



Fuel Cell & Hydrogen Technologies JP

SP2: Catalyst and Electrodes

Borovetz, Bulgaria

June 2nd and 3rd 2014

Electrochemical Impedance Study of the Poisoning Behavior of Ni-based Anodes at Low Concentrations of H₂S in a MCFC

EERA FCH2-SP2 WORKSHOP in frame of EIA10

Bridging experimental and numerical research:

development and optimization of advanced characterization tools – Electrochemical Impedance Spectroscopy



Italian national agency for new technologies,
energy and sustainable economic development

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ENEA

Background and objective

Challenge:

- **Biogas** from anaerobic digestion of organic wastes is a promising alternative in the *transition* from fossil to sustainable fuels and hydrogen



- Among biogas contaminants, **H₂S** is still the critical compound, even after clean-up **0.2 % vol. H₂S → 1 ppm**
- Need to *study* the H₂S **poisoning mechanism** in MCFC and *develop* more resistant components

ENEA approach:

- Develop tailored solutions to improve state-of-art industrial components
→ **Ceria coating**
- Characterize and validate modified components for performance
→ **Button & single cell testing (performance & durability)**

Generating sulphur-resistant anodes

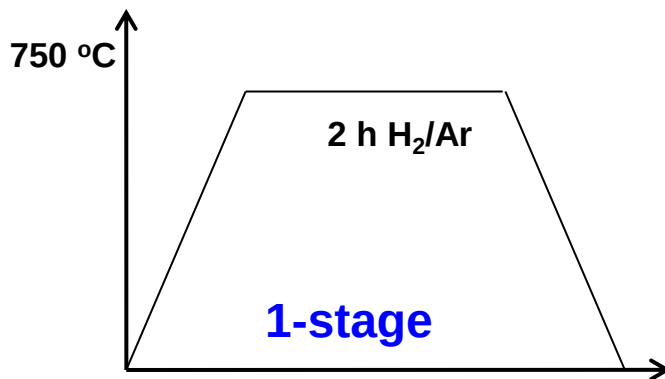
1) First tests on Ceria-coating of anode

- Industrial Ni-Cr anodes have been dipcoated with Ceria to create sacrificial layer
- IV plots showed no effects of coating on the poisoning tolerance of MCFC!
- Post-test analysis indicated no Ceria was left on the anode!
 → Out-of-cell leaching tests confirmed Ce dissolves in molten carbonates

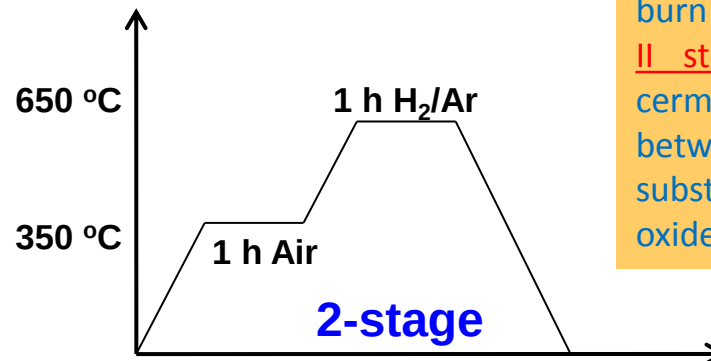


The coated electrode preparation has been optimized with a heat treatment before assembling in a cell in order to fix the ceria layer permanently to the substrate.

2) Pre-test heat treatments attempted



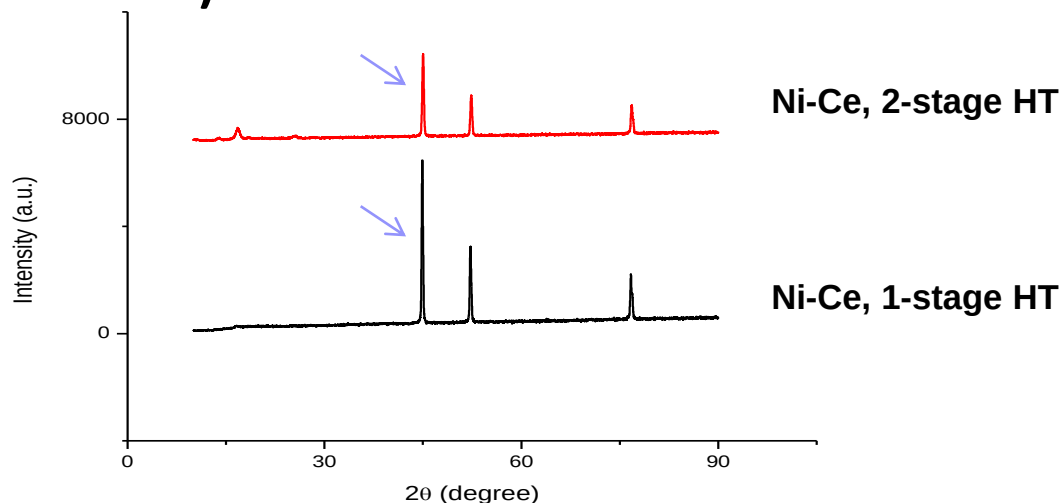
Vs.



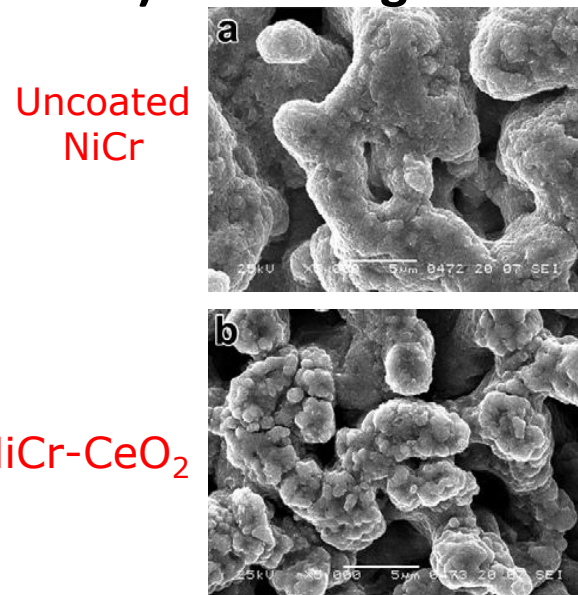
I step 350°C - you burn organic materials
 II step 650°C - a cermet is formed between the nickel substrate and the oxides coating

Generating sulphur-resistant anodes

3) XRD after heat treatment



4) SEM images



5) XRF after heat treatment

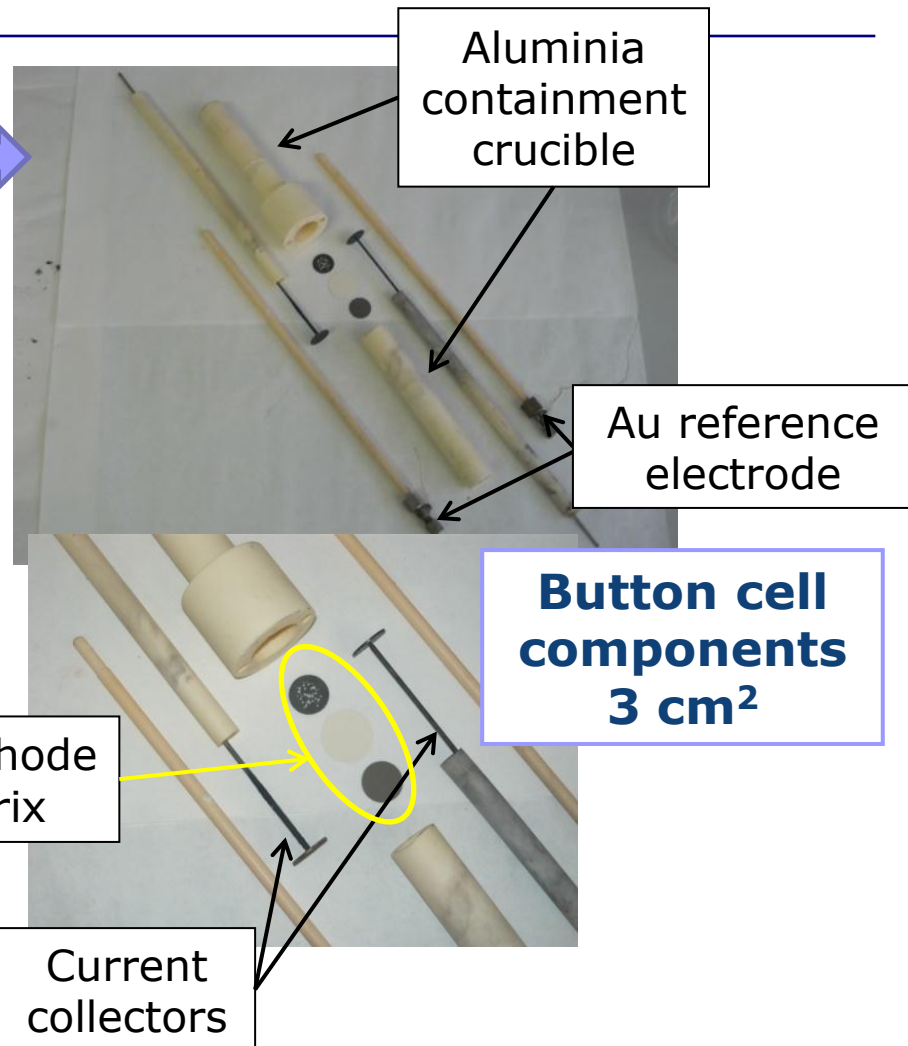
Out-of-cell tests in carbonates under anode atmosphere

Ex situ	Ce	Zr	Cr	Ni	Trace
CZ100_750	1.46	-	19.36	944.71	-
CZ100_350_650	0.35	-	19.19	905.43	-

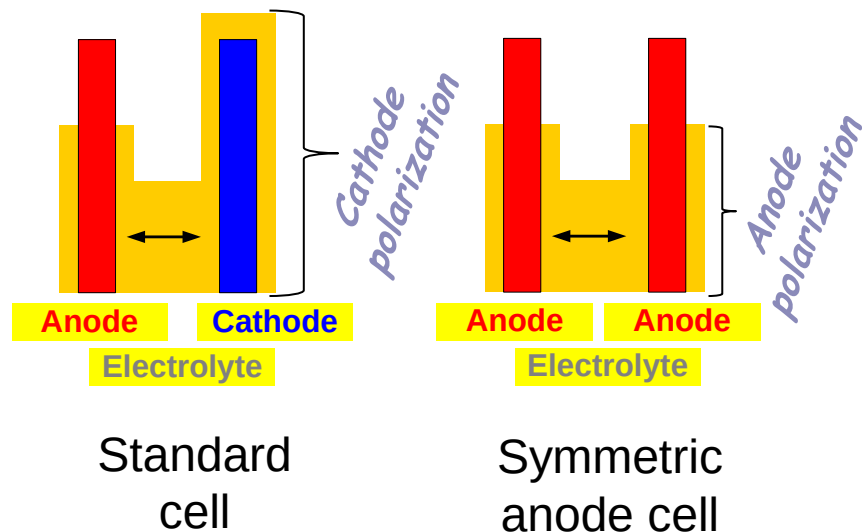
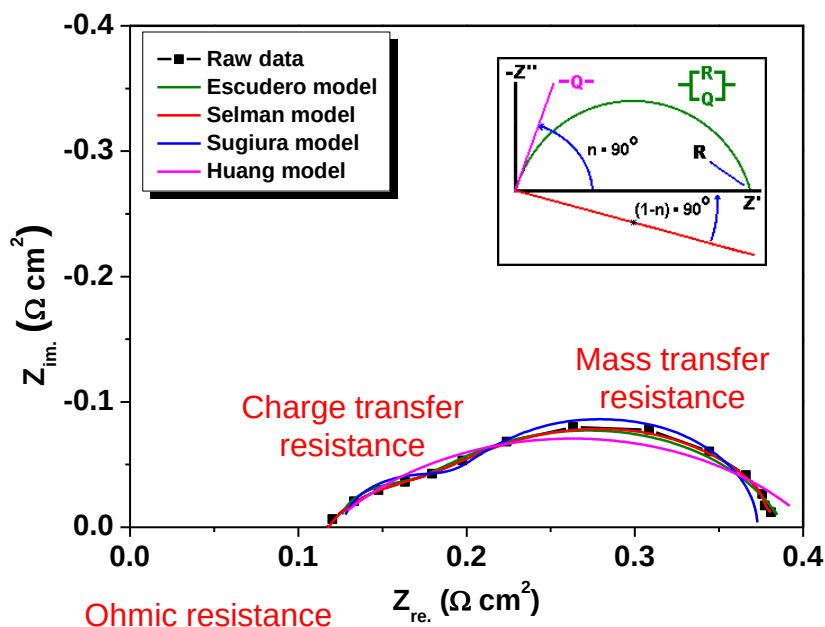
More Ce left!

→ 1 stage HT generates better coating

Fuel Cell experimental device

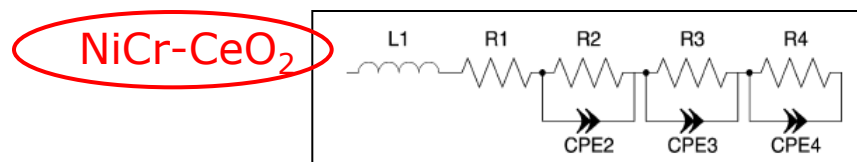
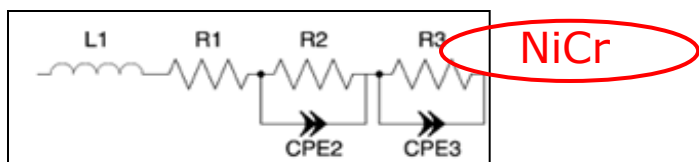


EIS spectra

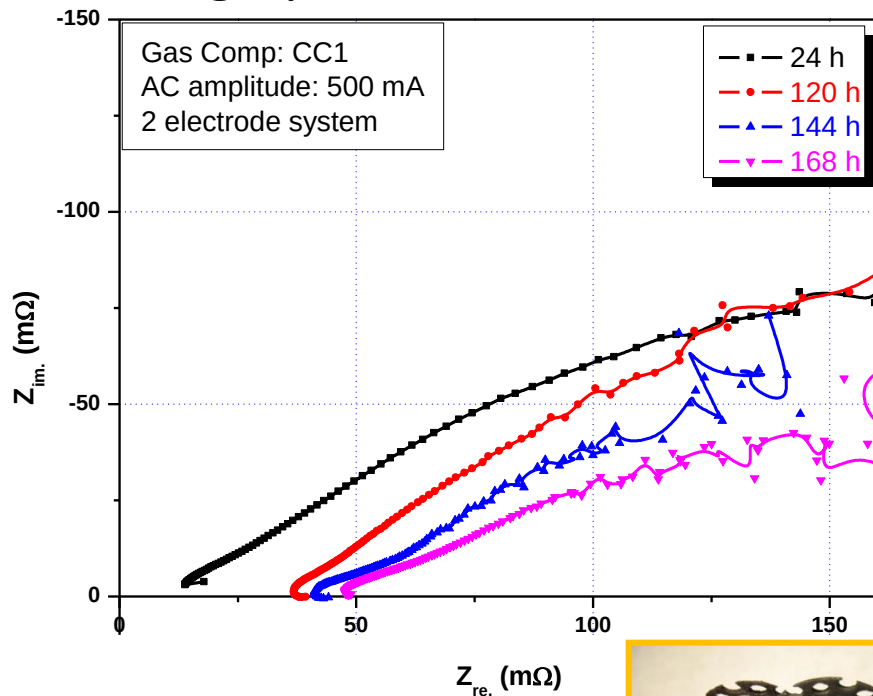


The symmetrical set up has been chosen to enhance the effects @ the anode. In case of standard single cell, the effects of the cathode polarizations are too large which makes the differences in anode polarization become less significant.

Equivalent circuit model for the Ni based anode with and without Ceria coating



Finding optimum characterization conditions: pre-experiment analysis



Optimized gas composition

Anode

H₂ = 3.5 NI/h (26%)
N₂ = 8.6 NI/h (64%)
CO₂ = 0.6 NI/h (4%)
H₂O = 0.6 g/h (5%)

Cathode

O₂ = 1.5 NI/h (13%)
N₂ = 6.5 NI/h (57%)
CO₂ = 3.5 NI/h (30%)

REF B

Anode

H₂ = 3.0 NI/h (25%)
N₂ = 5.6 NI/h (46%)
CO₂ = 0.5 NI/h (4%)
H₂O = 2.4 g/h (25%)

Cathode

O₂ = 1.9 NI/h (14%)
N₂ = 7.5 NI/h (55%)
CO₂ = 4.3 NI/h (31%)

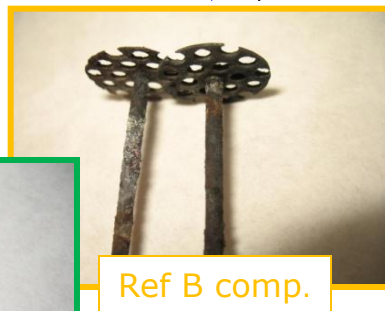
CC1

Anode

H₂ = 40.1%
N₂ = 3.9%
CO₂ = 7.1%
H₂O = 47.9%

Cathode

O₂ = 9.4%
N₂ = 69.6%
CO₂ = 3%
H₂O = 18%

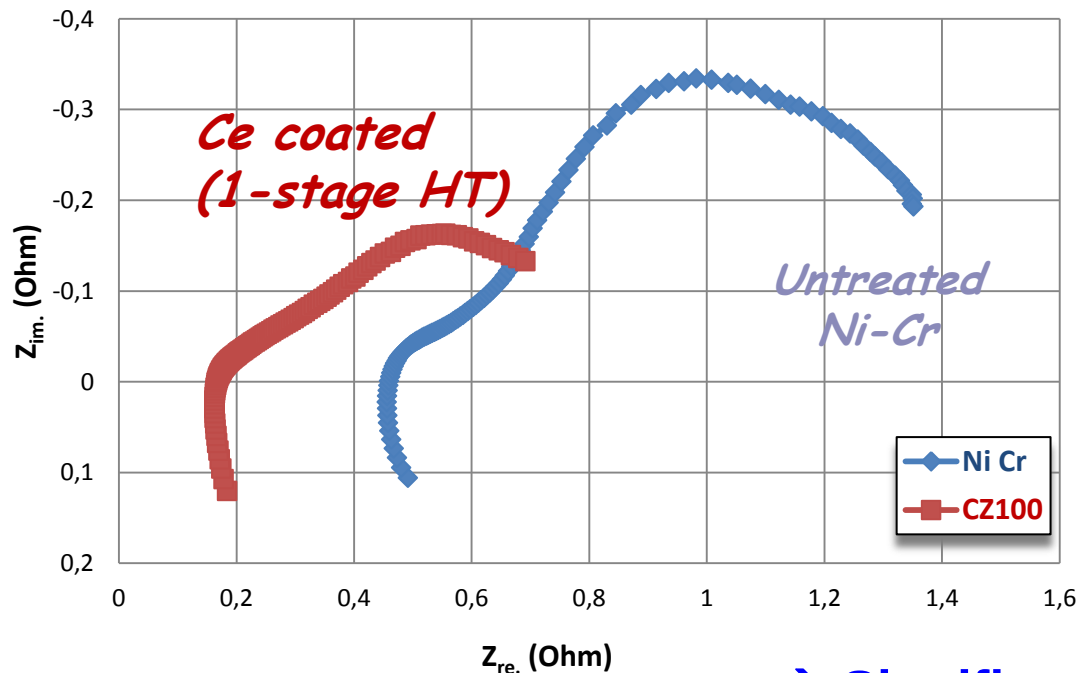


OPTIMIZED COMPOSITION
avoids corrosion and
scattered EIS spectra



EIS spectra of symmetric cell: 2 anodes

Nyquist plot @ 100 mA/cm² after 1-stage HT



- No difference in the first semiarc indicating the charge transfer polarization.
- Ceria coated anode show lower mass transfer polarization (second semi-arc) → when Ni is completely covered with S, hydrogen diffuses and penetrates through the electrode with difficulty

48 ppm of H₂S poisoning
Optimized composition

→ Significant increase in H₂S tolerance!

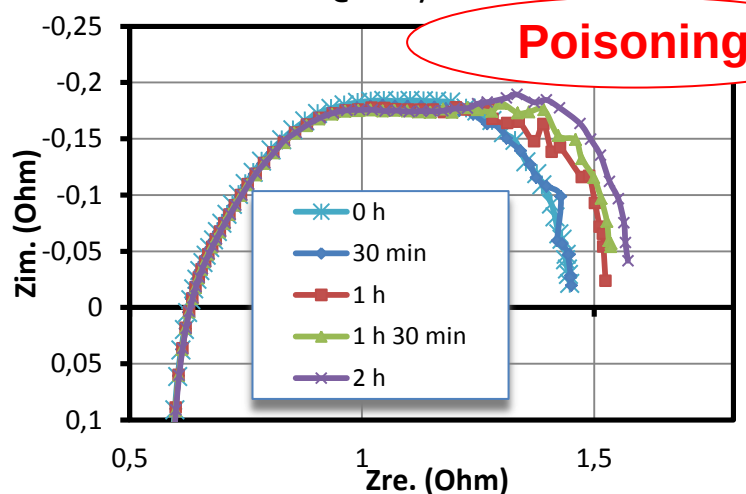
Electrochemical analysis & characteriz.

EIS: poisoning and regeneration kinetics

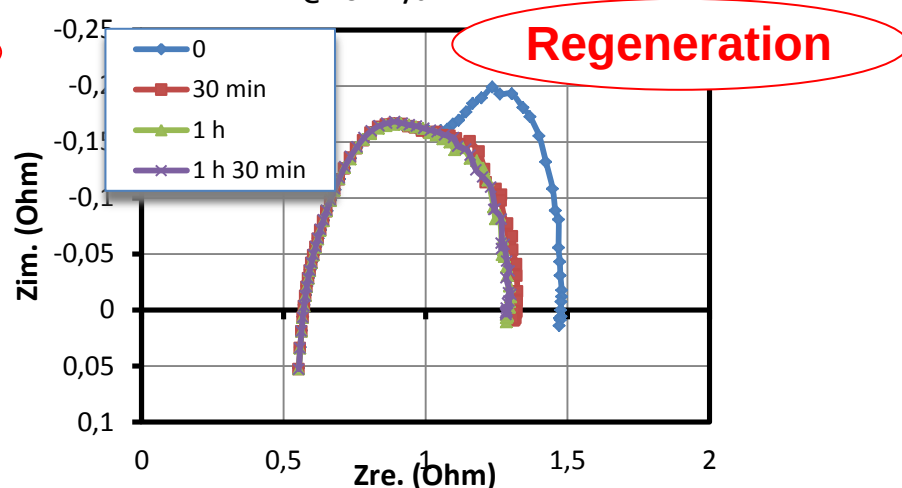
Button cells analysis

NiCr-CeO₂

Nyquist Plot of Poisoning as a Function of Time
@75mA/cm²



Nyquist Plot of Regeneration as a Function of Time
@ 75 mA/cm²



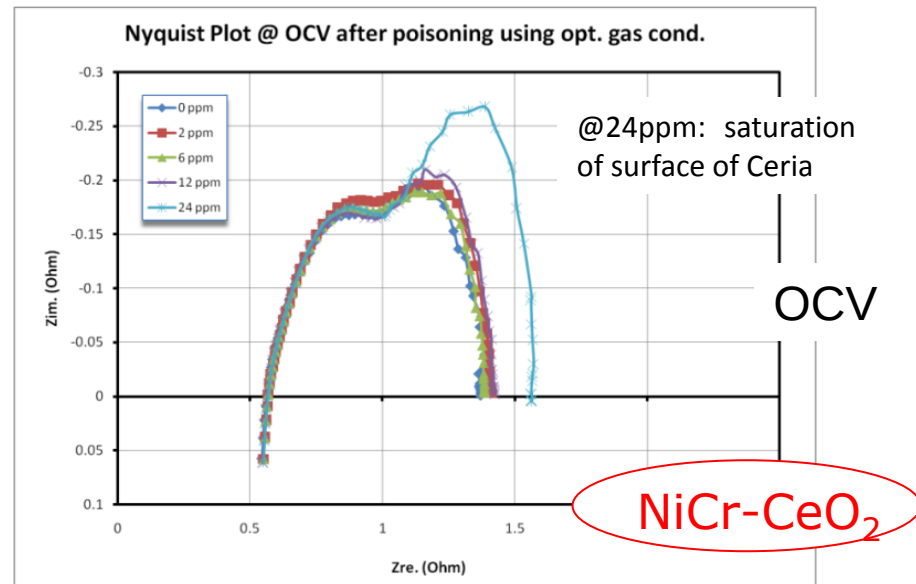
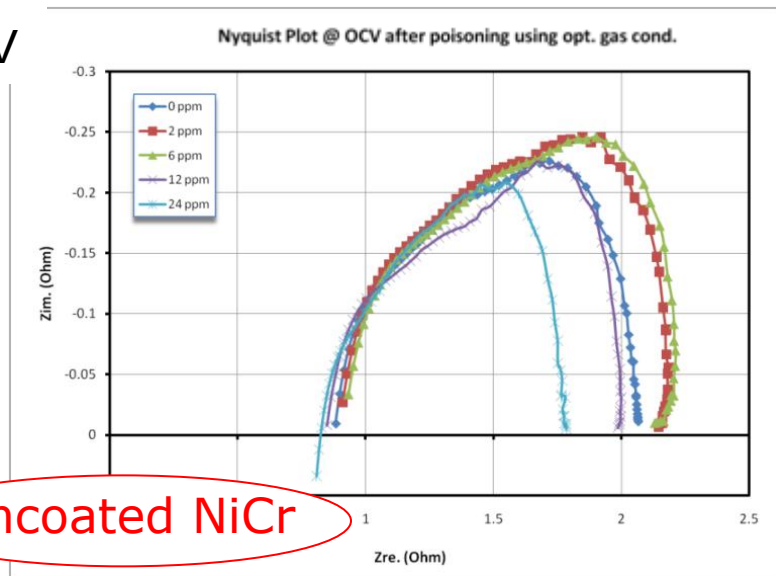
Nyquist diagram with 24 ppm H₂S as a function of time.

There is no difference in the intercept with the real impedance (ohmic polarization) and in the diameter of the first semicircle (charge transfer) during the first two hours of H₂S poisoning. Conversely, the diameter of the second semicircle (mass transfer) varies considerably, after 1 hour of H₂S exposure. The regeneration seems to be even faster.

EIS: Nyquist plots at various H_2S concentrations, comparison between uncoated and coated anodes

Nyquist diagrams of anode Ni-Cr and Ni-ceria at OCV during poisoning with 2, 6, 12, 24 ppm H_2S .

OCV



In case of Ni-Cr anode after the poisoning, the second semi-arc increases until 6 ppm and decreases afterwards. The increase of mass transfer polarization is due to the competition between H_2 and H_2S for Ni active sites. When the H_2S poisoning level reaches 12 ppm, mass transfer polarization decreases suggesting the high concentration of H_2S changes the component properties. In this particular case, probably better wetting of the anode by the electrolyte (compared to less or no poisoning) facilitates H_2 to reach triple phase boundary, resulting in better diffusion [ref].

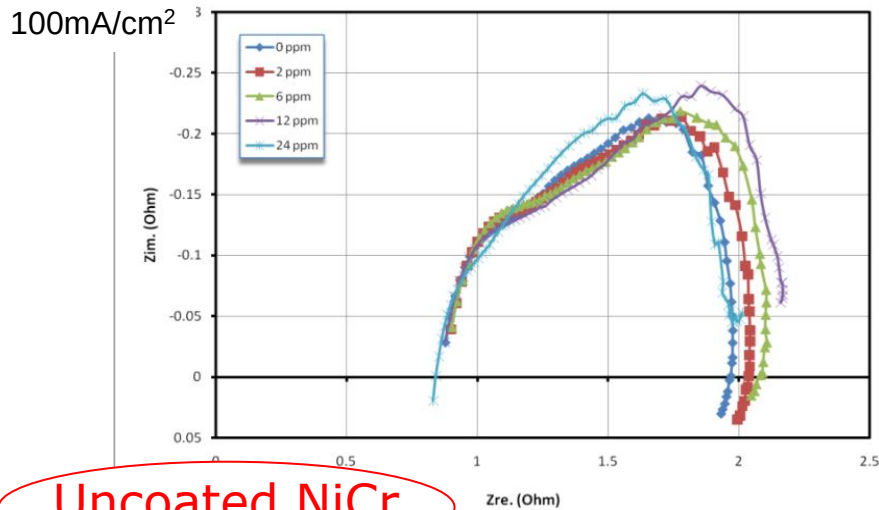
NiCr-CeO₂ → Poisoning takes effect only at > 12 ppm H_2S

Ceria proves to be an effective sacrificial compound that prevents Ni active sites from being poisoned.

EIS: Nyquist plots at various H_2S concentrations, comparison between uncoated and coated anodes

Nyquist diagrams of anode Ni-Cr and Ni-ceria at 100 mA/cm² during poisoning with 2, 6, 12, 24 ppm H_2S .

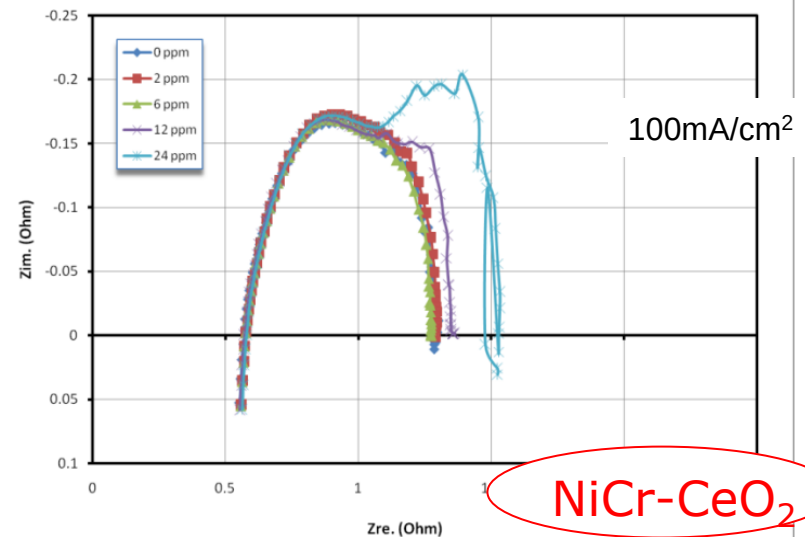
Nyquist Plot @ 100 mA/cm² after poisoning using opt. gas



The trend for the Nyquist plots at OCV and at 100 mA/cm² is the same. The only difference is the maximum point, which is 6 ppm and 12 ppm for OCV and 100 mA/cm², respectively.

This fact takes place due to the production of H_2O when the electrochemical reaction is also carried out. Higher water content decreases the effect of poisoning.

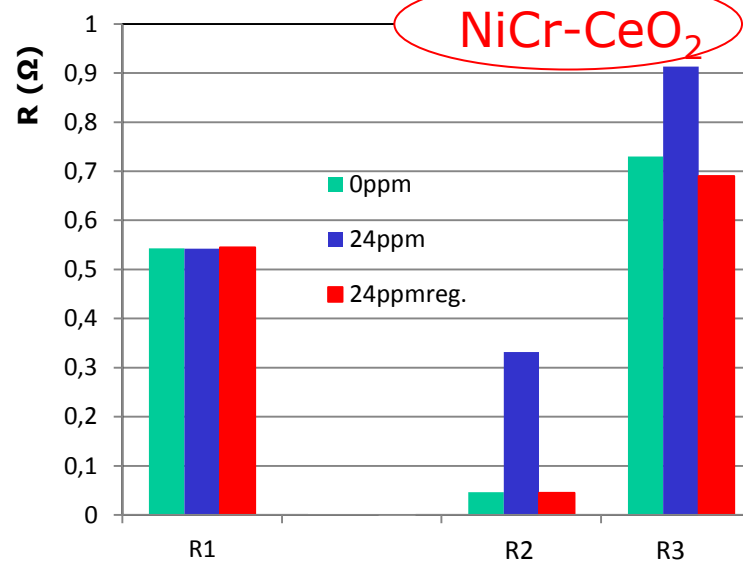
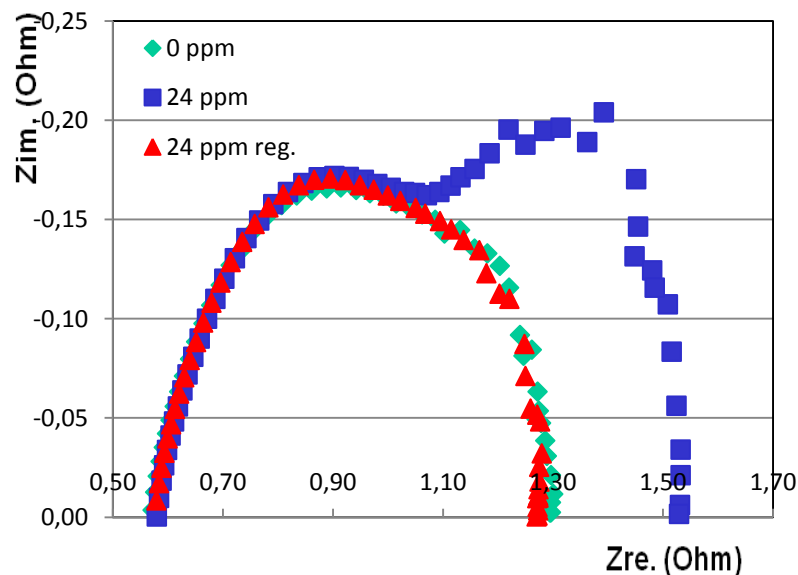
Nyquist Plot @ 100 mA/cm² after poisoning using opt. gas



The mass transfer polarizations are the same up to 6 ppm, and start to increase afterwards. Production of water shows an undesirable effect for ceria-coated anode, since the water probably competes with H_2S to be absorbed by ceria. Higher amounts of water maintained ceria in its fully oxidized state, making it difficult to absorb H_2S .

EIS: Nyquist plots after regeneration

Nyquist Plot @ 100 mA/cm² with
24 ppm H₂S and after regeneration



R1: ohmic resistance
R2: charge transfer resistance
R3: diffusion resistance

Cell performance does not show any residual effect of the H₂S presence and Nyquist diagrams before and after poisoning are perfectly coincident.

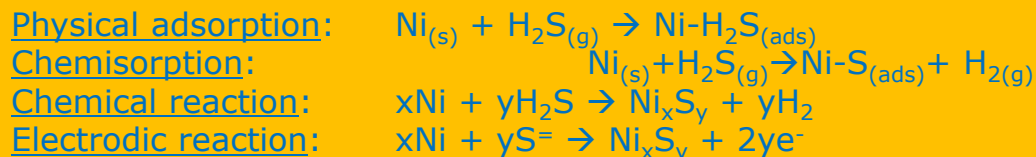
Conclusions

- ❑ EIS analysis on the cell seems to be a reliable tool to screen candidates of modified anodes that show an higher resistance to H_2S poisoning.
- ❑ Electrochemical impedance measurements (EIS) show that the coated electrodes have higher performance than the traditional ones.
- ❑ Ni-ceria anodes are effective in reducing damages of poisoning, especially at low concentrations of hydrogen sulfide.
- ❑ The coating with ceria is therefore a potential solution to reduce the poisoning of a MCFC fuelled with biogas.

Thanks
for your
attention

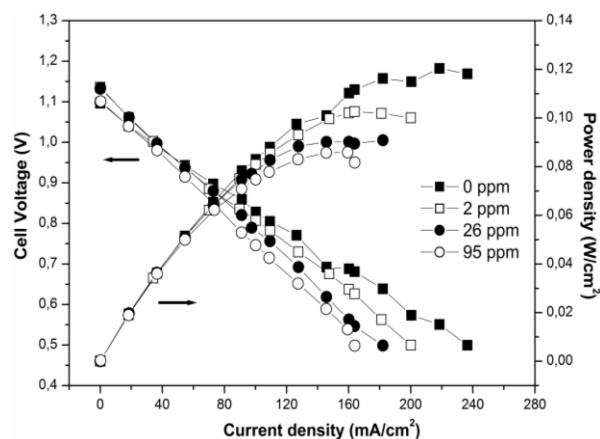
MCFC fuelled with biogas: H₂S poisoning

Poisoning by H₂S of Ni-based anode can occur either by chemical, physical or electrochemical reactions:

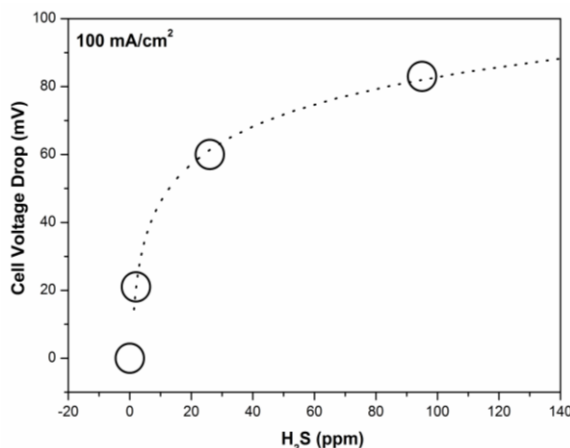


- ❑ Poisoning occurs predominantly via electrochemical reaction.
- ❑ When the anodic potential reaches the value of the potential for nickel sulphides download, the cell potential significantly decays (drop of potential).

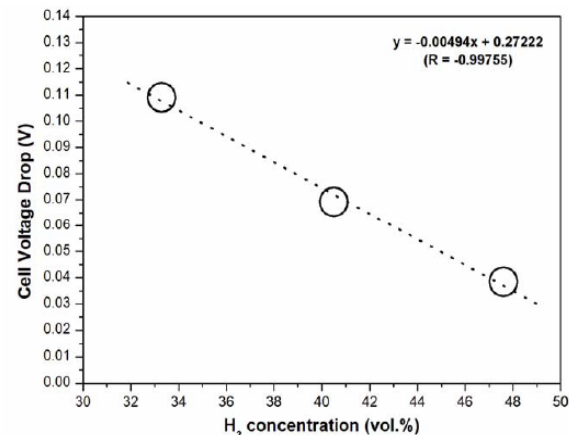
The poisoning degree depends on applied current, hydrogen sulphide and hydrogen concentration.



The Cell Voltage drop increase with the current density because the H₂S poisoning occurs with electrochemical mechanism



The anode surface is almost saturated by H₂S at high concentration



Cell voltage drop shows a linear dependence with H₂ concentration

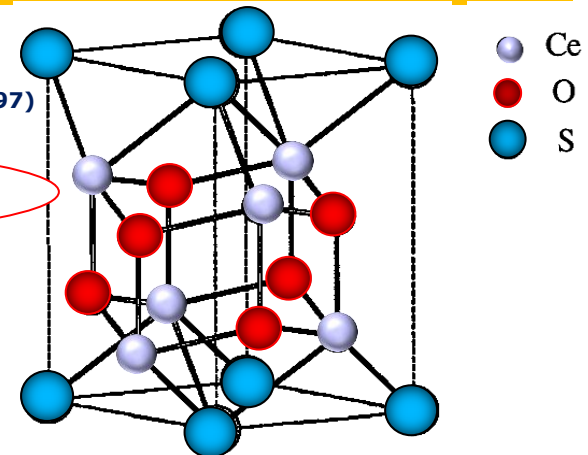
NiCr-CeO₂ anodes

- ❑ Ceria incorporates sulphur in presence of H₂S according to the redox reaction:

$$2\text{CeO}_2 + \text{H}_2\text{S} + \text{H}_2 \rightleftharpoons \text{Ce}_2\text{O}_2\text{S} + 2\text{H}_2\text{O}$$
- ❑ CeO₂ has high sulphur tolerance and high recovering capability.
- ❑ The addition of CeO₂ increases resistance to sintering and promotes the ability of anode regeneration for the high oxygen storage capacity.

C. Sourisseau, JOURNAL OF RAMAN SPECTROSCOPY, VOL. 28, 965-971 (1997)

Cerium oxide sulfide (Ce₂O₂S)

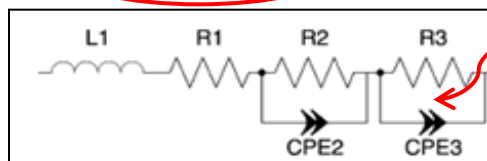


AIM OF THE WORK

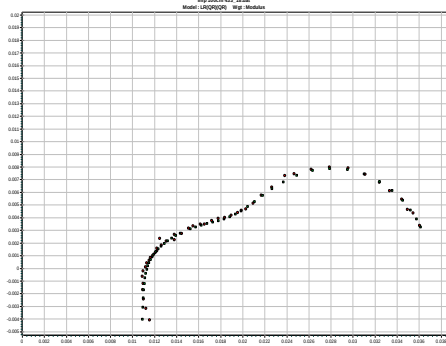
- ❑ Preparation of sulfur-tolerant alternative materials by protecting the traditional Ni-Cr anode with a layer of CeO₂ using **dip coating method**.
- ❑ Materials physical-chemical characterization: **SEM, EDX, XRD, conductivity measurements, neutron diffraction**.
- ❑ In cell test: **polarization curves, EIS measurements, iR**.
- ❑ Post test analysis: **SEM, EDX**.

Electrochemical Impedance Spectroscopy

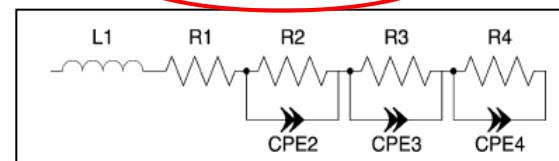
NiCr



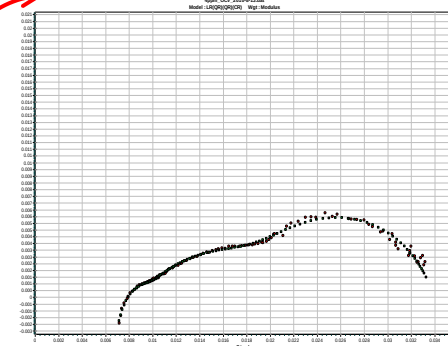
R1: ohmic resistance
R2: charge transfer resistance
R3: diffusion resistance



NiCr-CeO₂



R1: ohmic resistance
R2: ohmic resistance of the coating
R3: charge transfer resistance
R4: diffusion resistance



The Constant Phase Element (CPE) is a non-intuitive circuit element that was discovered (or invented) while looking at the response of real-world systems. In some systems the Nyquist plot (also called the Cole-Cole plot or Complex Impedance Plane plot) was expected to be a semicircle with the center on the x-axis. However, the observed plot was indeed the arc of a circle, but with the center some distance below the x-axis.

These depressed semicircles have been explained by a number of phenomena, depending on the nature of the system being investigated. The common thread among these explanations is that some properties (porosity, roughness of the surface) of the system are not homogeneous.