Carbon and Sulfur Tolerant anodes for SOFCs

Stylianos G. Neophytides

FORTH Institute of Chemical Engineering Sciences

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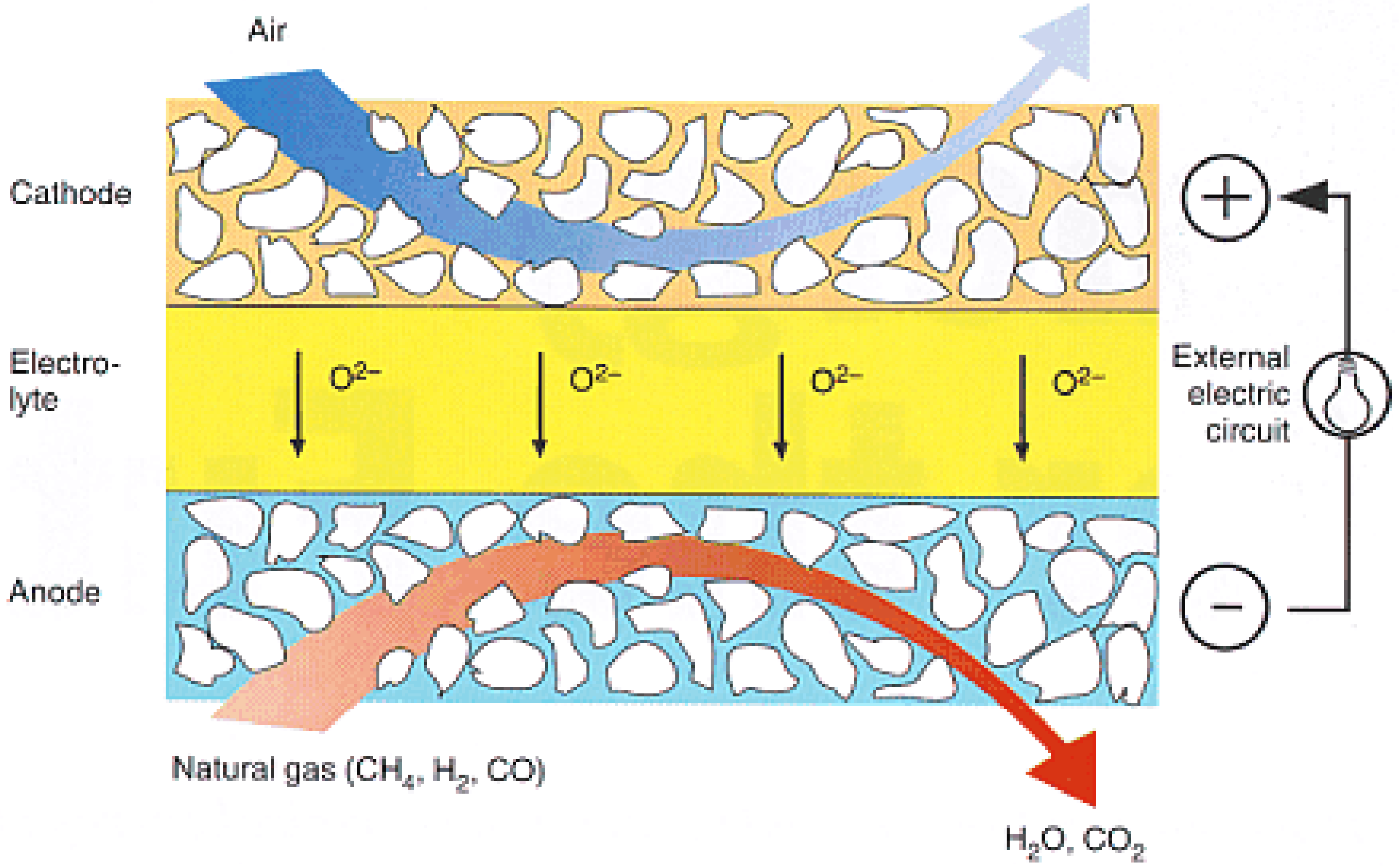
ITE/ΕΙΧΗΜΥΘ

Outline

- Introduction to SOFCs and and the Internal steam reforming process
- Carbon tolerance
  - NiAu/YSZ
  - NiAu/GDC, NiAuMo/GDC
  - Physicochemical characterization, catalytic, electrocatalytic and Abient Pressure Photoelectron spectroscopy experiments
- Sulfur tolerance
  - NiAu/GDC, NiAuMo/GDC

Basic Operational principles

Cathode reaction: ½ $O_2 + 2e^- = O^{2-}$



Electrical Energy (e^-)

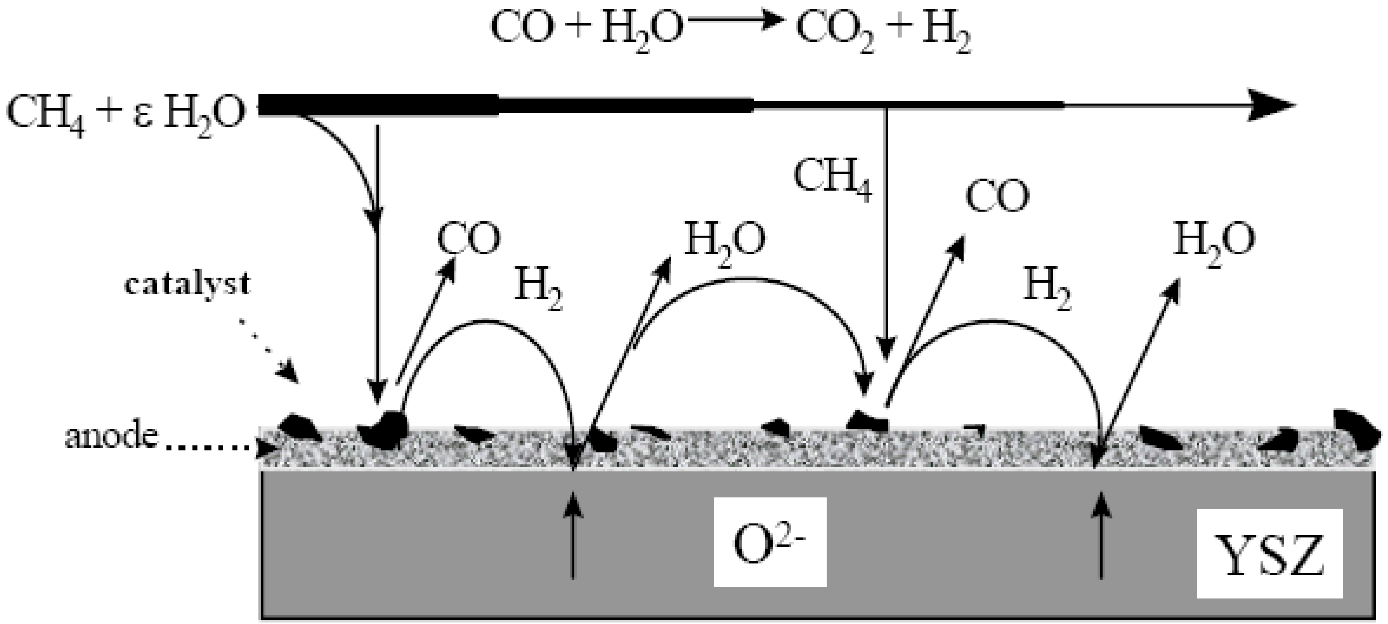
Anode reactions:

$H_2 + O^{2-} = H_2O + 2e^-$

$CO + O^{2-} = CO_2 + 2e^-$

$C_nH_{2n+2} + (3n+1)O_2 = nCO_2 + (n+1)H_2O + (6n+2)e^-$

Internal reforming proceeds through the water produced by the fuel at the anode



Internal Methane steam reforming reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

- ADVANTAGES
  - H_2 is directly produced in the SOFC
  - H_2 is readily oxidized for the production of electricity
- DISADVANTAGES
  - The exposure of the anode in high CH_4/H_2O may result in C deposition
  - Low CH_4/H_2O ratios cause a decrease in the cell's Nerst potential
- **Objectives**
  - **Development of anode electrocatalysts active for catalytic CH_4 steam reforming and resistive to graphitic carbon formation and sulphur poisoning**

Common SOFC materials[1]

Anode

- Ni based cermets, Ni/GDC, Ni/YSZ

- H_2 electrooxidation
- CH_4 steam reforming

Cathode

- Sr-doped $LaMnO_3$ (LSM)
- $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)
- $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)
- $Sm_{0.5}Sr_{0.5}CoO_3$

- dissociate O_2
- high electronic and ionic cond.
- thermal expansion coefficient

Electrolyte:

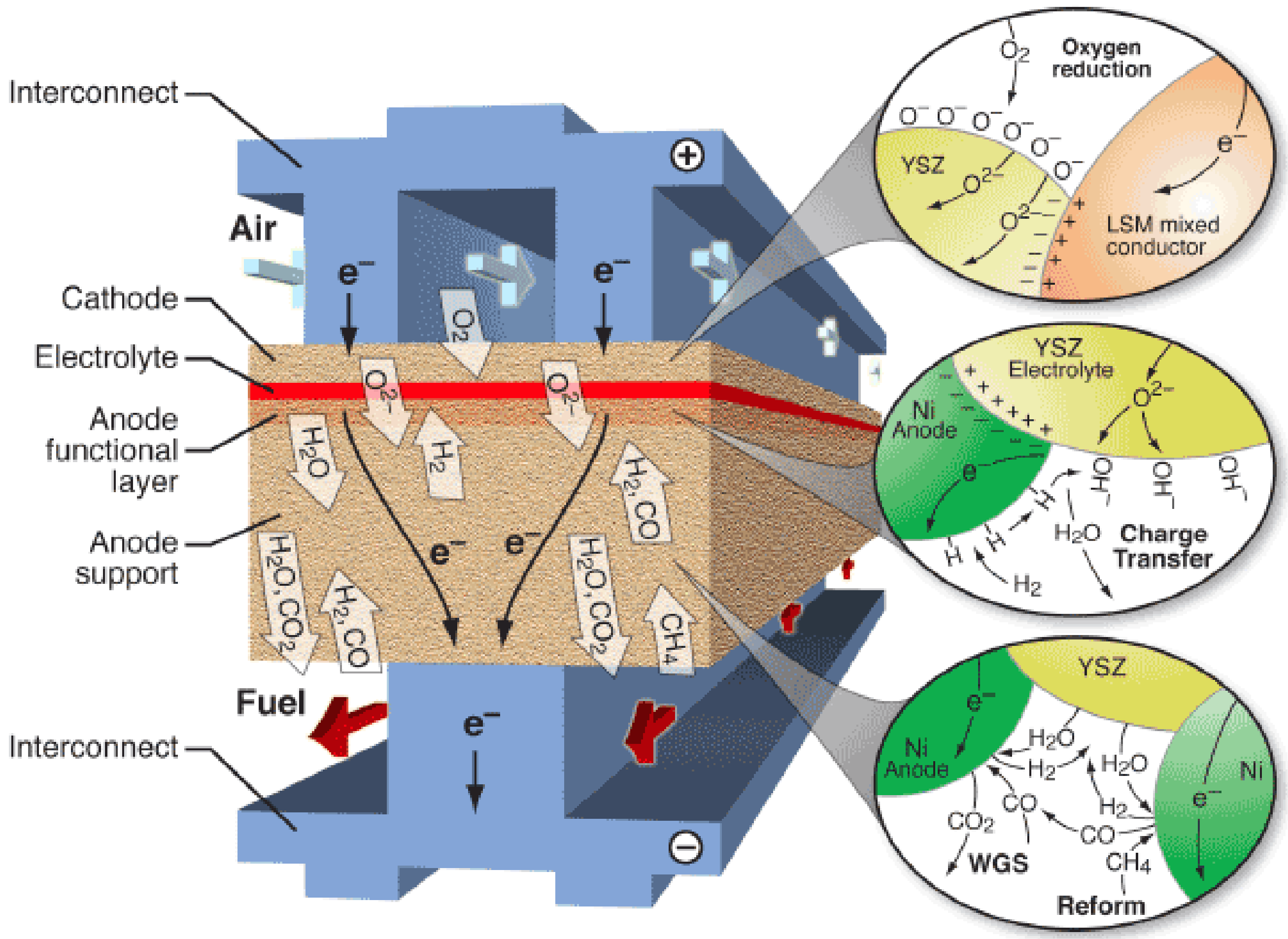
- $ZrO_2(Y_2O_3)$ (YSZ)
- $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM)
- Samaria doped Ceria (SmDC)
- Scandia doped ceria (ScDC)
- Scandia stabilized zirconia (ScSZ)

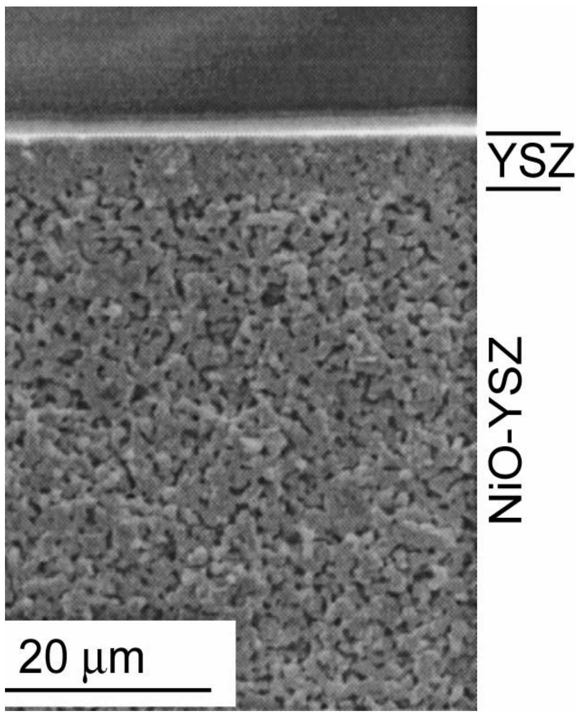
- dense
- high ionic conductivity
- electronic insulators

[1] C. Sun and U. Stimming, Journal of Power Sources 171 (2007) 247.

Basic SOFC designs-Configurations

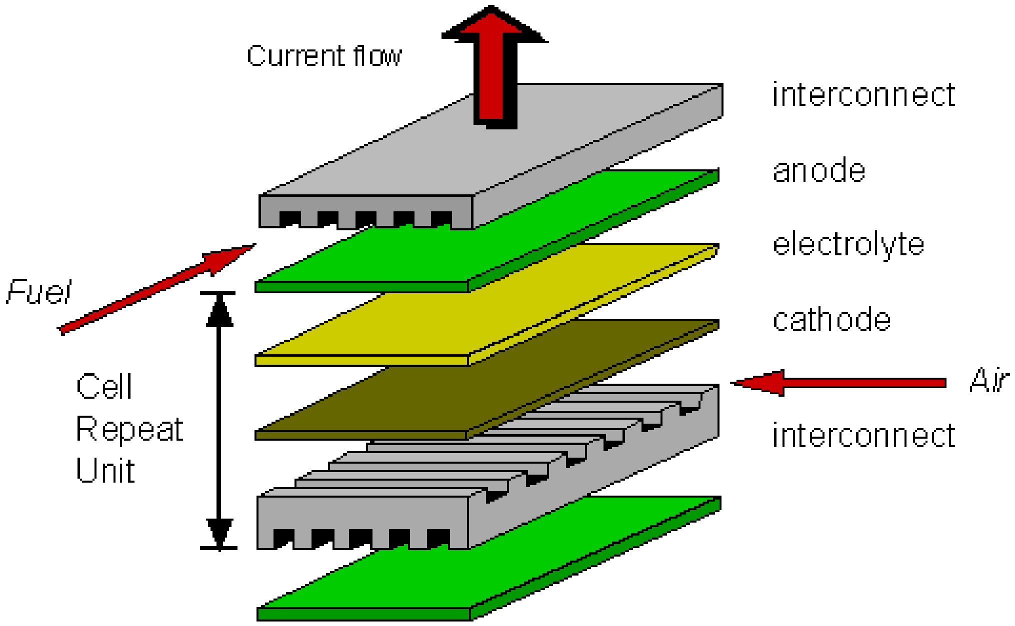
❑ Planar: Anode-Supported



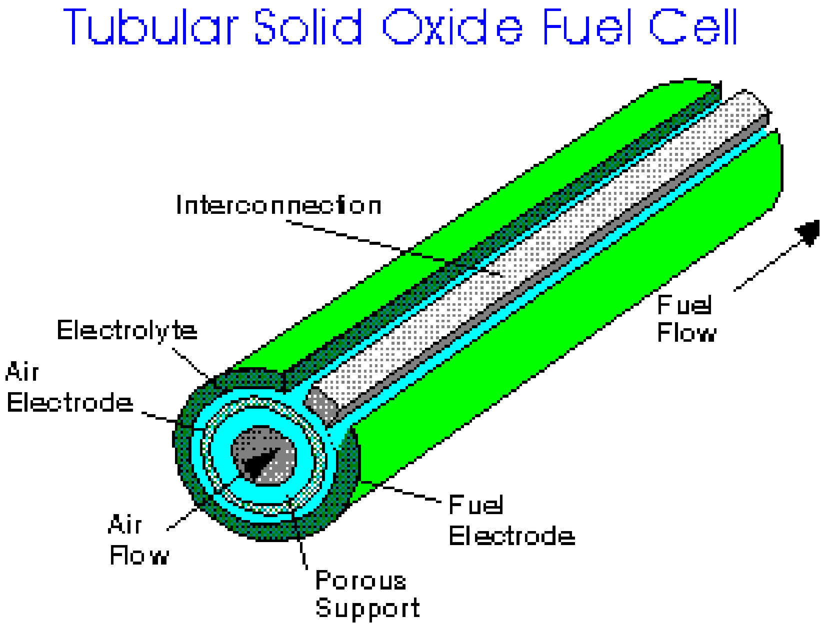


Basic SOFC designs-Configurations

- Electrolyte-Supported
- Cathode-Supported
- Metal-Supported



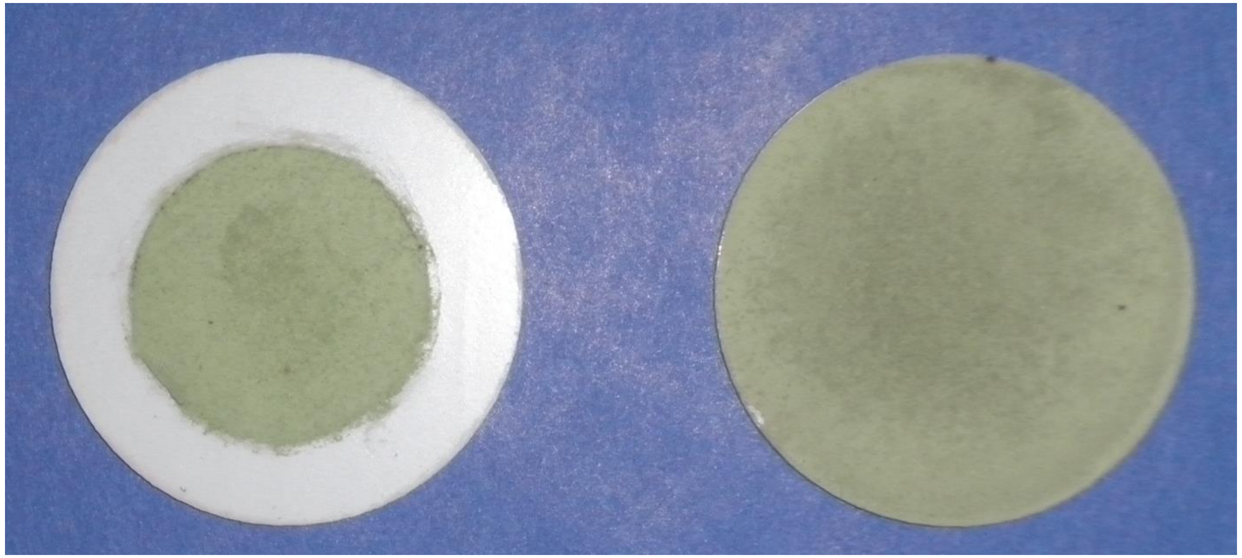
Flat design



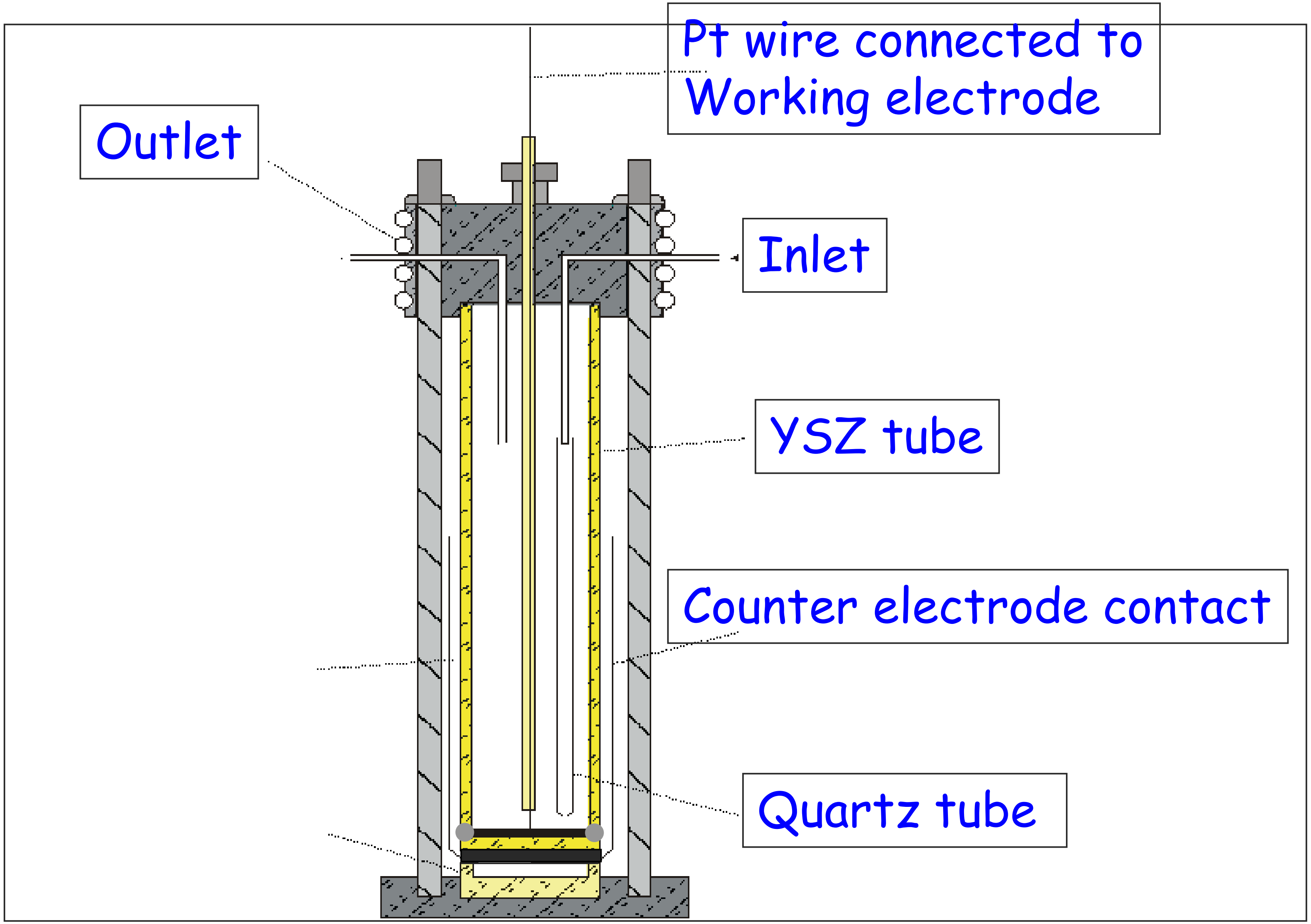
Tubular design

Basic SOFC designs-Configurations

❑ Planar: Electrolyte-Supported



Experimental electrochemical reactor



Ni-Au/YSZ anode

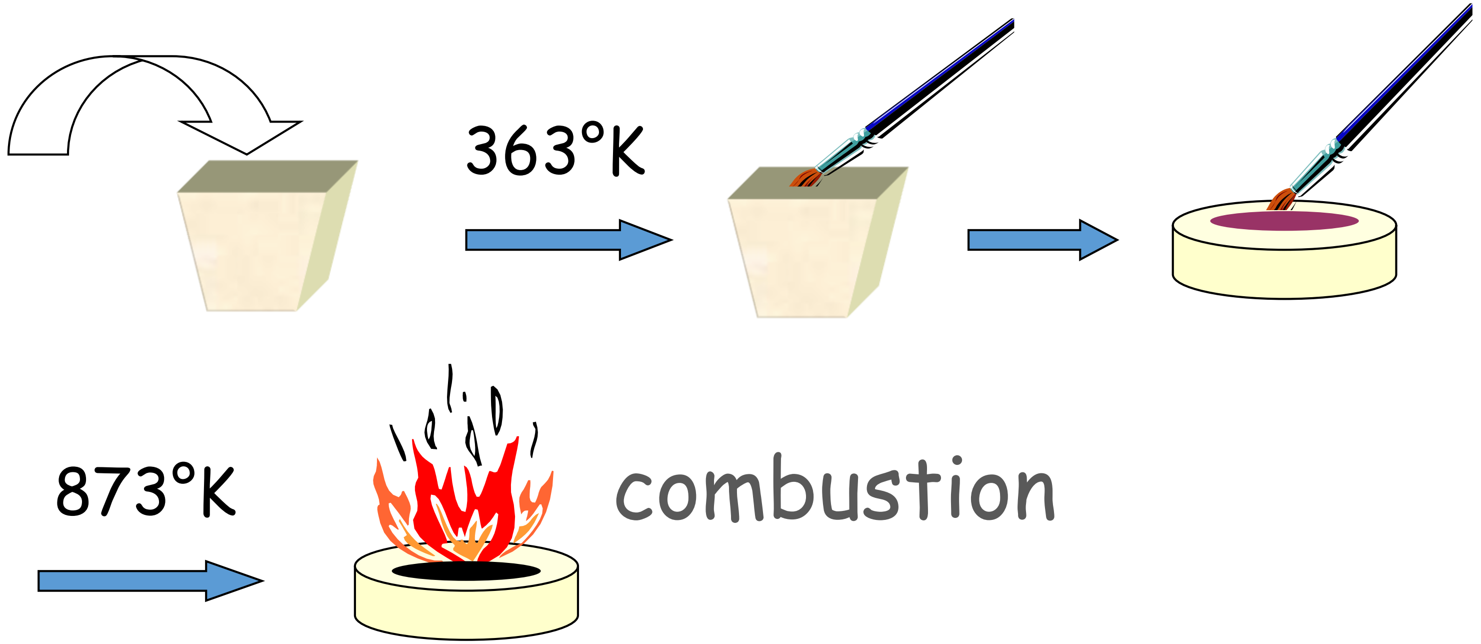
Carbon Tolerant Ni-Au SOFC Electrodes operating under Internal Steam Reforming Conditions, Ilias Gavrielatos , Vasilis Drakopoulos and Stylianos G. Neophytides, Journal of Catalysis 259 (2008) 75–84

The combustion synthesis method

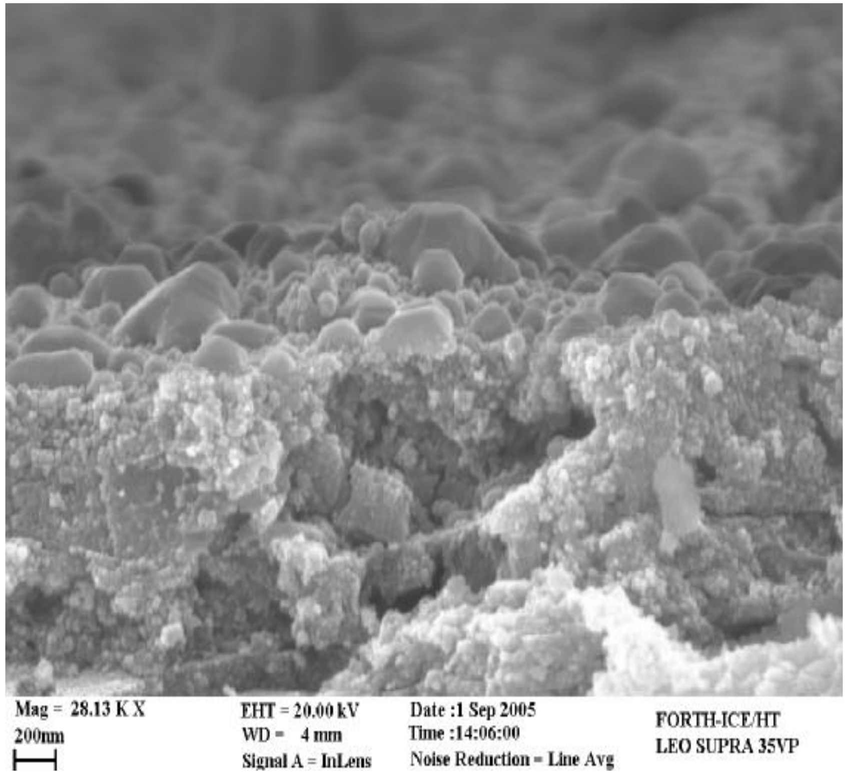
Precursors

$Ni\ (NO_3)_2$, $HAuCl_4$, $ZrO(NO_3)_2$

$Y(NO_3)_3$, CH_4N_2O

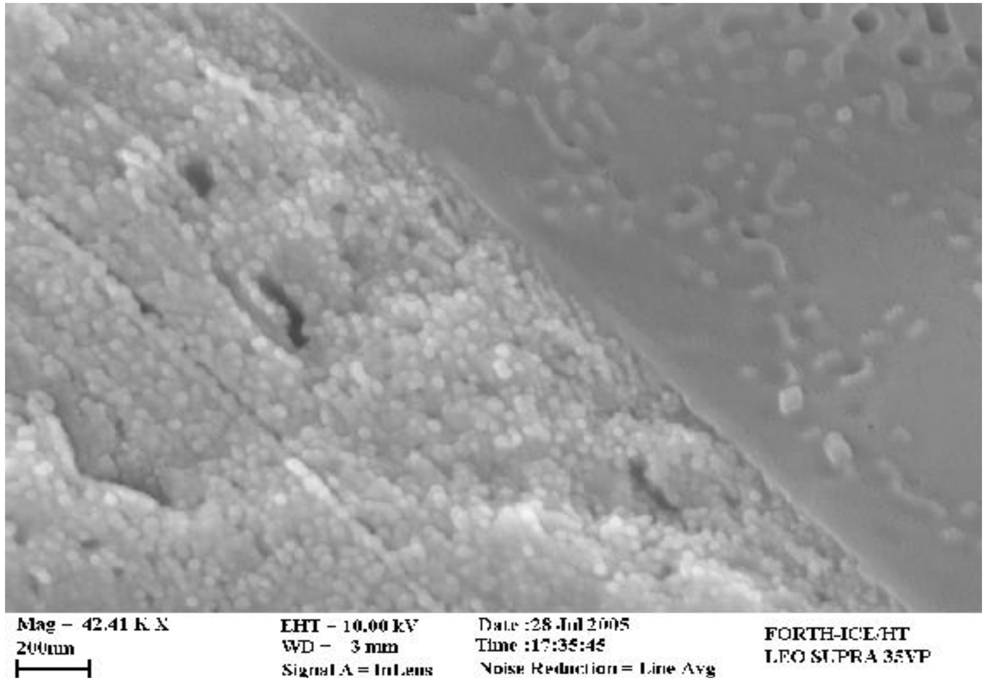


Cross section images of reduced NiAu/YSZ

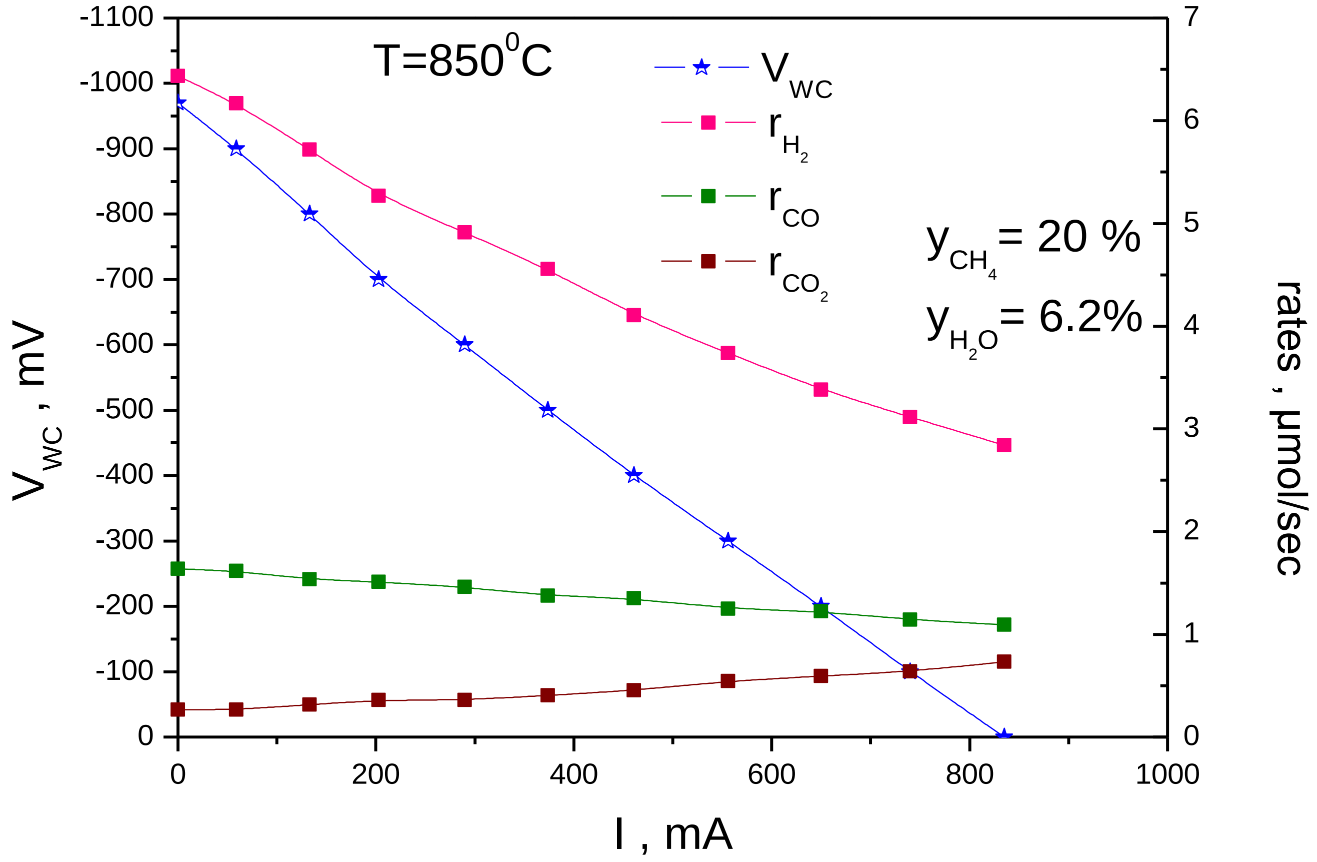


Electrode/gas phase interface

The electrode-electrolyte three phase boundary

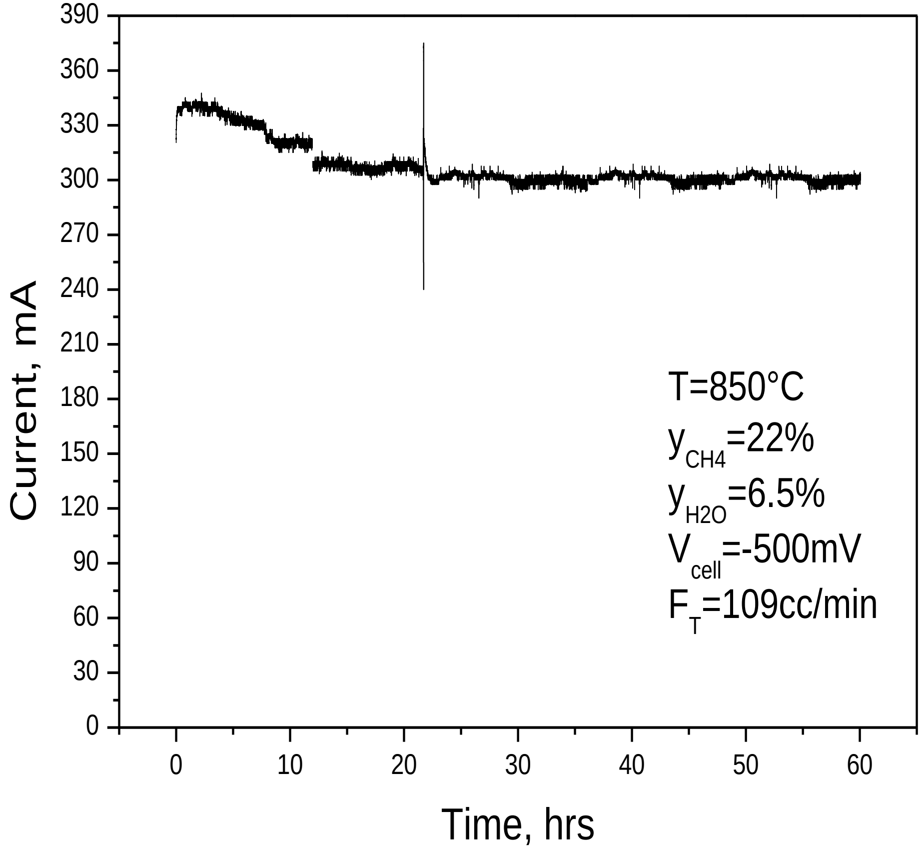


Electrokinetic measurements under internal steam reforming conditions on Ni/YSZ

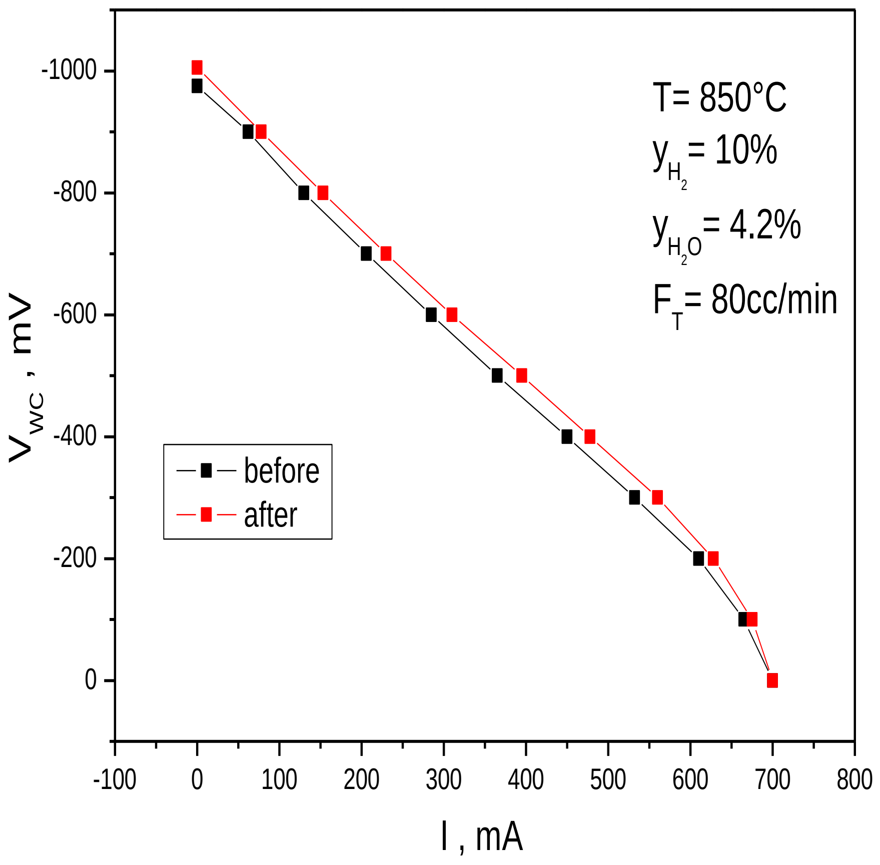


Carbon Tolerant Ni-Au SOFC Electrodes operating under Internal Steam Reforming Conditions, Ilias Gavrielatos , Vasilis Drakopoulos and Stylianos G. Neophytides, Journal of Catalysis 259 (2008) 75–84

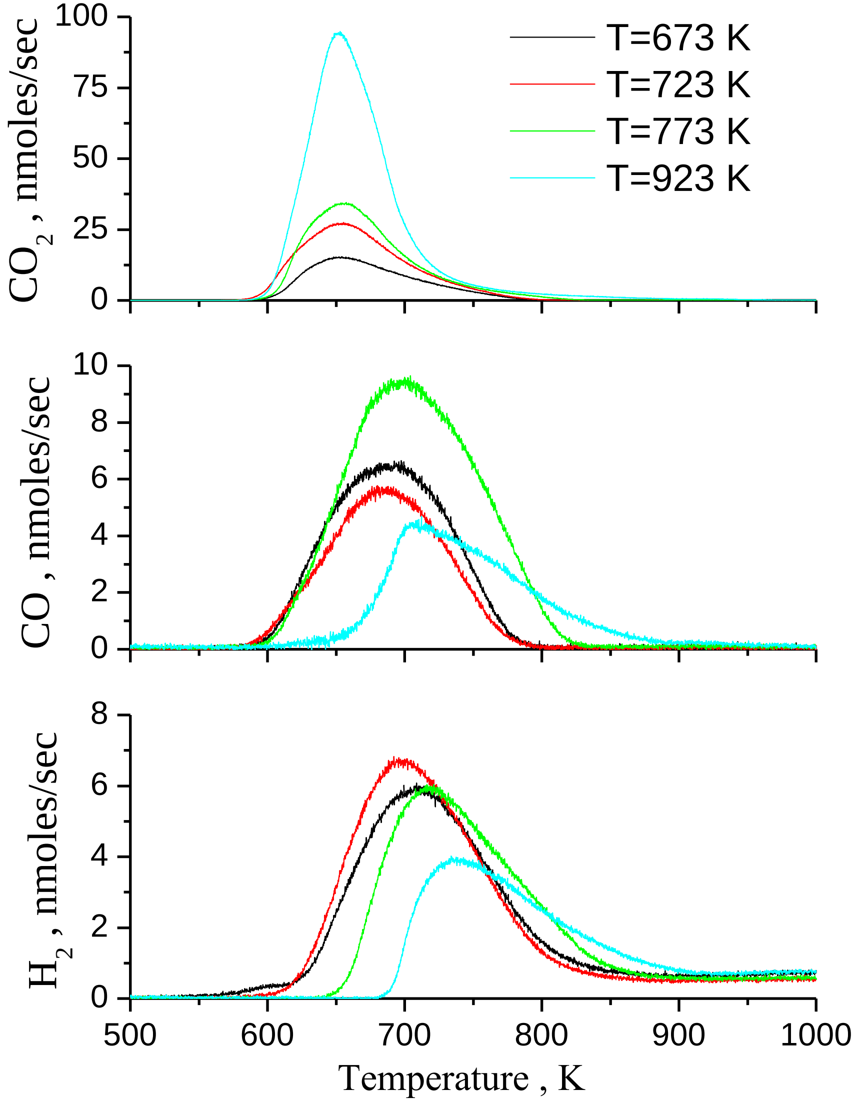
Short term stability test



Electrocatalytic performance under 10% H_2 before and after the stability test



TPO following CH_4 dissociative adsorption Ni(1%at Au)-YSZ

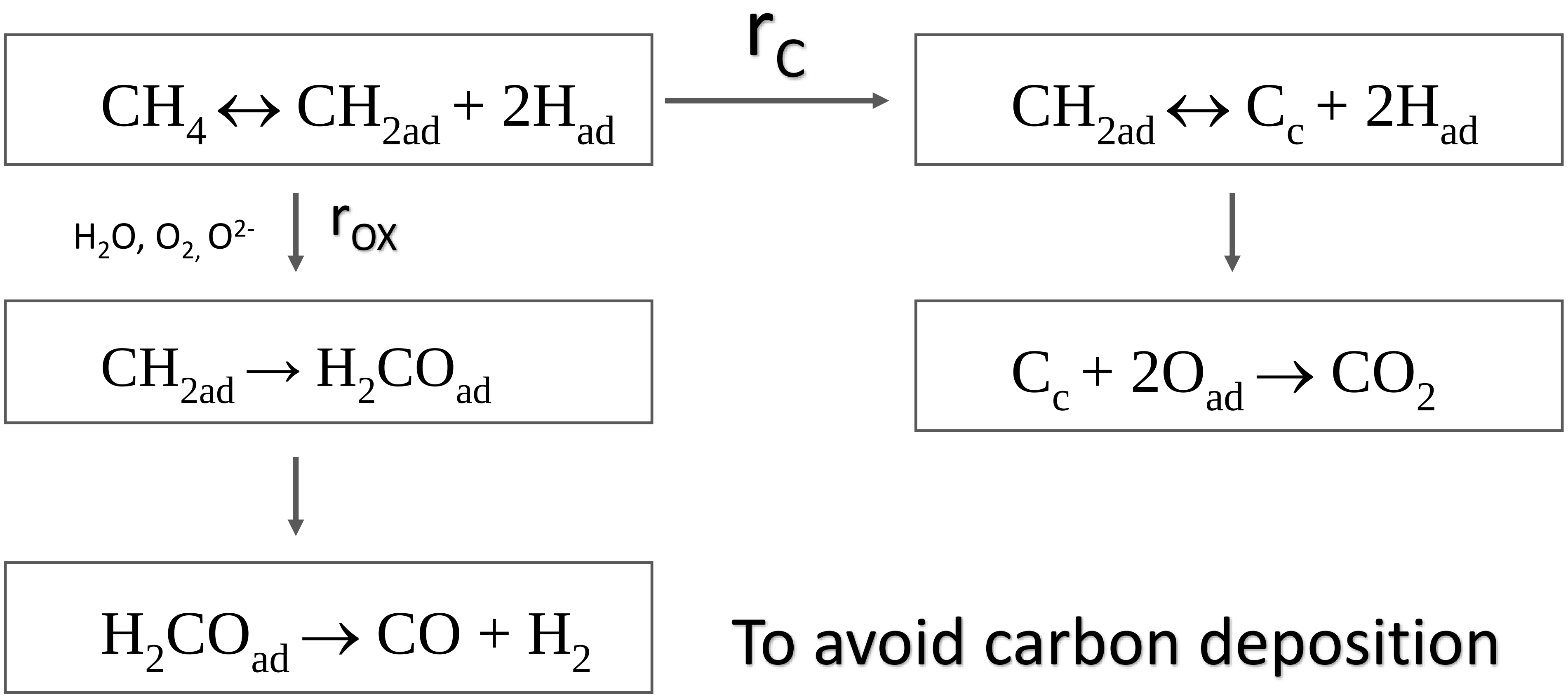


Pulse of O_2 at T< 450 K , O_2/C=2
20°/min, F_t=26 μmoles/sec

- Simultaneous evolution of CO and H_2
- Decomposition of CH_xO species at elevated Temperature

N.C.Triantafyllopoulos,S.G.Neophytides, J. Catalysis **239**, 187-199 (April 2006)

REACTION MECHANISM



To avoid carbon deposition

$$r_{OX} > r_C$$

Ni/GDC

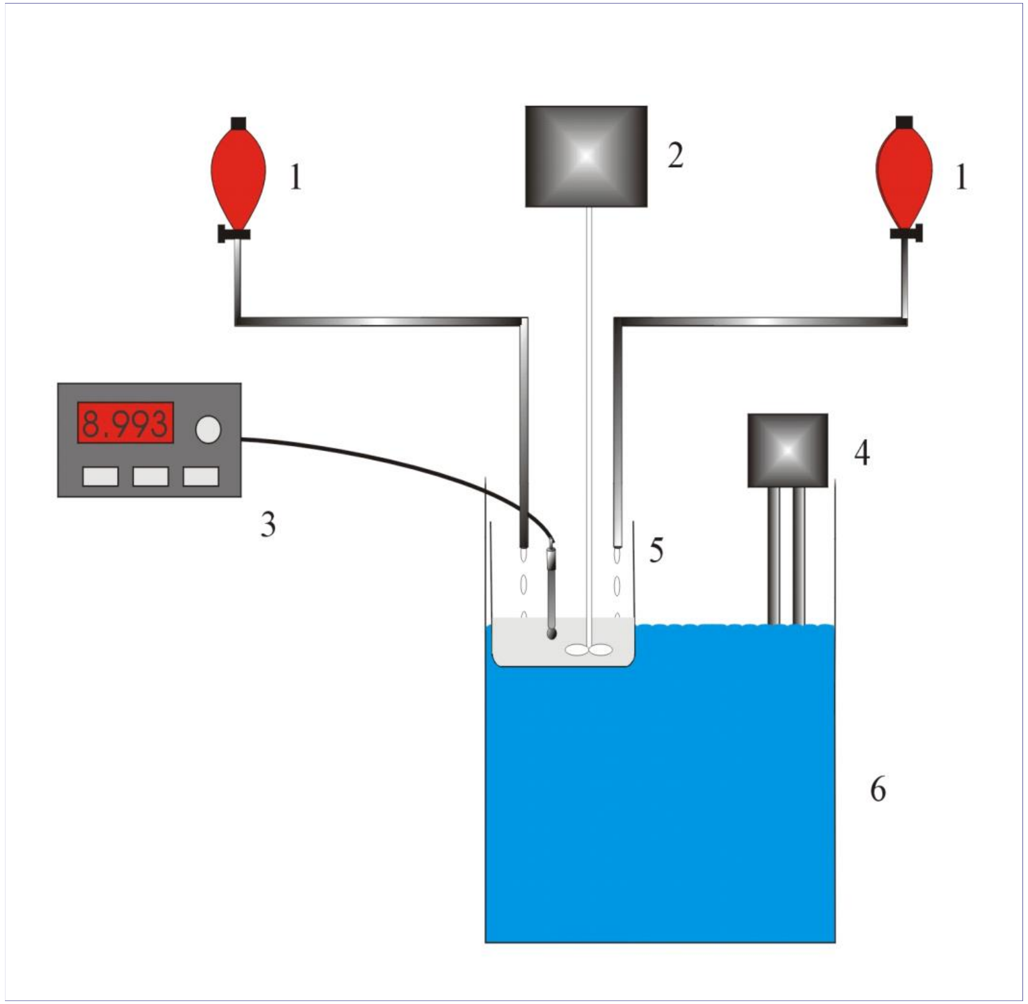
NiAu/GDC

NiAuMo/GDC

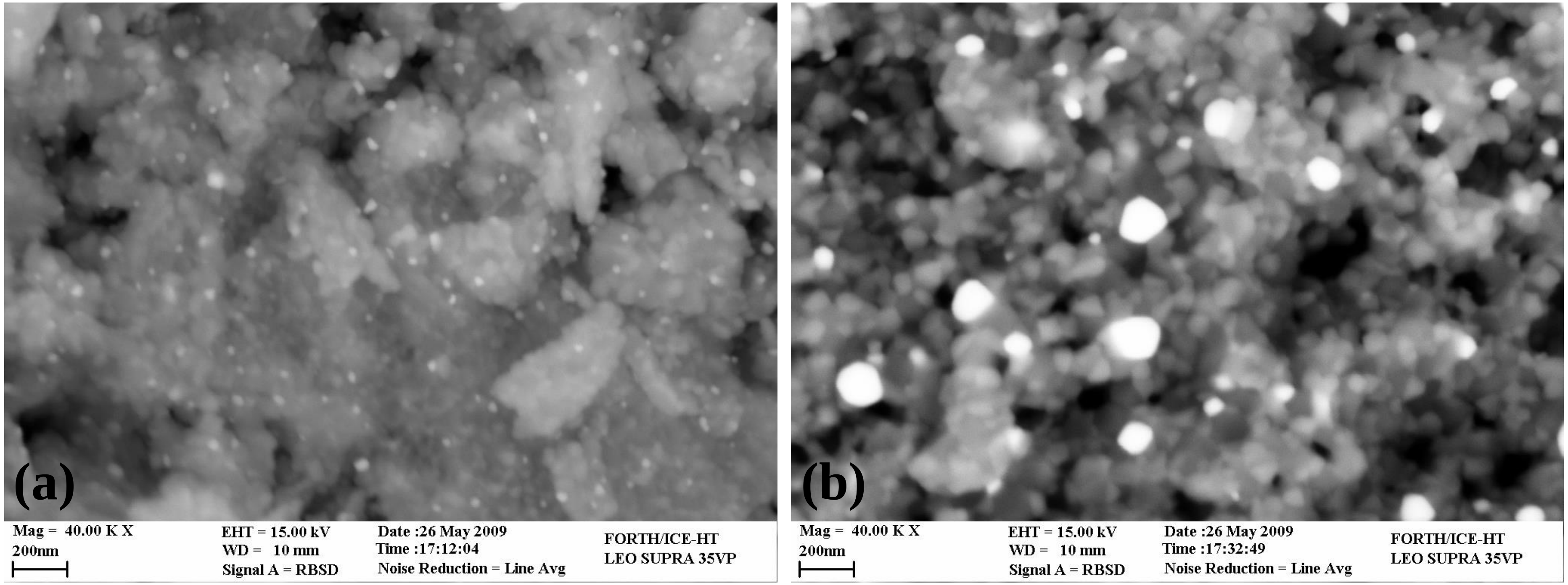
Study of the synergistic interaction between nickel, gold and molybdenum in novel modified NiO/GDC cermets, possible anode materials for CH_4 fueled SOFCs, Niakolas, D.K., Athanasiou, M., Dracopoulos, V., Tsiaoussis, I., Bebelis, S., Neophytides, S.G. Applied Catalysis A: General 456 , pp. 223-232 (2013)

Deposition Co-Precipitation

- **Commercial NiO/GDC** powder as the support, hydrogen tetrachloroaurate **($HAuCl_4$)** and ammonium heptamolybdate **[(NH4)6Mo7O24 4H2O]**
- Adjustment of **pH** and **Temp.** of the suspension
- NH_3 as precipitant agent
- Filtering, drying and final calcination at 850 & 1100 °C



SEM-BSE on Au-Mo-NiO/GDC

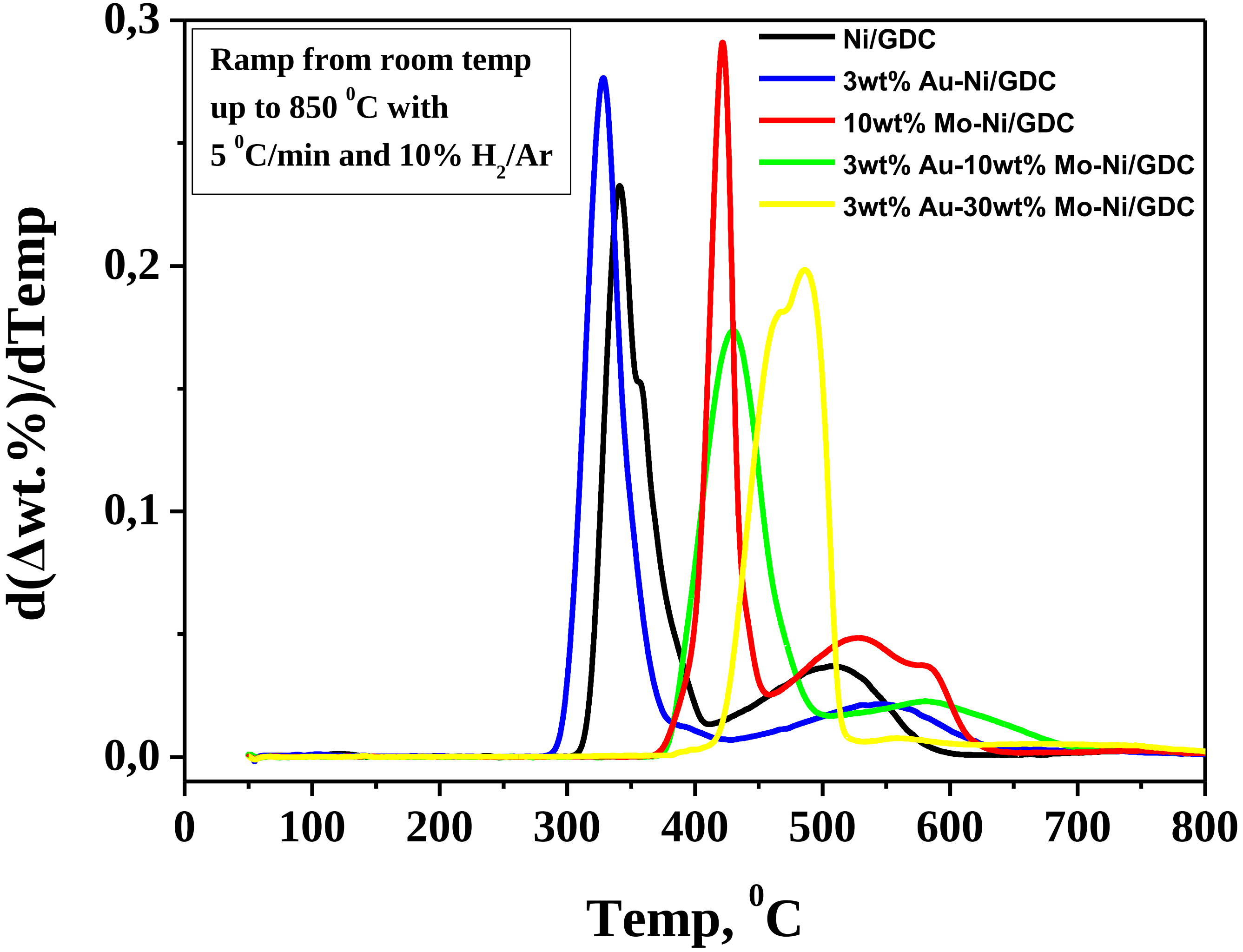


- Au^0 varies 10-50 nm
- Calcined at 850°C

- Au^0 varies 10-150 nm
- Calcined at 1100°C

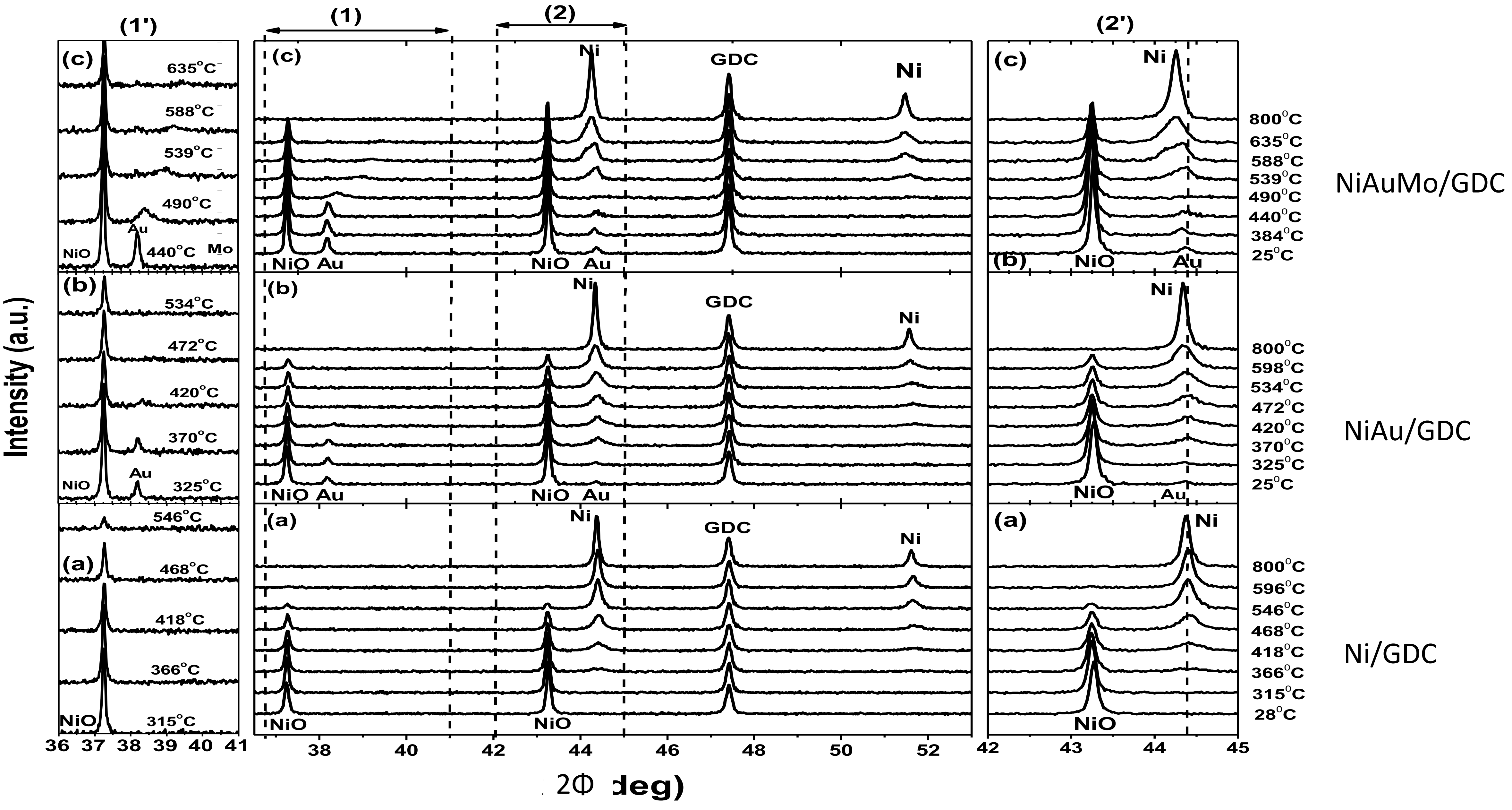
- **MoO_x species could not be detected**

H_2-TPR on Au-Mo-NiO/GDC

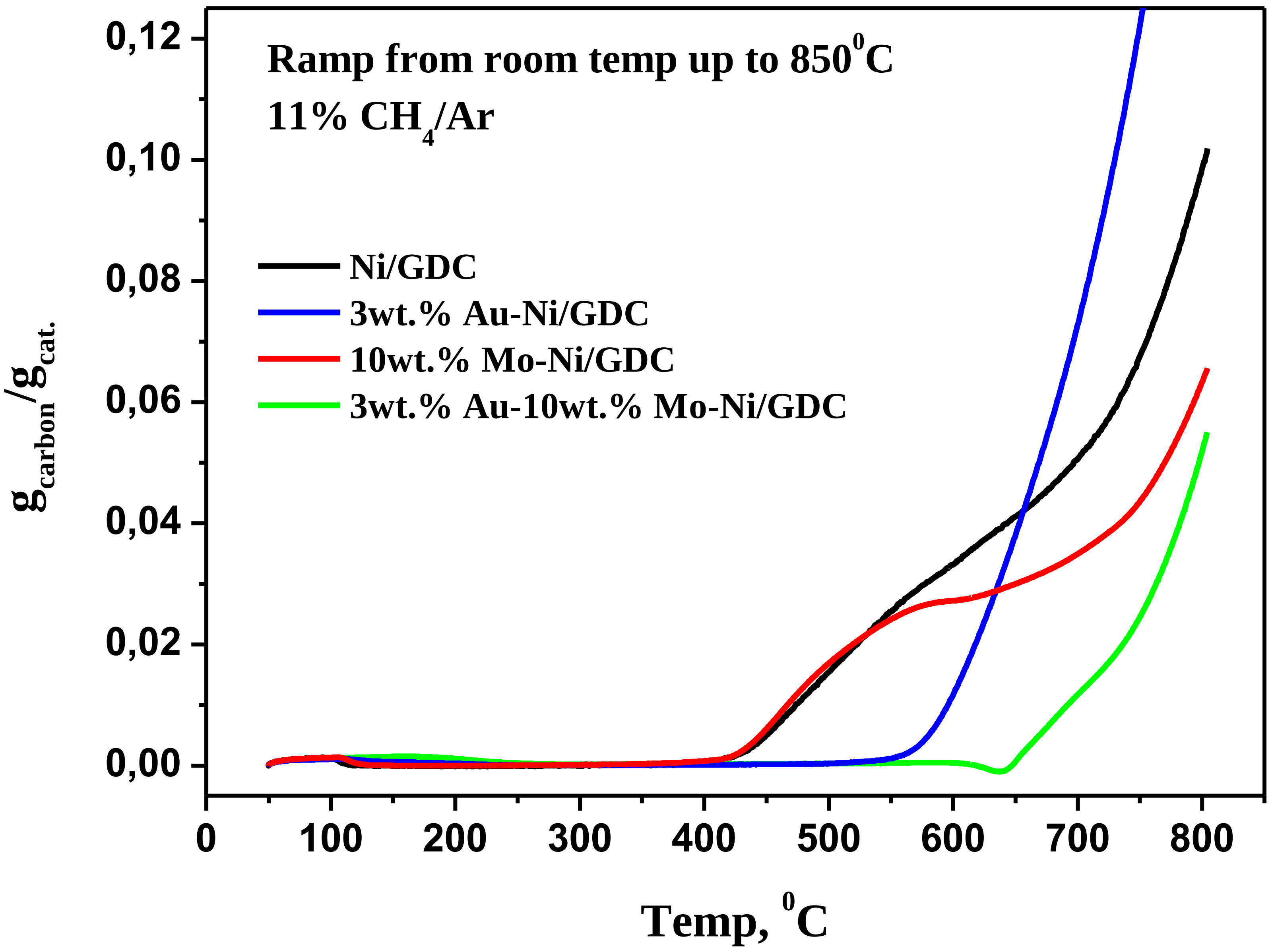


Study of the synergistic interaction between nickel, gold and molybdenum in novel modified NiO/GDC cermets, possible anode materials for CH4 fueled SOFCs, Niakolas, D.K., Athanasiou, M., Dracopoulos, V., Tsiaoussis, I., Bebelis, S., Neophytides, S.G. Applied Catalysis A: General 456 , pp. 223-232 (2013)

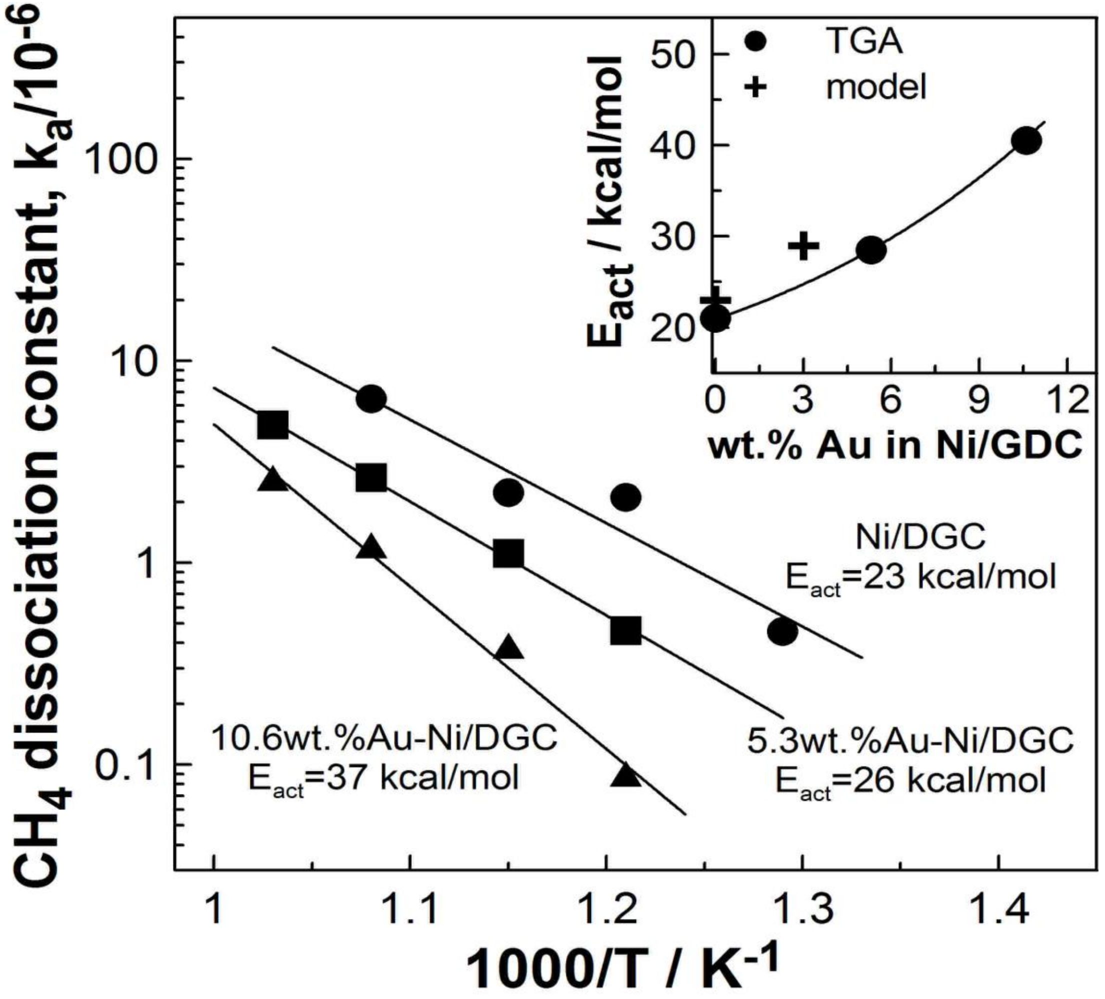
TPR-XRD on Au-Mo-Ni/GDC



TGA on Au-Mo-NiO/GDC



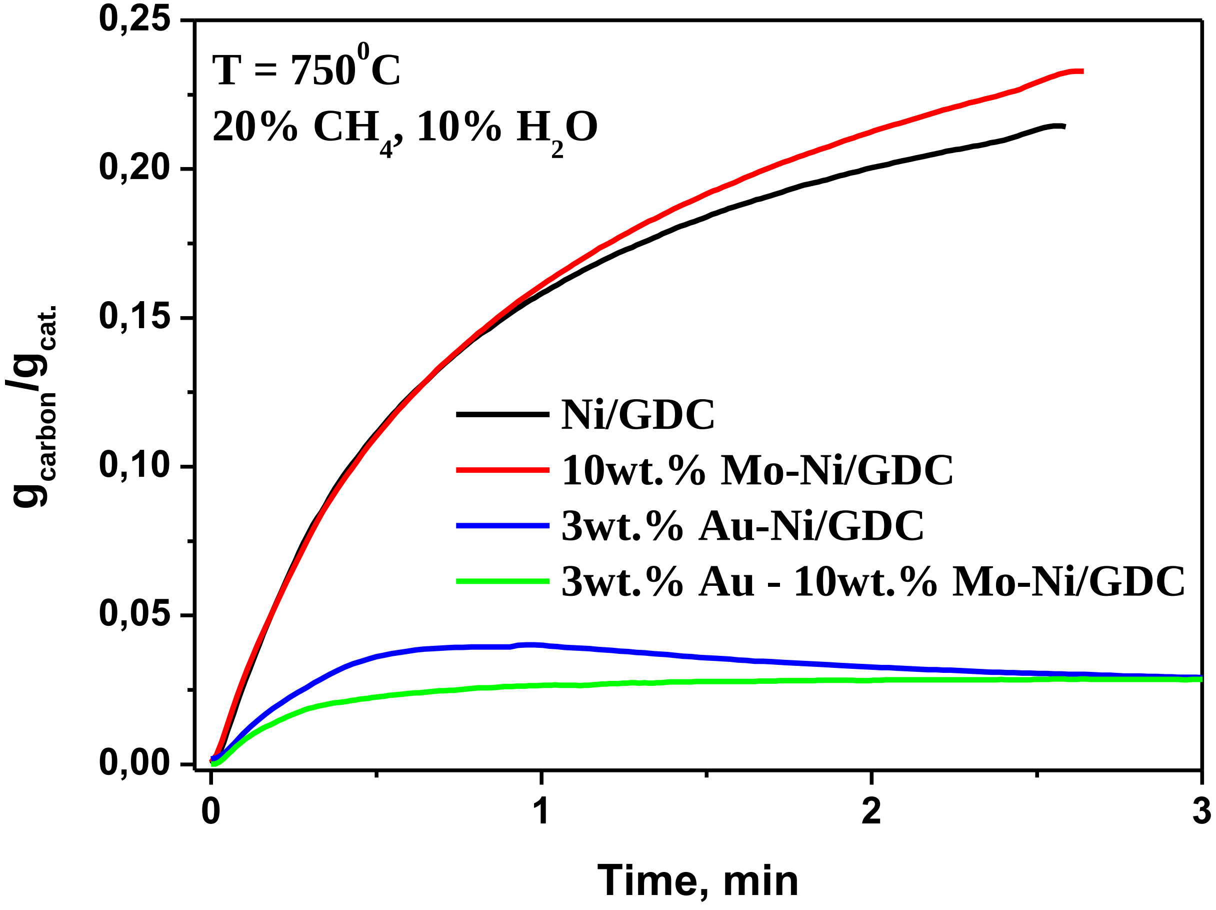
Activation energies of CH_4 dissociation on various NiAu/GDC powders



The activation energy of CH_4 dissociation increases with increasing Au content

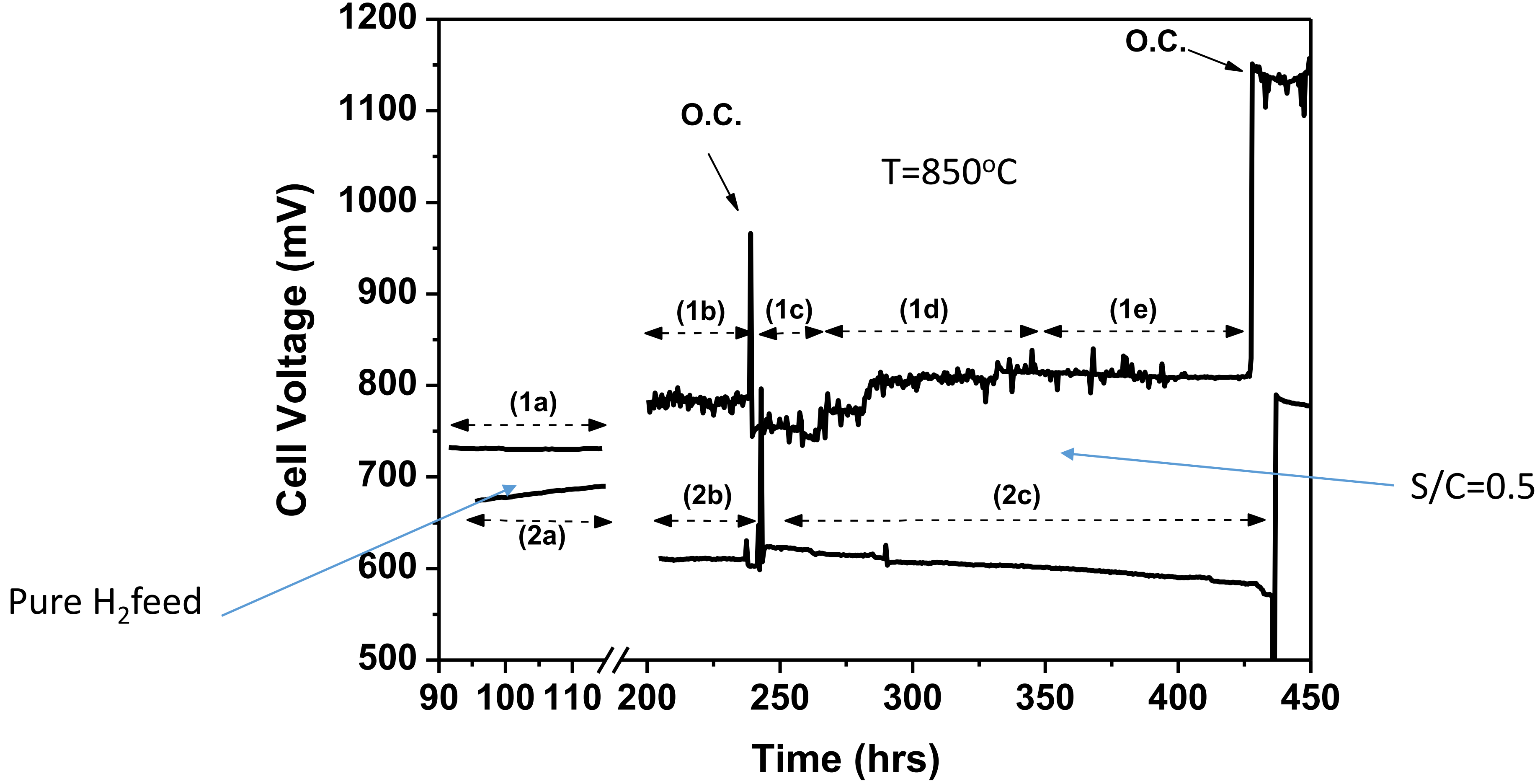
TGA-MS on Au-Mo-NiO/GDC

Sample	Ni/GDC	10wt.%Mo	3wt.% Au	3wt.Au -10wt.% Mo
r_{H2} (mmol m^{-2} s^{-1})	1.2	1.0	0.5	0.3
r_{Carbon} (mmol m^{-2} s^{-1})	0.116	0.127	0.041	0.039



- Binary and ternary cermets are active.
- Less active for H_2 production and carbon deposition, compared to Ni/GDC.
- Synergy between **Ni**, **Au** and **Mo** for decrease of carbon deposits.

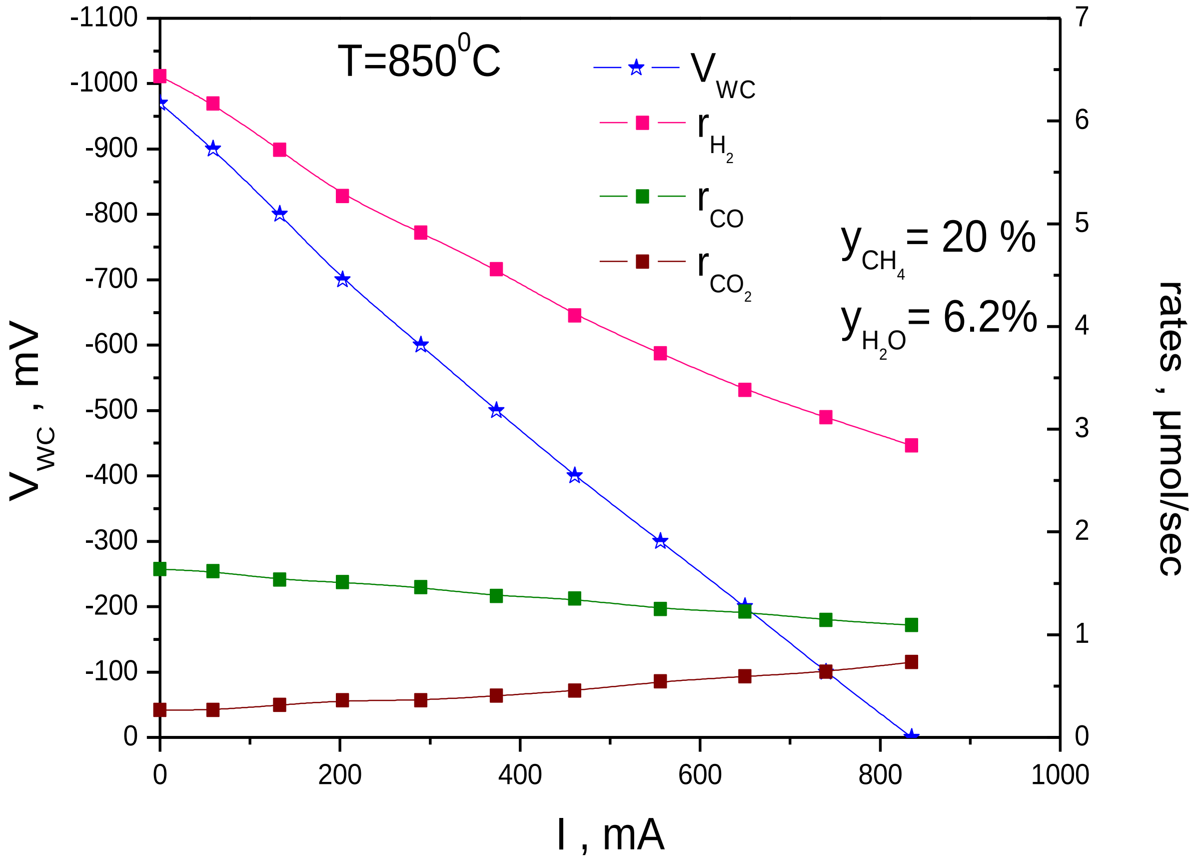
Stability of the Ni/GDC and NiAu/GDC under S/C=0.5 at 0.5A/cm^2



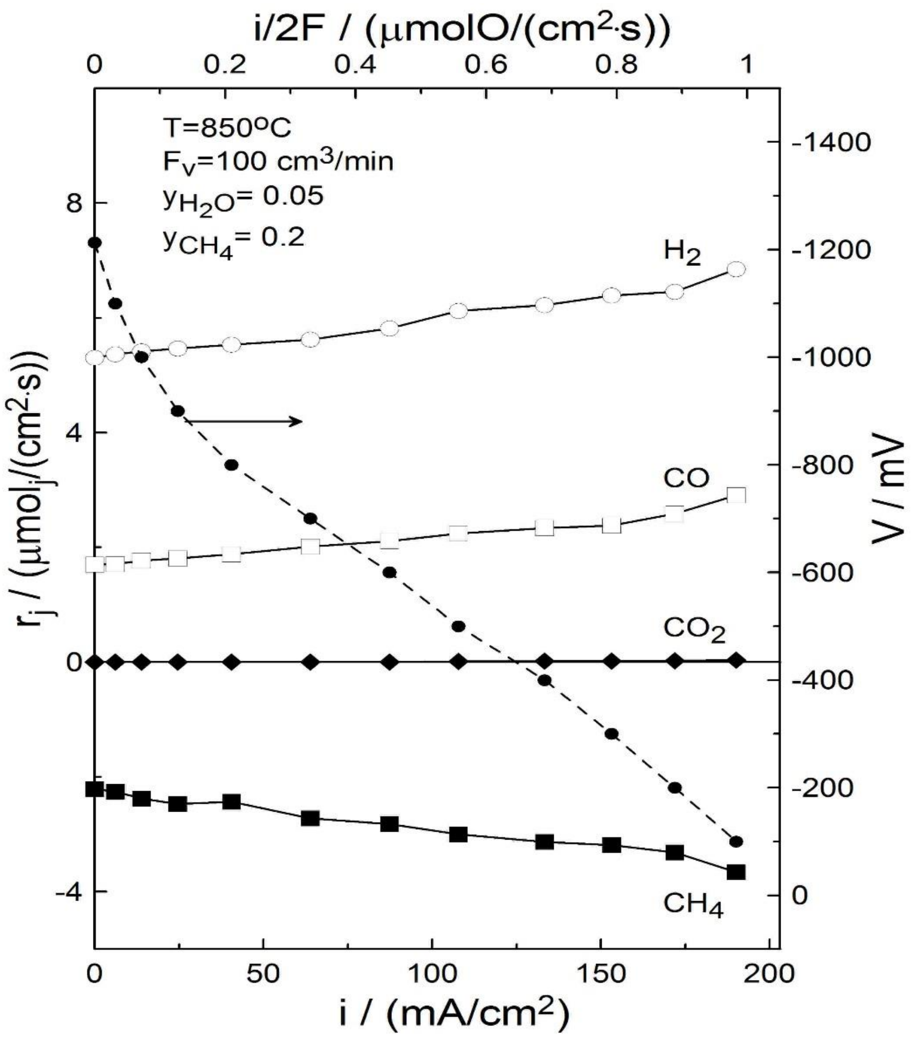
Au doped Ni/GDC as a new anode for SOFCs operating under rich CH4 internal steam reforming, Niakolas D.K., Ouweltjes J.P., Rietvelt G., Dracopoulos V., Neophytides S.G., International Journal of Hydrogen energy, 35(15), 7898-7904, (2010)

Electrokinetic behavior of NiAu/YSZ and NiAu/GDC

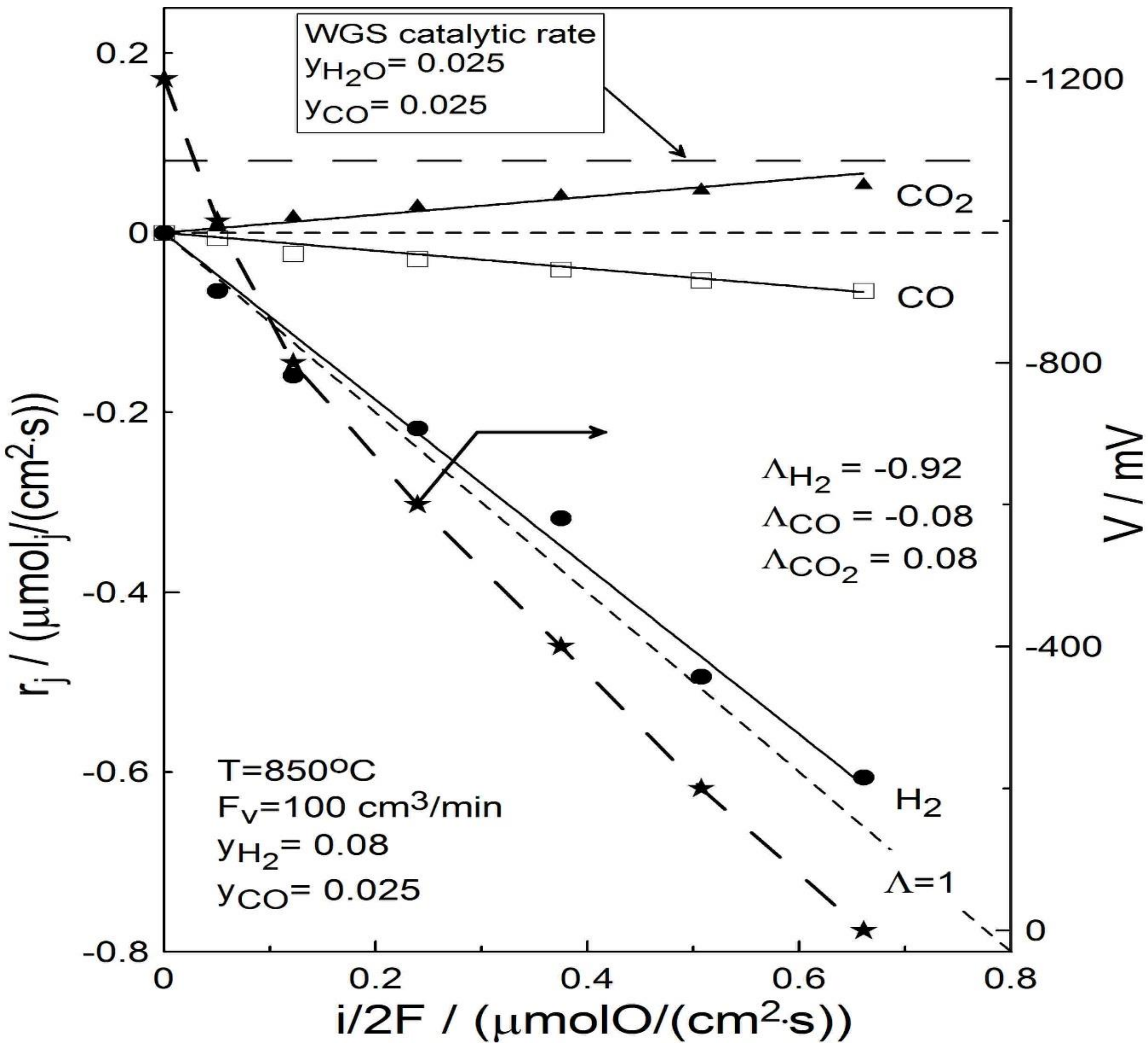
NiAu/YSZ



NiAu/GDC



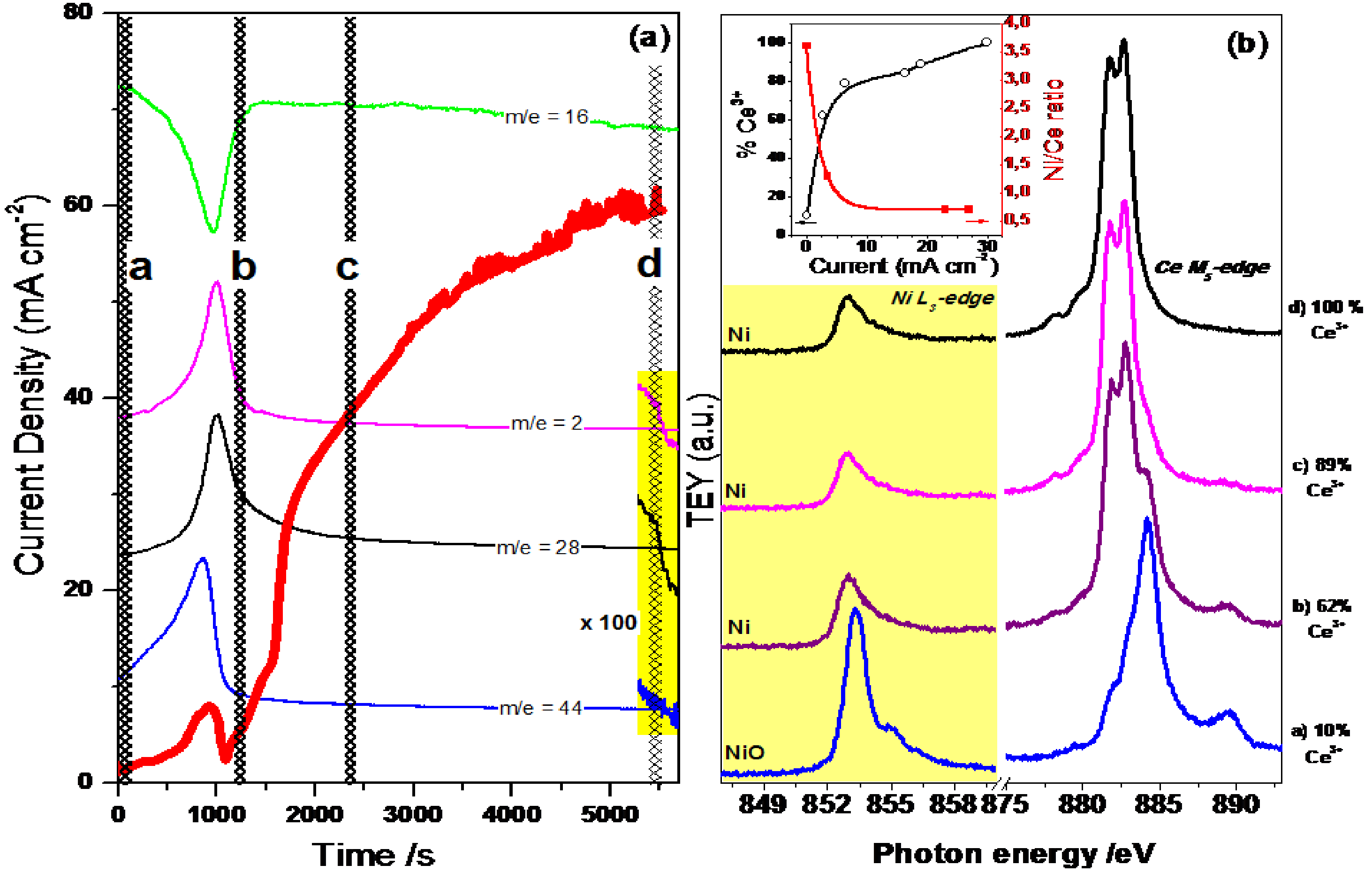
During current application CO is being oxidized into CO_2 only through WGS reaction

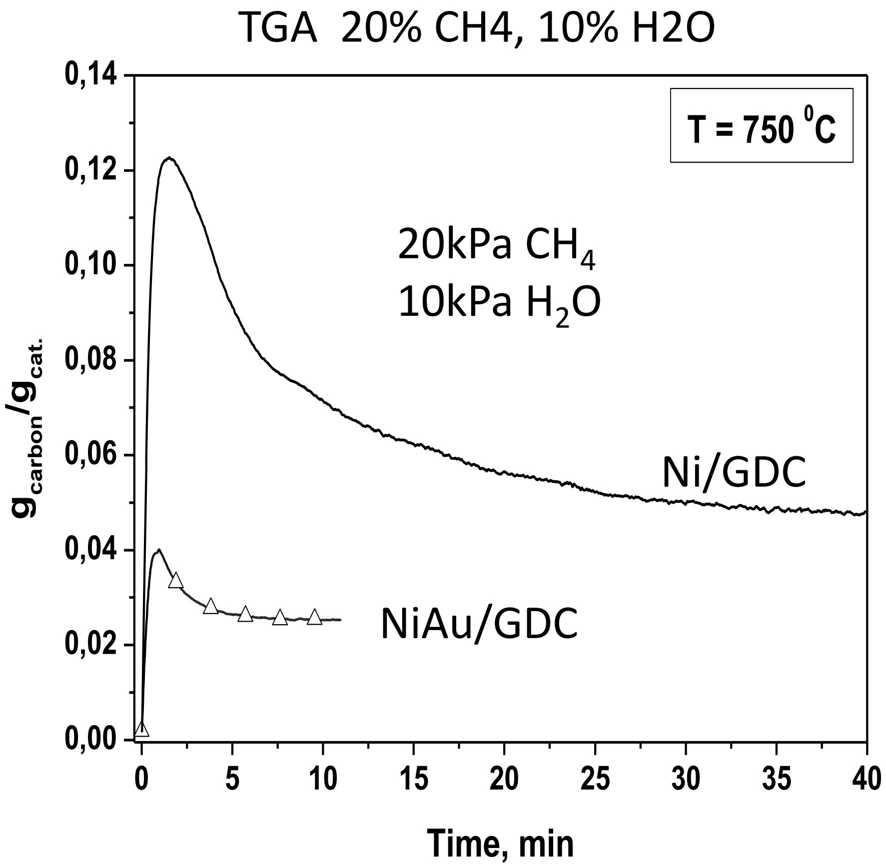


Mathematical modeling of Ni/GDC and Au-Ni/GDC SOFC anodes performance under internal methane steam reforming conditions, Souentie, S., Athanasiou, M., Niakolas, D.K., Katsaounis, A., Neophytides, S.G., Vayenas, C.G. Journal of Catalysis 306 , pp. 116-128 (2013)

Ambient pressure X-ray photoelectron spectroscopy

shows massive reduction of CeO_2 into Ce_2O_3 and enhancement in the current





On the active surface state of nickel-ceria solid oxide fuel cell anodes during methane electrooxidation, Papaefthimiou, V., Shishkin, M., Niakolas, D.K., Athanasiou, M., Law, Y.T., Arrigo, R., Teschner, D., (...), Zafeiratos, S. Advanced Energy Materials 3 (6) , pp. 762-769 (2013)

REACTION MECHANISM NiAu/GDC

$$CH_4 \leftrightarrow CH_{2ad} + 2H_{ad}$$

r_C activated on Ni

$$CH_{2ad} \leftrightarrow C_c + 2H_{ad}$$

$$C_c + 2O_{ad} \rightarrow CO_2$$

H_2O, O_2, O^{2-} — r_{OX} activated on Ce_2O_3

$$CH_{2ad} \rightarrow H_2CO_{ad}$$

Ni activated decompomposition

$$H_2CO_{ad} \rightarrow CO + H_2$$

To avoid carbon deposition

$r_{OX} > r_C$

Comparison of NiAu/YSZ and NiAu/GDC

NiAu/YSZ

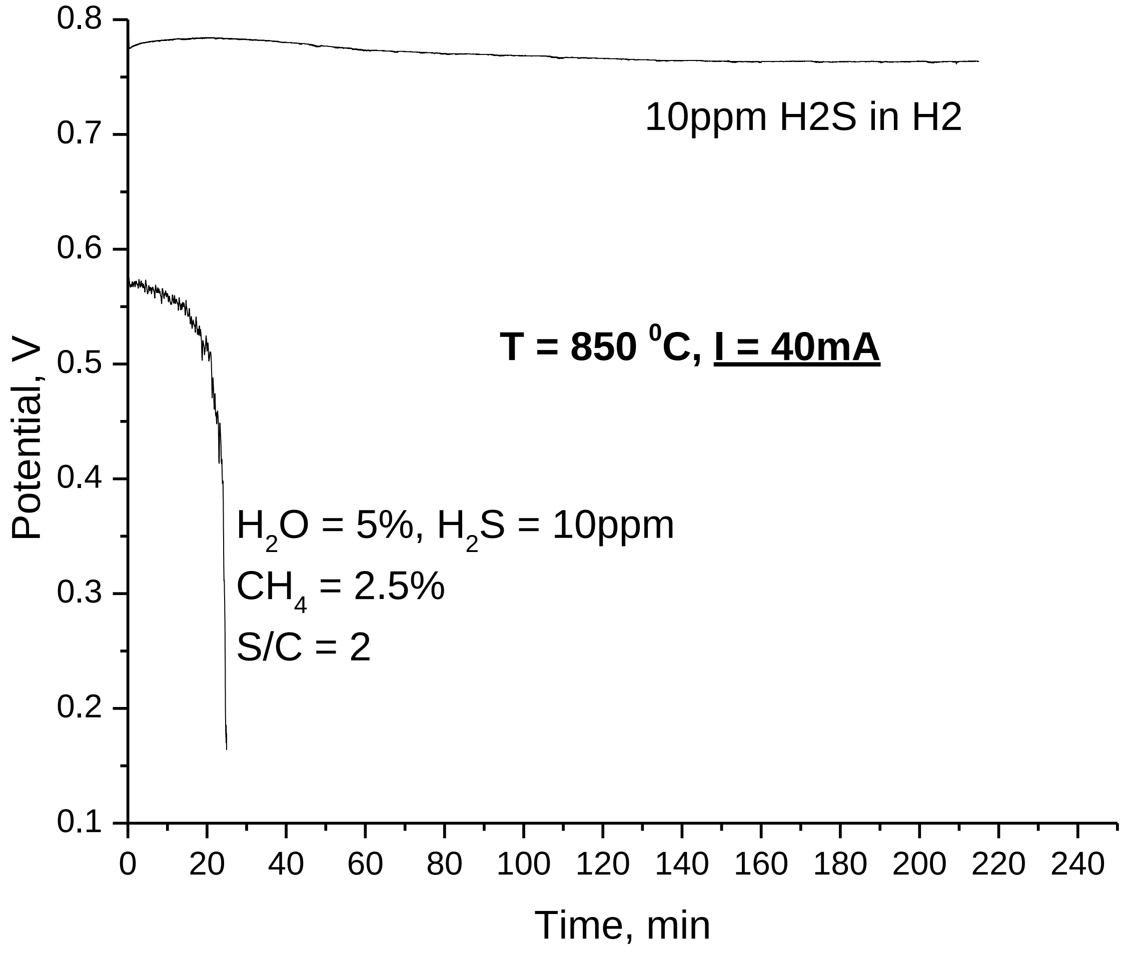
- CH_4 activation takes place on Ni
- CH_xO formed on Ni is an intermediate and decomposes into CO and H_2
- Au hinders CH_4 dehydrogenation Ni into C deposites
- Under lean S/C NiAu/YSZ is selectively electrooxidizing H_2 due to the low coverage of CH_xO

NiAu/GDC

- CH_4 activation takes place on Ce_2O_3
- CH_xO is formed on Ce_2O_3 and decomposes on Ni into CO and H_2
- Au hinders CH4 dehydrogenation Ni into C deposites
- Under lean S/C NiAu/GDC is selectively catalyzing CH_4 partial electrooxidation due to the abundant formation of CH_xO

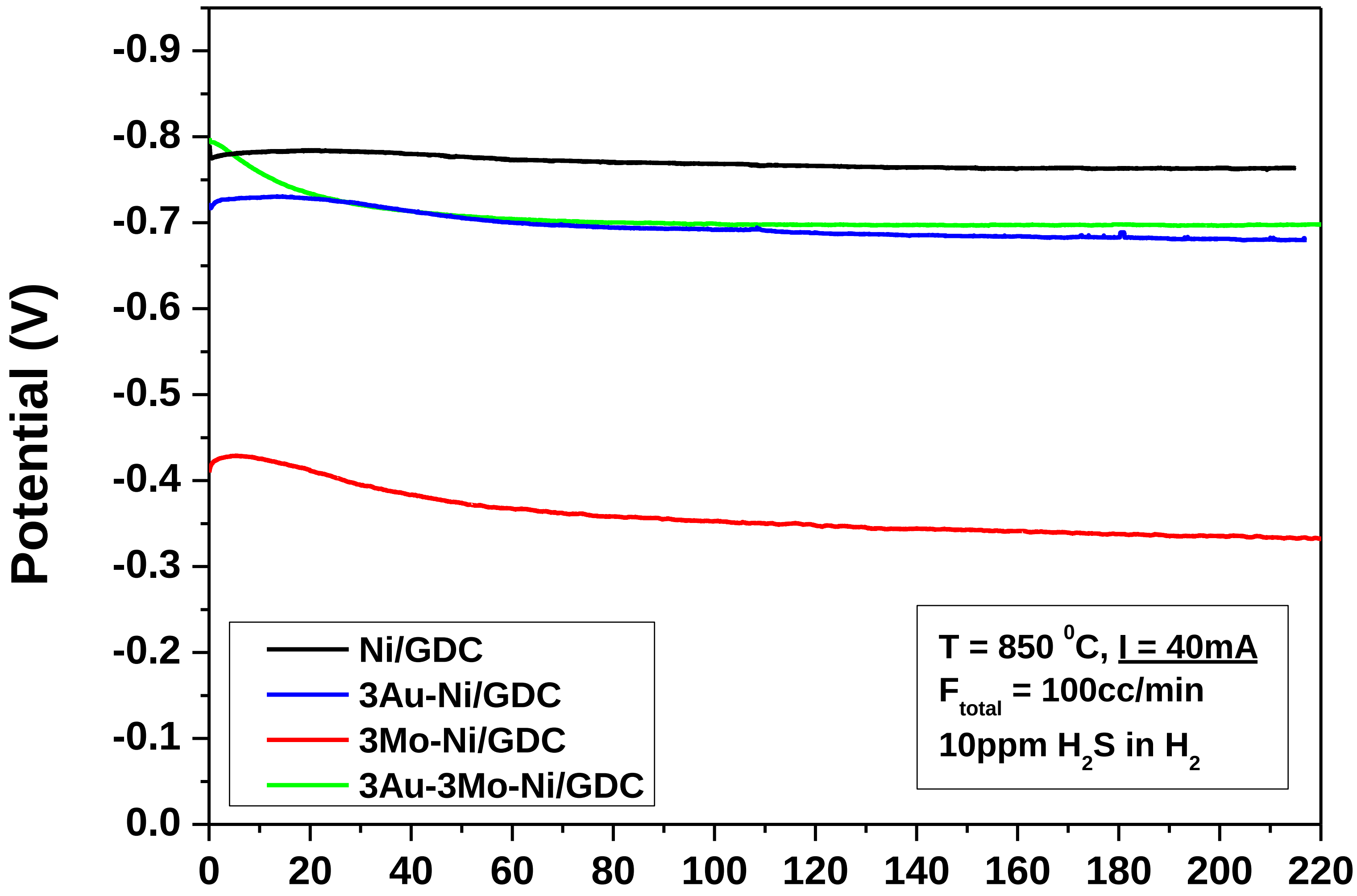
Sulfur Tolerance

Effect of H_2S on Ni/GDC under H_2 and reforming conditions



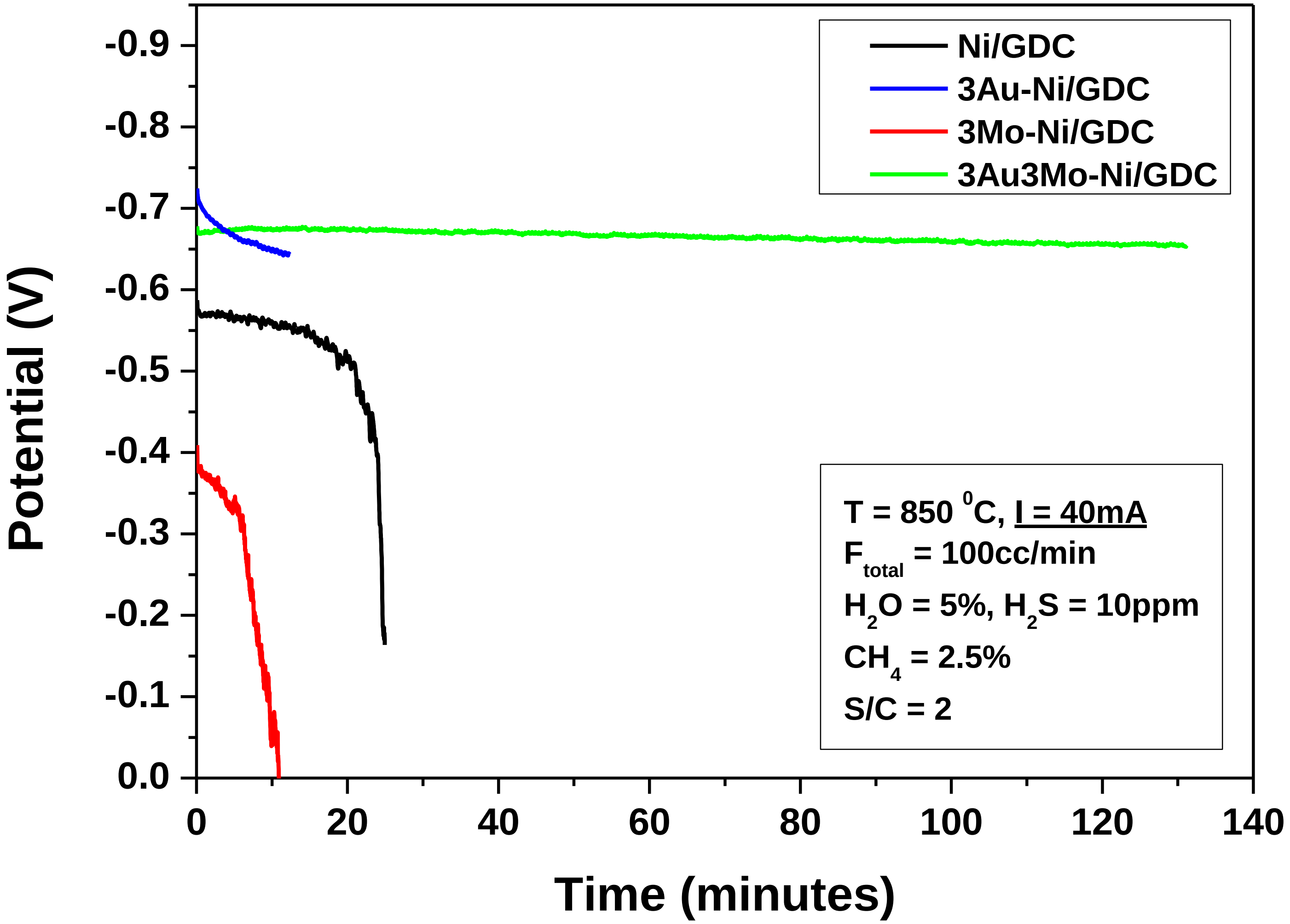
Stability in the presence of H_2S

■ 10ppm H_2S/H_2



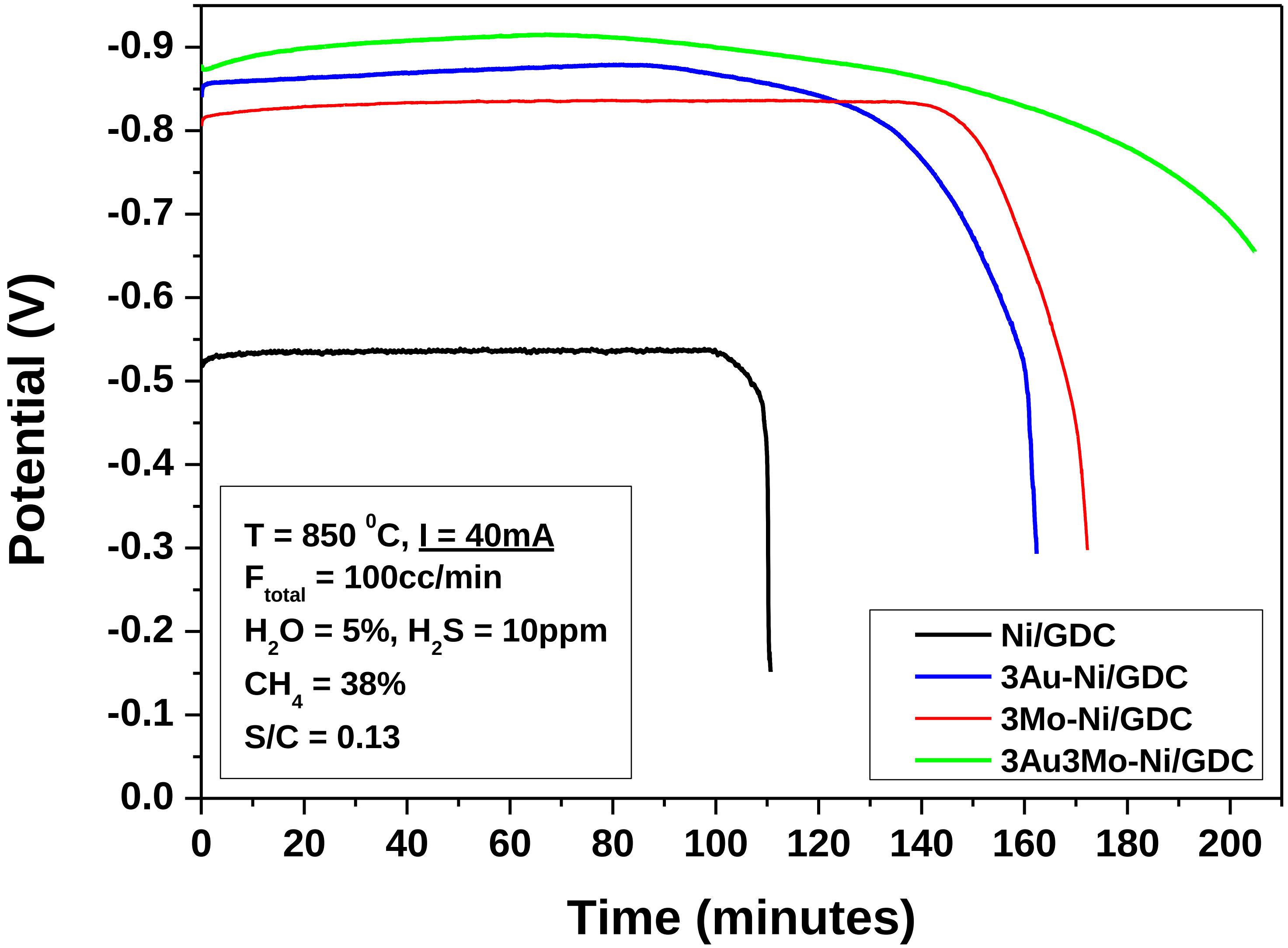
Stability in the presence of H_2S

■ CH_4 SR, S/C=2 + 10ppm H_2S



Stability in the presence of H_2S

■ CH_4 SR, S/C=0.13 + 10ppm H_2S



Conclusions – Current status

- The introduction of Au modified Ni/YSZ into a carbon tolerant catalyst by the formation of NiAu1%at/YSZ syrface alloy
- Modification of commercial NiO/GDC with D.P. and/or D. CP. of Au and/or Mo resulted in new binary and ternary materials, possible anodes in CH_4 plus H_2S fueled SOFCs
- Binary and ternary samples show catalytic activity though lower than the undoped Ni/YSZ
- Synergistic interaction between Ni, Au and Mo towards the decrease of carbon deposition for the catalytic CH_4 dissociation and steam reforming reactions
- Synergy is attributed to the formation of Ni-Au-Mo solid solution

Research Team

- Dr Dimitris Niakolas
- Dr Nikos Triantafyllopoulos
- Dr Ilias Gavrielatos
- Michalis Athanasiou

Acknowledgements

- FCH-JU project **Understanding and minimizing anode degradation in hydrogen and natural gas fuelled SOFCs,** Acronym:ROBANODE
- FCH-JU project **Innovative SOFC Architecture based on Triode Operation,** Acronym:T-cell