0.5 – 9.0 kPa) partial pressures (see indicatively **Figure 8**).

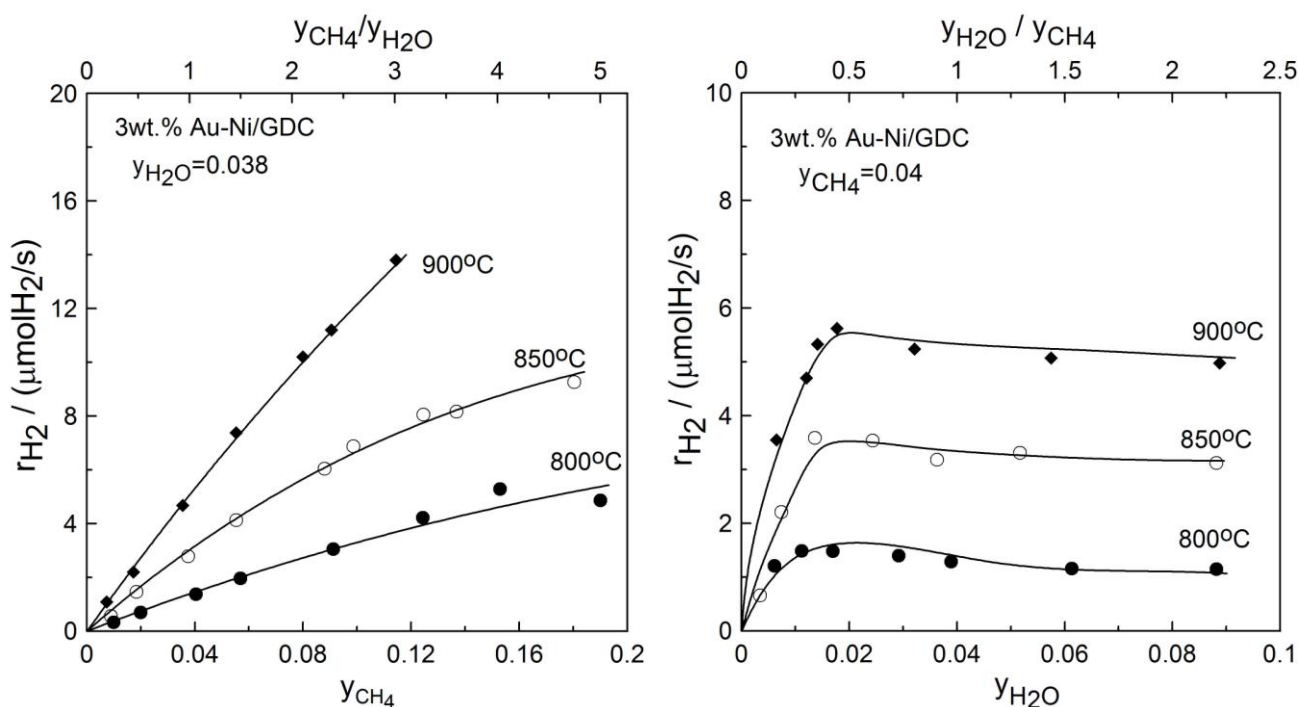


Figure 8: Steady-state effect of H₂O molar fraction of (y_{H_2O}) on the H₂ formation rate under open-circuit conditions and fixed CH₄ molar fraction ($y_{CH_4} = 0.03$). 3wt.% Au-Ni/GDC, differential conditions [4].

The electrocatalytic data were obtained with a 1wt.% Au-Ni/GDC catalyst electrode, at 850 °C and for two different steam-to-carbon (S/C) ratios ($S/C = 1$ and $S/C = 0.25$). The comparison of the mathematical model predictions with the observed anode performance has finally yielded a simple kinetic model, describing the catalytic and electrocatalytic performance of Ni-based anodes operating under internal CH₄ steam reforming reaction conditions, under both low and high steam-to-carbon ratio values.

The model accounts for surface dissociation of CH₄ and formation of methyl-species which then react with H₂O from the gas phase to form CO and H₂. Under high steam-to-carbon ratios (see **Figure 9**) it was found that the electrochemical oxidation of H₂ and CO is favored. In this case the model suggests that H₂ selective oxidation occurs at carbon-free adsorption sites and CO oxidation on sites covered by a carbonaceous adsorbate (see **Figure 10**).

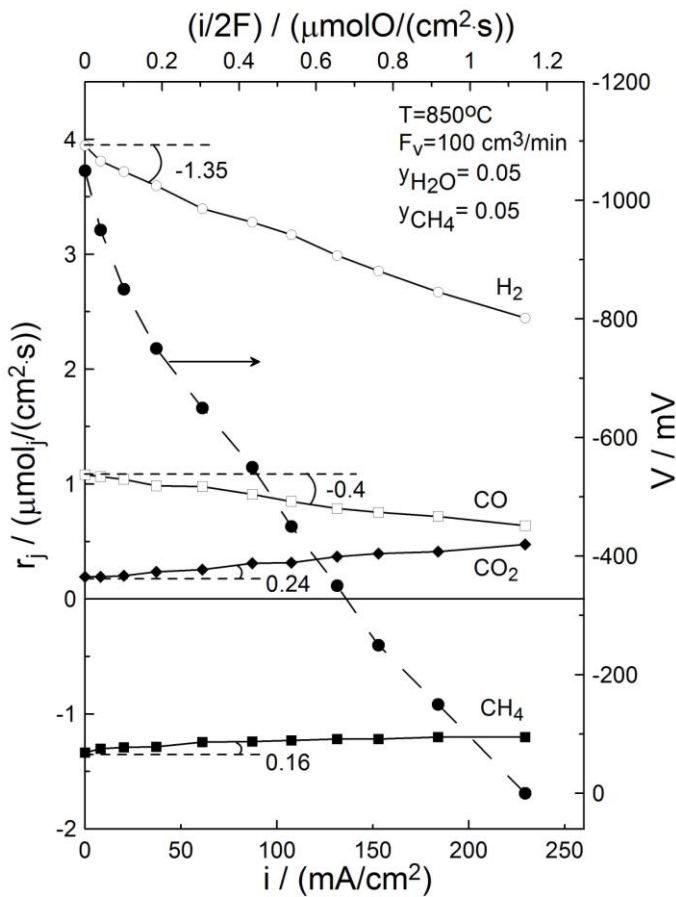


Figure 9: Effect of current density, i , on the potential, V , and on the reaction rates of H_2 , CH_4 , CO and CO_2 . $y_{H_2O} / y_{CH_4} = 1$, $T=850^\circ C$, 1wt.% Au-Ni/GDC anode, $T=850^\circ C$ [4].

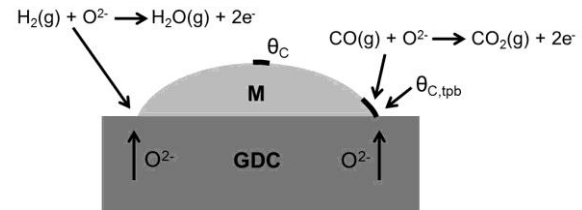


Figure 10: Schematic of the physical model developed for high steam-to-carbon ratio cases. It suggests H_2 electrochemical oxidation at carbon-free adsorption sites and CO electrochemical oxidation on sites covered by a carbonaceous adsorbate [4].

Under low steam-to-carbon ratios (see **Figure 11**) electrochemical partial oxidation of CH_4 to CO and H_2 in parallel with electrochemical oxidation of H_2 was found to take place. In this case, the model suggests (see **Figure 12**) that H_2 is also oxidized at carbon-free adsorption sites while CH_4 on sites covered by a carbonaceous adsorbate.

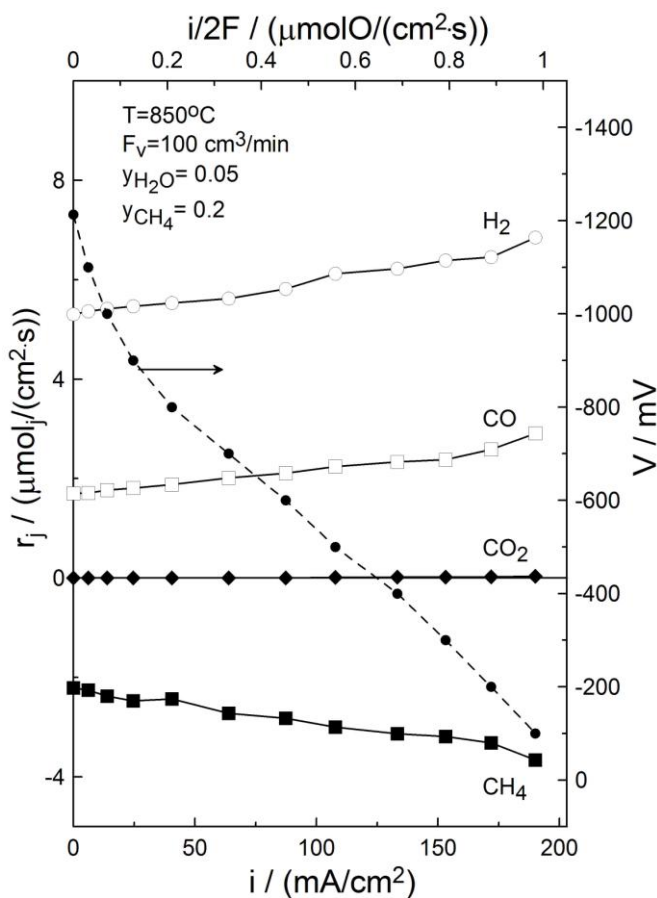


Figure 11: Effect of current density, i , on the potential, V , and on the reaction rates of H_2 , CH_4 , CO and CO_2 . $S/C=0.25$, $T=850^\circ C$, 1wt.% Au-Ni/GDC [4]

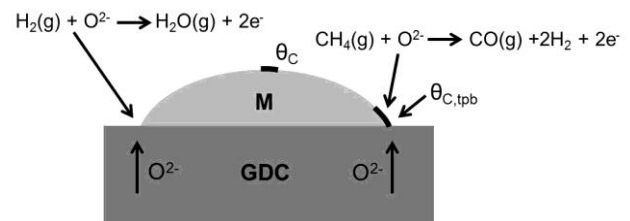


Figure 12: Schematic of the physical model developed for low steam-to-carbon ratio cases. It suggests H_2 electrochemical oxidation at carbon-free adsorption sites and CH_4 electrochemical oxidation on sites covered by a carbonaceous adsorbate [4].

Interestingly, in both cases the model predicts that the coverage of methyl-type species on the catalyst surface coincides with that at the three-phase boundaries (**Figure 13**). The model was found to be in good agreement with experiment, under both open-circuit and fuel cell operation conditions. Details can be found in a very recent publication [4]. Regarding the coverage of the carbonaceous species (θ_c), both CO and CO_2 formation must originate from the same carbonaceous species through two parallel electrochemical processes involving the oxidation of the adsorbed CH_2^* species. In the case of Ni/GDC the presence of Au and its interaction with Ni seems to retard CH_4 dissociation into carbon species, thus improving the carbon tolerance of the catalyst.

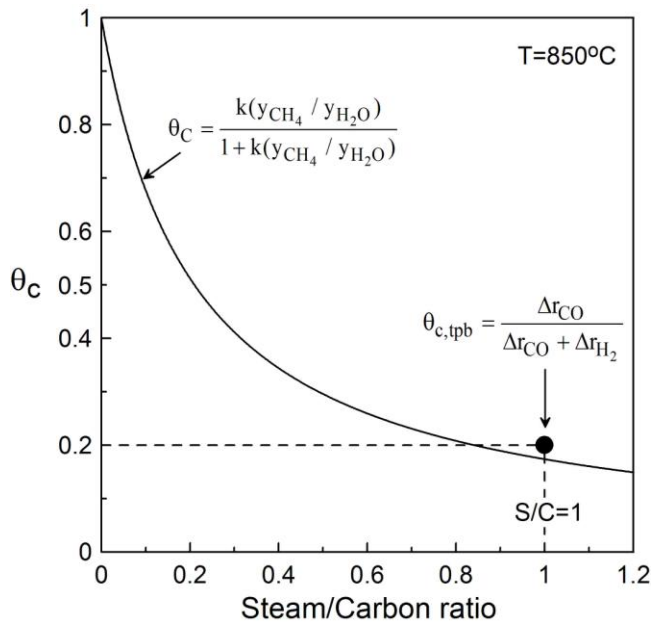


Figure 13a: Comparison between the model predicted methyl-type species coverage of the catalyst surface, θ_C , and methyl-type species coverage of the catalyst tpb, $\theta_{C,tpb}$. $S/C=1$, $T=850^\circ\text{C}$, 1wt.% Au-Ni/GDC [4].

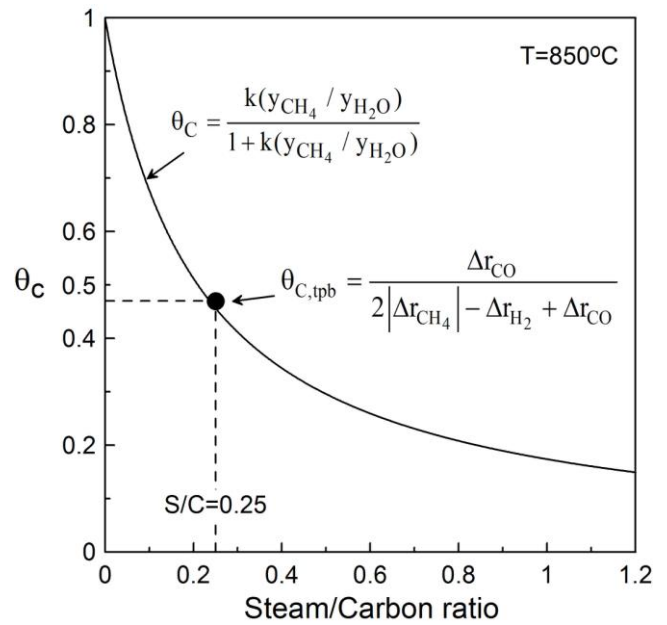


Figure 13b: Comparison between the model predicted methyl-type species coverage of the catalyst surface, θ_C , and methyl-type species coverage of the catalyst tpb, $\theta_{C,tpb}$. $S/C=0.25$, $T=850^\circ\text{C}$, 1wt.% Au-Ni/GDC [4].

A noteworthy remark, which was combined with the model predictions, resulted from the experiments carried out by CNRS [2]. These experiments concerned *in situ* APPEs and NEXAFS at 700°C combined with electrochemical measurements, under different ambient gas phase composition (0.1 mbar CH_4 , H_2O and 0.2 mbar for O_2 and H_2). They revealed that Ni/GDC cermet anodes play a vital catalytic and electrocatalytic role in the activation of CH_4 toward its electrochemical oxidation in SOFCs. Specifically, it was concluded that CH_4 reduces surface Ce^{4+} into Ce^{3+} , with parallel enhancement of the electrocatalytic performance of the anode. In combination with DFT calculations it was proposed that CH_4 is partially oxidized electrochemically by O^{2-} to CO and H_2 on the reduced Ce^{3+} sites. The CH_2^* or CH_2O^* species diffuse onto the Ni surface, where they are correspondingly oxidized to CO_2 and H_2O or decompose to CO and H_2 . In the case of methane lean conditions, CH_4 activation takes place rather on Ni, whereas ceria can be partially reduced thus promoting the selectivity of H_2 and CO oxidation reaction to H_2O and CO_2 , respectively. This can be rationalized by the observation that Ni is encapsulated in GDC, in particular under methane reducing atmosphere, which causes total reduction of surface Ce^{4+} into Ce^{3+} .

In addition, the observed [4] non-Faradaic rate changes during the electrocatalytic measurements and especially under fuel lean conditions can be attributed to the effect of Electrochemical Promotion of Catalysis (EPOC) or non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA effect) [5]. The appearance of electrochemical promotion at such elevated temperatures (800-850°C) is not normally expected, since EPOC has been observed at temperatures below 600°C, due to desorption at higher temperatures of the adsorbed promoting oxygen anionic species which cause EPOC in the case of O^{2-} conductors [5]. However, the metal-oxygen interaction is very strong in the case of nickel, which explains the detected by CNRS accumulation of ionic oxygen species on the catalyst surface during current application (i.e. O^{2-} pumping to the Ni/GDC). It can be claimed that the accumulated excess of oxygen ionic species can act as the $O^{\delta-}$ promoting species and affect the catalytic properties of the Ni/GDC anode, according to the theoretical basis of EPOC [5]. This claim can be substantiated through the enhancement of the oxidation and decomposition catalytic reaction steps and the concomitant promotion of the overall steam reforming catalytic reaction rate. The non-Faradaic behavior of the Au-Ni/GDC anode under CH_4 rich conditions can be proven as a potential example pointing to the wide application of SOFCs as chemical co-generation reactors for production of electricity and synthesis gas.

In the frame of ROBANODE, another mathematical model was also developed that describes the effect of polarization in the metal particles size and the three phase boundary length (l_{tpb}). This model allows the prediction of the catalyst deactivation rate due to sintering of the metal particles under closed-circuit conditions, and is based on a correlation of sintering with anode overpotential [6]. The performed study in the frame of the project was a step towards development of a model for the whole anode electrode starting from a model which concerned a single metal particle [6].

Specifically, the investigation regarding the effect of cell polarization on the metal particle size resulted in a mathematical expression, with which it is possible to calculate the work of adhesion of metal particles (for example Ni), for any degradation curve obtained experimentally. Previous relevant studies concerning the Ni - YSZ system [7] have shown that the calculated work of adhesion values are in very good agreement with the corresponding literature values [8]. As it concerns the model prediction of the decrease in the three – phase boundary length (l_{tpb}), the starting point is the Butler-Volmer equation, which relates the current density with the electrode overpotential. One basic assumption used in the model is that the exchange current i_0 for the particular electrode/electrolyte interface is proportional to l_{tpb} . The model predicts that the variation of l_{tpb} with time depends on the variation of electrode potential U with time, or, equivalently, with the degradation rate $r_{deg} = dU/dt$, thus making possible the calculation of the reduction l_{tpb} with time, for various degradation rates.

Alternatively, by measuring experimentally the reduction of the three phase boundary length, the degradation rate can be predicted.

The aforementioned mathematical model predicting (i) the effect of cell polarization in the metal particle size and (ii) on the three-phase boundary length will be provided with experimental data, from measurements of the micro-structural changes of Ni-based cermets. Such measurements have been performed by EPFL, as described above, but due to the fact that they were time-consuming it did not become possible to use the corresponding data as feed to the model by the end of ROBANOde. Nevertheless, this is in the process and the corresponding results and conclusions will be disseminated in the form of scientific publications in the near future.

Summarizing, two mathematical models were developed in the frame of ROBANOde which, combined with reliable experimental data, can provide an adequately integrated approach regarding modeling of key-processes that are responsible for anode degradation during SOFC operation.

In conclusion, the overall progress of ROBANOde is considered satisfactory. The majority of the reported tasks have been elaborated efficiently, although certainly not to the same extent. Moreover, though there were some delays in few deliverables, these did not affect the final outcome of the project. It has to be stressed that all partners showed high responsibility and appreciable interaction through their activities. This resulted in quality research and noteworthy results, relative to the objectives of the project. Finally, though some of the conclusions are not fully presented in the Final report, there will be detailed scientific publications soon after the completion of ROBANOde that will integrate the aims of the project, thus making the final outcome a useful contribution to the scientific and industrial community.

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