

Fuel cells and hydrogen

Joint undertaking

Programme Review Day 2012
Brussels, 28-29 November



<http://www.fch-ju.eu/>

Fuel Cells and Hydrogen

Joint Undertaking

ROBANODE (245355)

Coordinator: Prof. Symeon Bebelis^{1,2}

Speaker: Dr. Dimitrios K. Niakolas¹











*¹Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences,
GR-26500, Patras, Greece (FORTH/ICE-HT)*



²Department of Chemical Engineering, University of Patras, GR-26504, Greece

Fuel Cells and Hydrogen

Joint Undertaking

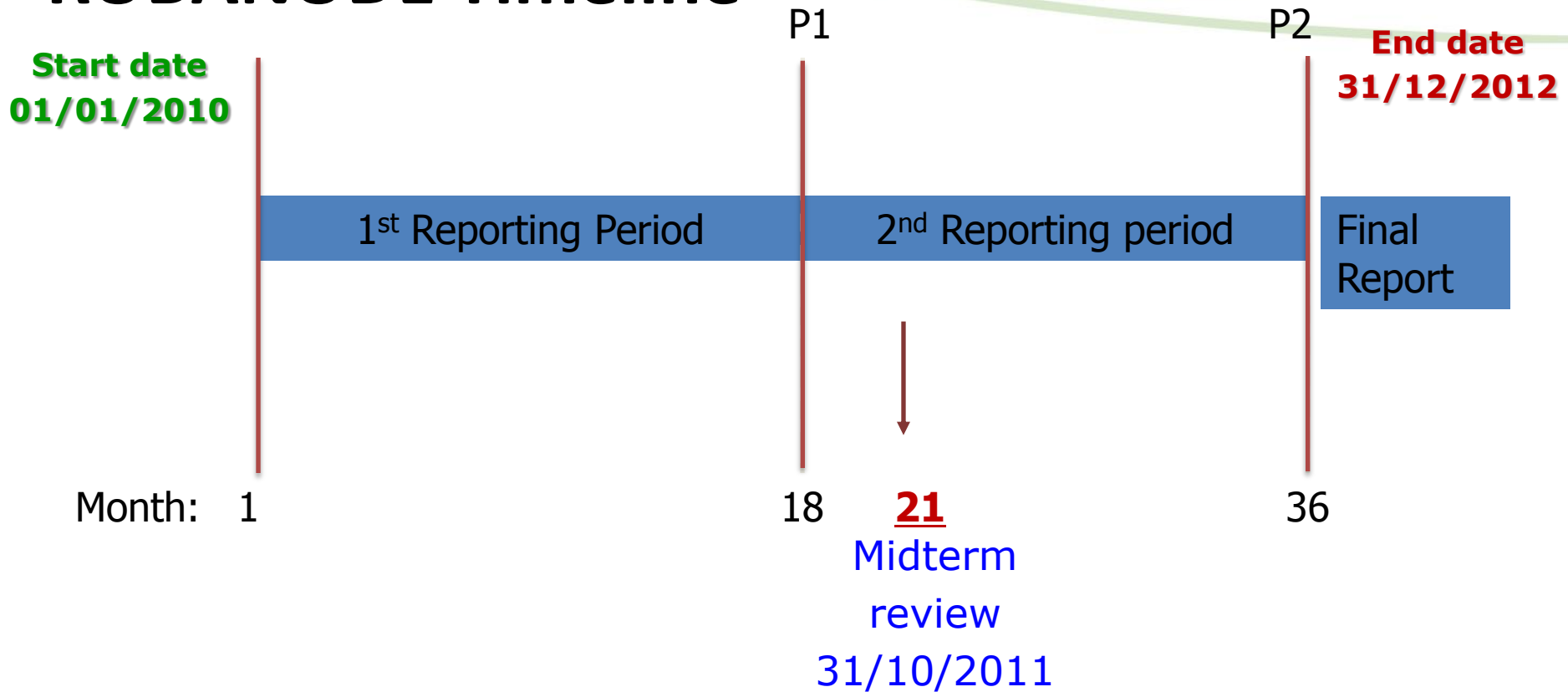
| No | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------|-------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| Partner Short Name & Logo | FORTH/ ICE-HT  | TUC  | NTUA  | EPFL  | CSIC  | CNRS  | CERECO S.A.  | Saint Gobain CREE  |
| Country | Greece | Germany | Greece | Switzerland | Spain | France | Greece | France |

- Four (4) EU members (France, Germany, Greece, Spain) and Switzerland
- Six (6) Research organizations (FORTH/ICE-HT, TUC, NTUA, EPFL, CSIC, CNRS)
- One (1) SME (MIRTEC S.A.)
- One (1) Industrial partner (Saint Gobain CREE)

Fuel Cells and Hydrogen

Joint Undertaking

ROBANODE Timeline



Fuel Cells and Hydrogen

Joint Undertaking

Aims of ROBANODE

A **deeper insight** with regards to the interference and the concerted action of the **various factors** that contribute to **degradation of Ni - based cermet anodes in SOFCs**:

- **Agglomeration** of Ni particles due either to **thermal** or **electrochemical sintering**
- Degradation due to **carbon deposition and improvement of tolerance** under CH₄ Internal Steam Reforming (ISR) (S/C = 0.5 or less).
- Degradation due to **sulfur contamination** and tolerance improvement under CH₄ ISR conditions in the presence of H₂S (5 – 30ppm).
- **RedOx tolerance** of the cermet anodes.

Fuel Cells and Hydrogen

Joint Undertaking

Main Objectives

- **Understanding the interrelations between the aforementioned degradation factors** so that targeted modifications in the structure and morphology of the Ni-based anodes can be made
- **Modeling of the degradation processes** in correlation with experimental observations
- **Simulation** of the chemical and physicochemical processes under SOFC operation

Fuel Cells and Hydrogen

Joint Undertaking

Strategy

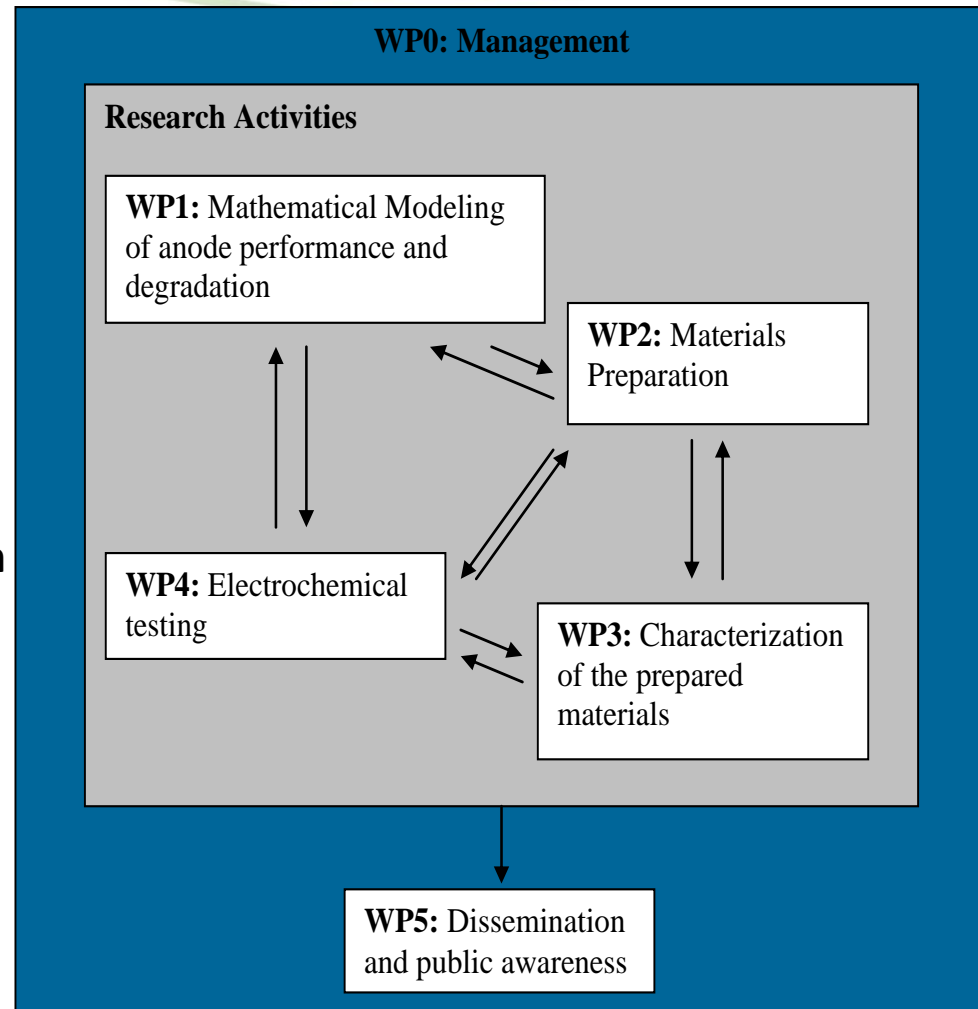
- ❖ Study of the **performance** of *state-of-the-art* **Ni-based** cermet anodes (e.g. NiO/GDC) modified with a second metal (**e.g. Au, Mo and other**), concerning *carbon and sulfur tolerance*
- ❖ Investigation of the degradation processes **in the modified anodes** using **various techniques** (including XPS, UPS, SEM, TEM, XRD, TPR impedance spectroscopy and other...)
- ❖ Use of the outcome of the aforementioned studies as **feedback to a mathematical model for prediction of the anode behavior**
- ❖ **Fabrication of cells for catalytic and electrochemical testing** of the modified anodes and for investigation of their **long-term performance**

Fuel Cells and Hydrogen

Joint Undertaking

Milestones

- ✓ Implementation of **management**
- ✓ **Model** describing the degradation processes
- ✓ Preparation of **modified anode powders**
- ✓ Preparation of **cells**
- ✓ **Comparison** of the **model predictions** with the **observed electrochemical behavior** of the anode.
- ✓ Establishment of **communication** with **scientific community, other projects** and **wide public**.



Fuel Cells and Hydrogen

Joint Undertaking

Alignment to MAIP/AIP & Innovation

- ❑ According to MAIP/AIP: *“Fuel cell stacks for stationary power applications require an operational lifetime up to 40,000 hours”*
- ❑ This target has not been achieved yet and anode degradation is one of the main reasons
- *The ultimate goal of ROBANODE is the study, understanding and modeling of the degradation mechanisms of state-of-the-art (SoA) Ni-based cermet anodes*
- *ROBANODE fits exactly to the objectives of: “Degradation and lifetime fundamentals of SOFCs”*

Fuel Cells and Hydrogen

Joint Undertaking

Alignment to MAIP/AIP & Innovation

- Main output of ROBANO
- ❖ Development of a model for prediction of the (SoA) Ni-based anode performance and degradation
- ❖ Development and improvement/optimization of (SoA) Ni-based anodes, easily commercialized, for CH₄ fuelled SOFCs (under Internal Reforming or Direct Oxidation conditions)
- ❖ Study of the degradation mechanism due to thermal and electrochemical sintering
- ❖ Study of the degradation mechanism due to carbon deposition and sulfur poisoning

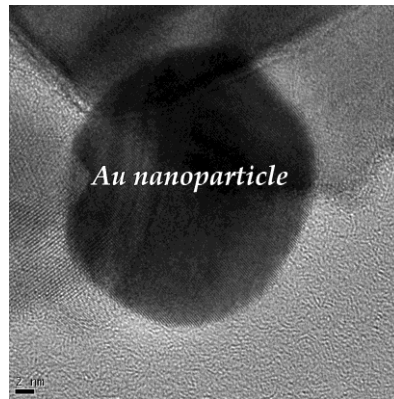
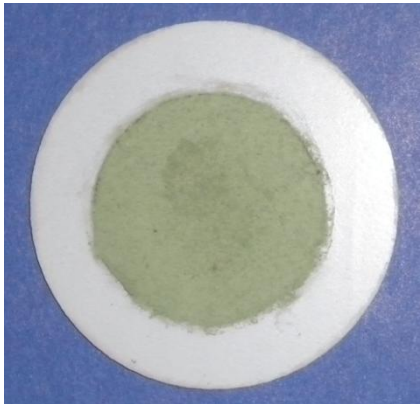
Fuel Cells and Hydrogen

Joint Undertaking

Alignment to MAIP/AIP & Innovation

□ *Modified (SoA) anodes and cells preparation/characterization*

- Au-NiO/GDC, Mo-NiO/GDC, Re-NiO/GDC, Au-Mo-NiO/GDC, Au-Re-NiO/GDC
- Studies of degradation due to carbon deposition and sulphur poisoning.



- Electrolyte-Supported Cells (ESC)
- Anode-Supported Cells (ASC)

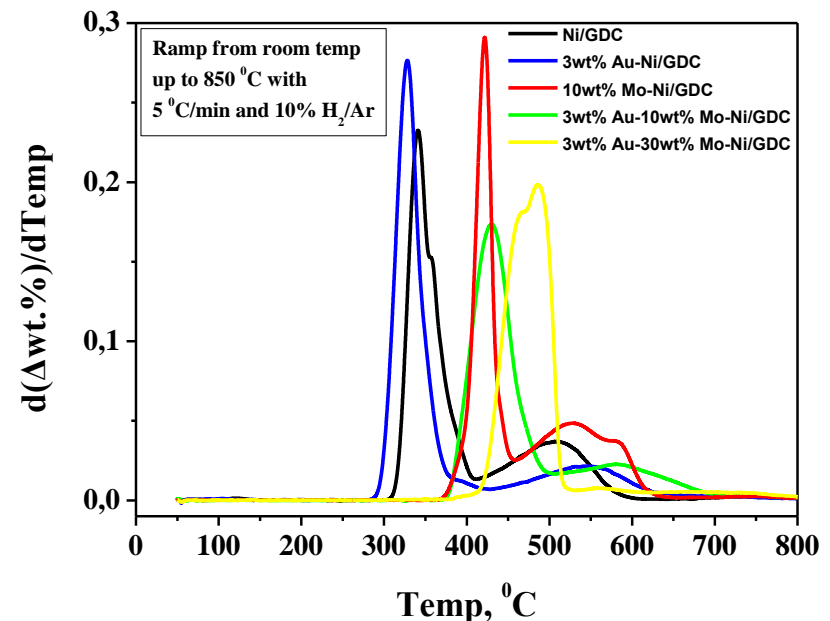
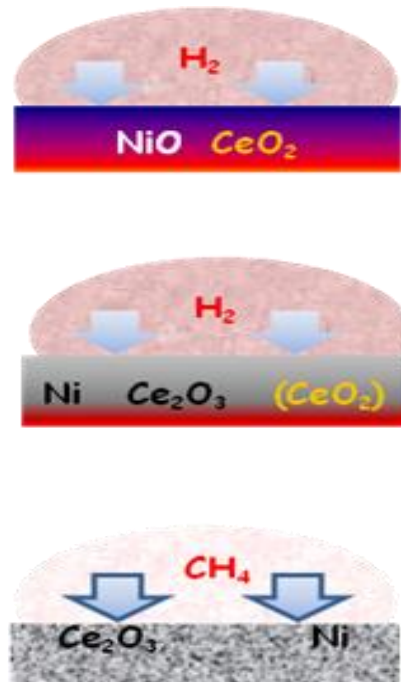
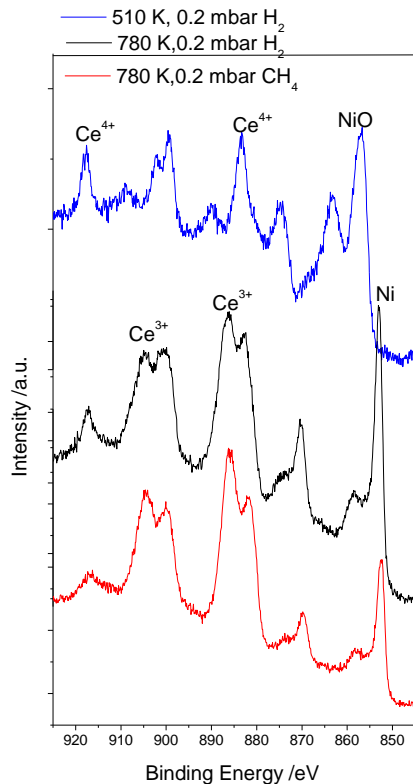
Fuel Cells and Hydrogen

Joint Undertaking

Alignment to MAIP/AIP & Innovation

□ **Modified (SoA) anodes and cells preparation/characterization**

- Several *ex situ* techniques...
- *In situ* XPS, NEXAFS XRD, e.t.c.



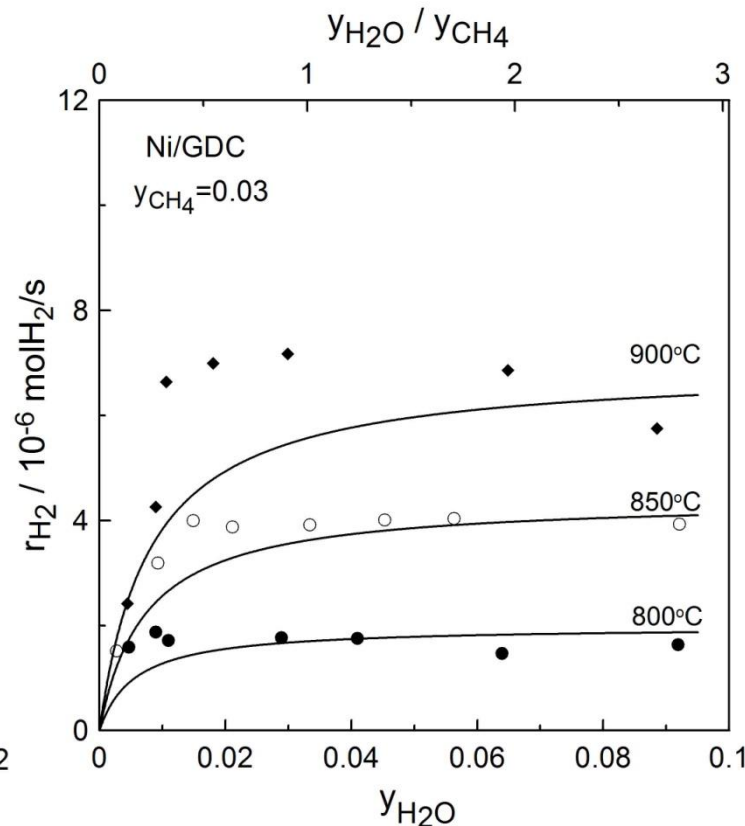
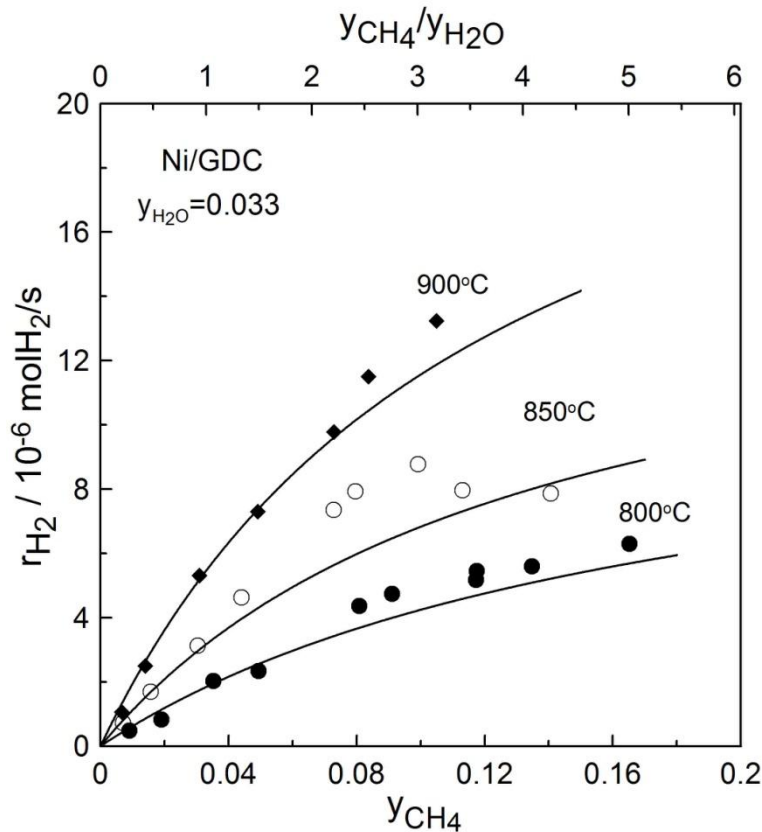
Fuel Cells and Hydrogen

Joint Undertaking

Alignment to MAIP/AIP & Innovation

ESC and ASC performance and stability testing

Catalytic-
Kinetic
experiments



$$r_{CH_4} = \frac{k_a P_{CH_4}}{1 + \frac{k_a P_{CH_4}}{k_r P_{H_2O}}}$$

$$r_{H_2} = 3 |r_{CH_4}|$$

$$r_{H_2} = 3 \frac{k_a P_{CH_4}}{1 + \frac{k_a P_{CH_4}}{k_r P_{H_2O}}}$$

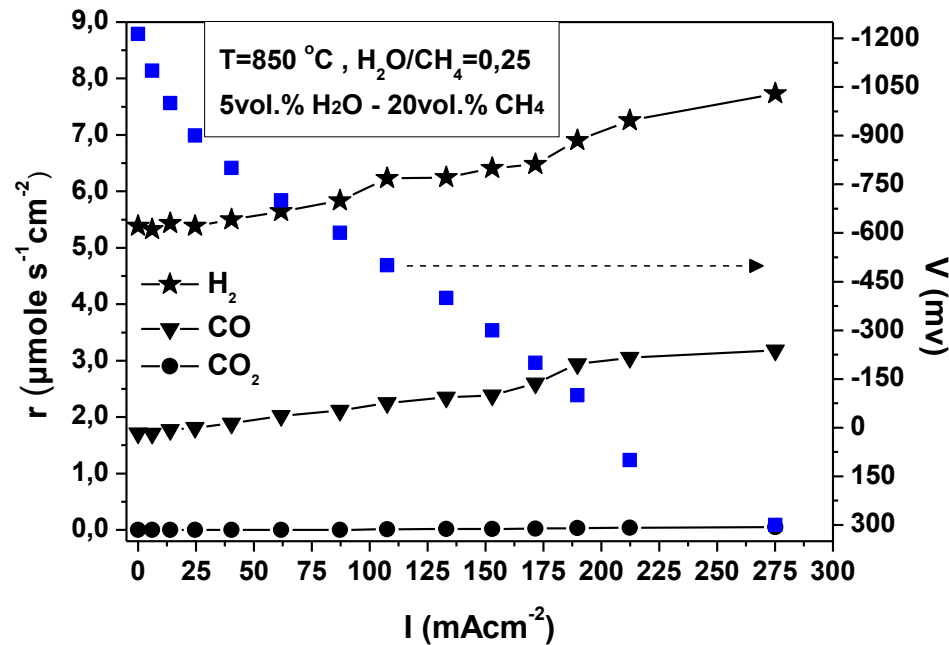
Fuel Cells and Hydrogen

Joint Undertaking

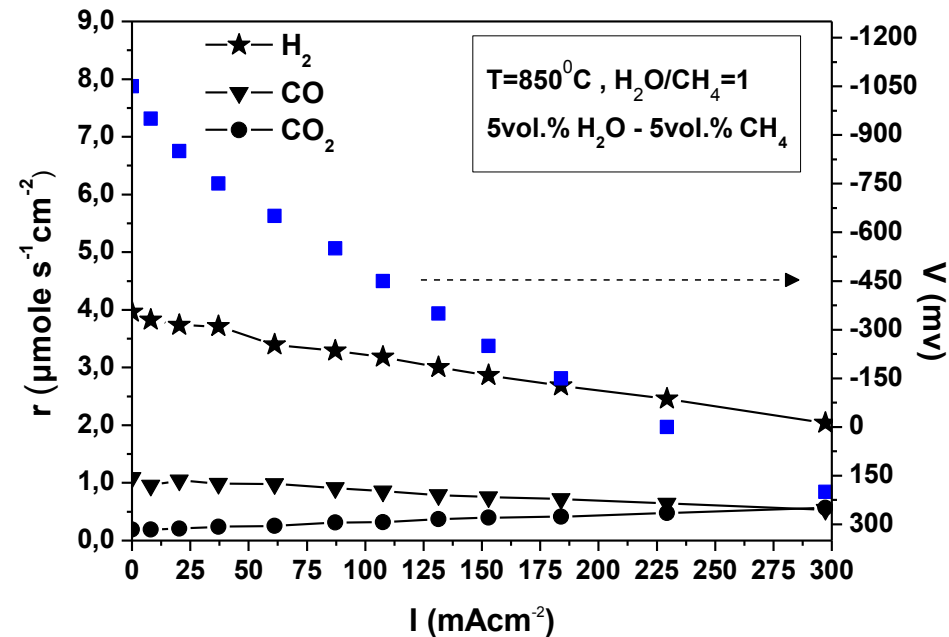
Alignment to MAIP/AIP & Innovation

□ ESC and ASC performance and stability testing

➤ Electrocatalytic experiments under various S/C ratios



➤ At **low S/C**: Partial CH₄ oxidation



➤ At **high S/C**: Low activity

Fuel Cells and Hydrogen

Joint Undertaking

Alignment to MAIP/AIP & Innovation

Model vs Experiment

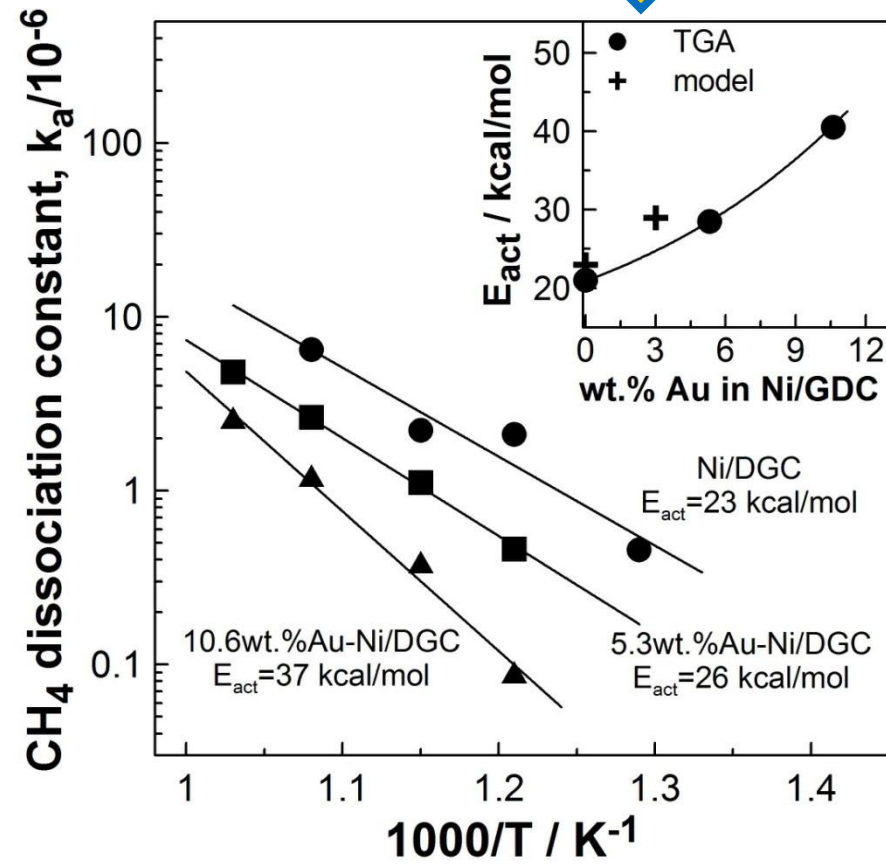


ESC and ASC performance and stability testing

- Cell & Stack testing – RedOx stability
- All tests provide feedback data for the mathematical model development



2D mathematical model for description of the fuel cell performance (power production) under CH₄ steam reforming conditions and concomitant production of H₂



Fuel Cells and Hydrogen

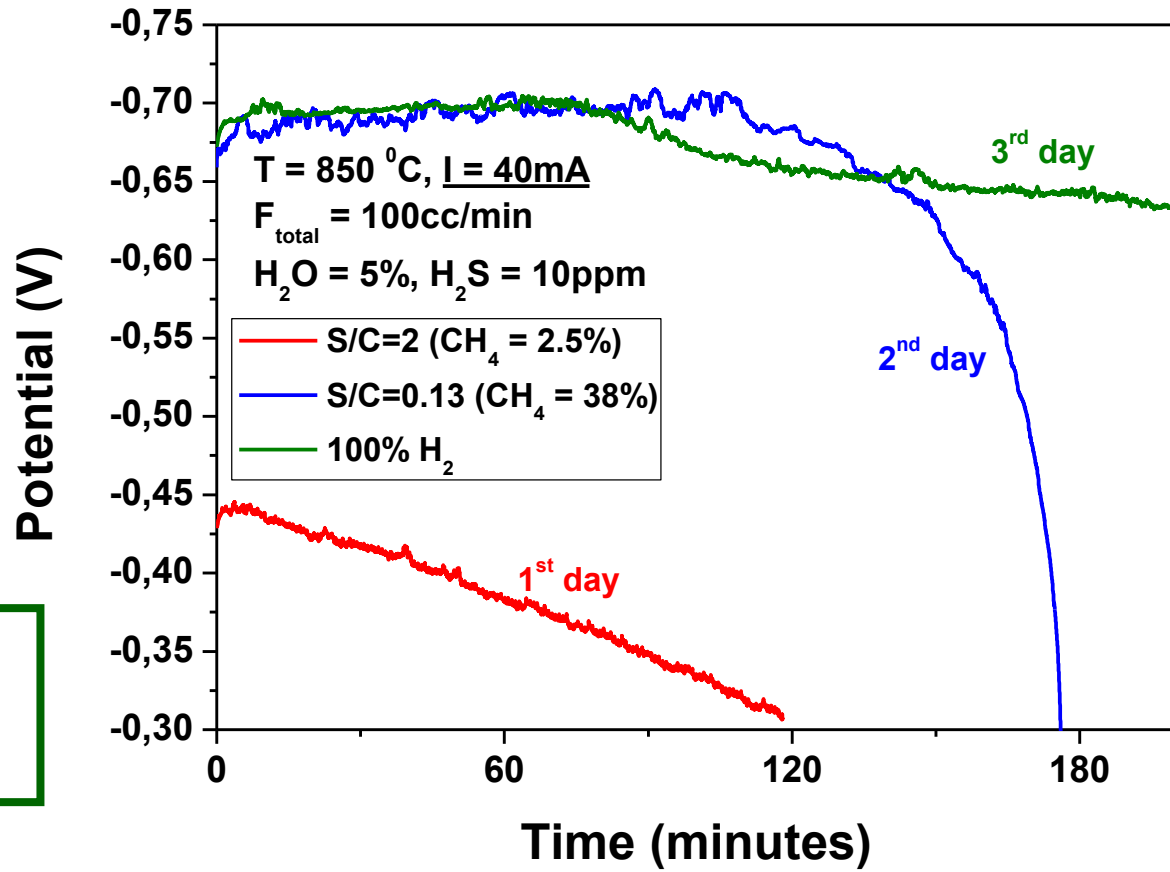
Joint Undertaking

Alignment to MAIP/AIP & Innovation

□ ESC and ASC *performance and stability* testing

- 3wt.% Au-3wt.% Mo-Ni/GDC
- Various S/C ratios plus H₂S
- Promising tolerance, in particular under pure H₂

Similar stability tests on the modified anodes are in the process of being carried out



Fuel Cells and Hydrogen

Joint Undertaking

Alignment to MAIP/AIP & Innovation

□ Medium and long-term impact of ROBANODE

- ❖ Improvement and optimization of the properties and design of (SoA) Ni-based anodes
- ❖ Long-term stability and reliability of natural gas fuelled SOFCs operating at 700- 900°C (degradation rate less than 0.5% /1000 h and operational lifetime of 40000 h)
- ❖ Minimization of degradation due to carbon deposition and sulfur poisoning in CH₄ fuelled SOFCs operating at 700-900°C under H₂O / CH₄ < 1 and in the presence of H₂S (up to 30 ppm)

Fuel Cells and Hydrogen

Joint Undertaking

Cross-cutting issues – Dissemination - Cooperation

- ❖ Proper **dissemination activities** through **peer reviewed publications**, **participation in conferences** and **other related events**
- ❖ The **established contact** through ROBANODE between **academia** and **high technology industry** is expected to stimulate **scientific career opportunities**
- ❖ **Results coming out of the project** are being shared not only with the project partners but also **with all SOFC stakeholders**, coming both from the **scientific community** and the related **industry**, as well as with the **wider public**
- ❖ **ROBANODE web site**: <http://robanode.iceht.forth.gr>

Fuel Cells and Hydrogen

Joint Undertaking

Cross-cutting issues – Dissemination - Cooperation

- ❖ ROBANODE has the potential to contribute to the **rapid penetration** of the (SoA) Ni-based **SOFCs into market**
- ❖ ROBANODE partners have extended experience in the **exploitation of the research results**
- ❖ **MIRTEC S.A.** and **Saint Gobain CREE** can ensure **fast dissemination of the expected via ROBANODE technology improvement to additional industrial end-users**
- ❖ The **results** so far have **triggered the interest** of other **research and industrial organizations**

Fuel Cells and Hydrogen

Joint Undertaking

Thank you all for your attention!