

# International Symposium on DIAGNOSTICS TOOLS FOR FUEL CELL TECHNOLOGIES

**“Current interruption: a method to characterize  
a 100 cm<sup>2</sup> class molten carbonate fuel cell”**

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1

- The current interruption / potential relaxation method was applied to a Molten Carbonate Fuel Cell (MCFC) as a suitable tool to provide information about cell components degradation.

2

- A 100 cm<sup>2</sup> class single cell was operated for about 2000 hours: effect of poisoning with small concentration of H<sub>2</sub>S in the anode gas was tested.

3

- Current interruption measurements at different time ranges were carried out on the same cell to separate and measure cell voltage losses before and during H<sub>2</sub>S poisoning.

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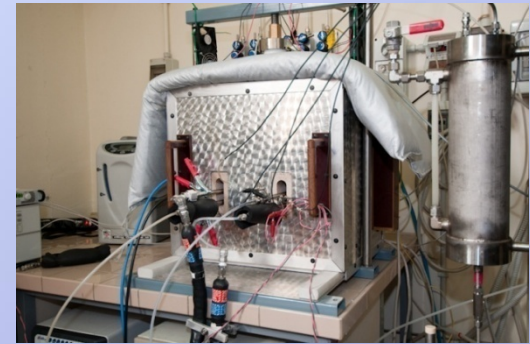
- Two different software were compiled by LABVIEW language:
  - **FC-TF** (Fuel Cell Test Facility) to manage the MCFC facility, and **FC-EC** (Fuel Cell Electrochemical Check) to carry out automatically electrochemical measurements.

In the effort to maximize the energetic yield from alternative energy sources like biomass sewage sludge, manure... and wanting to minimize environmental impact in terms of polluting emissions, the coupling of high-temperature fuel cells to the fuel gas produced from these sources is an attractive option. However, the contaminant levels are often unacceptable for performing and durable operation of a molten carbonate fuel cell (MCFC). The effect of  $H_2S$  in the fuel gas was investigated on the electrochemical performance of a single MCFC cell.

## Experimental

The cell was a cross flow type, water on the anodic side was fed by a CEM (controlled evaporator mixer) and hydrogen was produced by an electrolyser. Various compositions for cathodic gases were used: the  $O_2/CO_2$  gas mixtures range was from 1/1 to 1/6. The utilization factors of anode and cathode gasses are represented by  $U_f$  and  $U_{ox}$  which are calculated as the percentage of consumed gas to the feed gas.

## 100 cm<sup>2</sup> MCFC



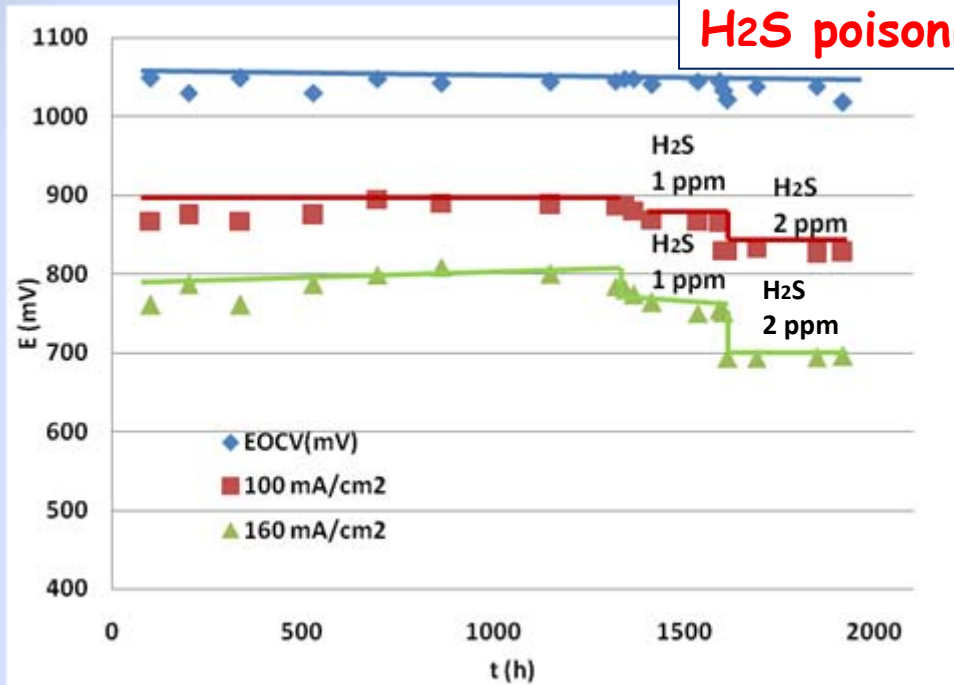
## Cathode and anode materials and operative conditions

Item	Operating conditions
Effective electrode area (cm <sup>2</sup> )	55
Cathode	NiO
Electrolyte	Li <sub>2</sub> CO <sub>3</sub> /K <sub>2</sub> CO <sub>3</sub> = 62/38%
Anode	Ni + 10 %wt Cr
Tile	$\gamma$ - Lithium aluminate
Temperature (°C)	650
Pressure (atm)	1
Reference anode gas	$H_2/N_2/CO_2 = 47.6/47.6/4.7$
Reference cathode gas	$O_2/N_2/CO_2 = 14/56/30$

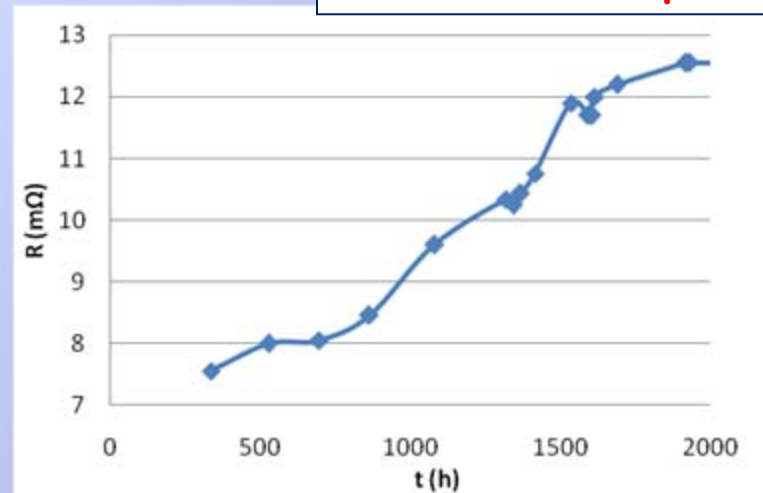
Current interruption measurements were carried out before and during anode poisoning with  $H_2S$

$H_2S$  has an immediate effect on cell performance, even at 1 ppm. The effects of low concentrations of  $H_2S$  in the fuel are due to interaction with the electrolyte and with the anode surface.

### $H_2S$ poisoning



### IR versus time plot



Cell potential at OCV and different current densities as a function of time for NiO cathode. At 1320 and 1594h poisoning with 1ppm and 2ppm of  $H_2S$  takes place.

Cell internal resistance slowly increases during 2000 Hr.

# Fuel Cell-Test Facility

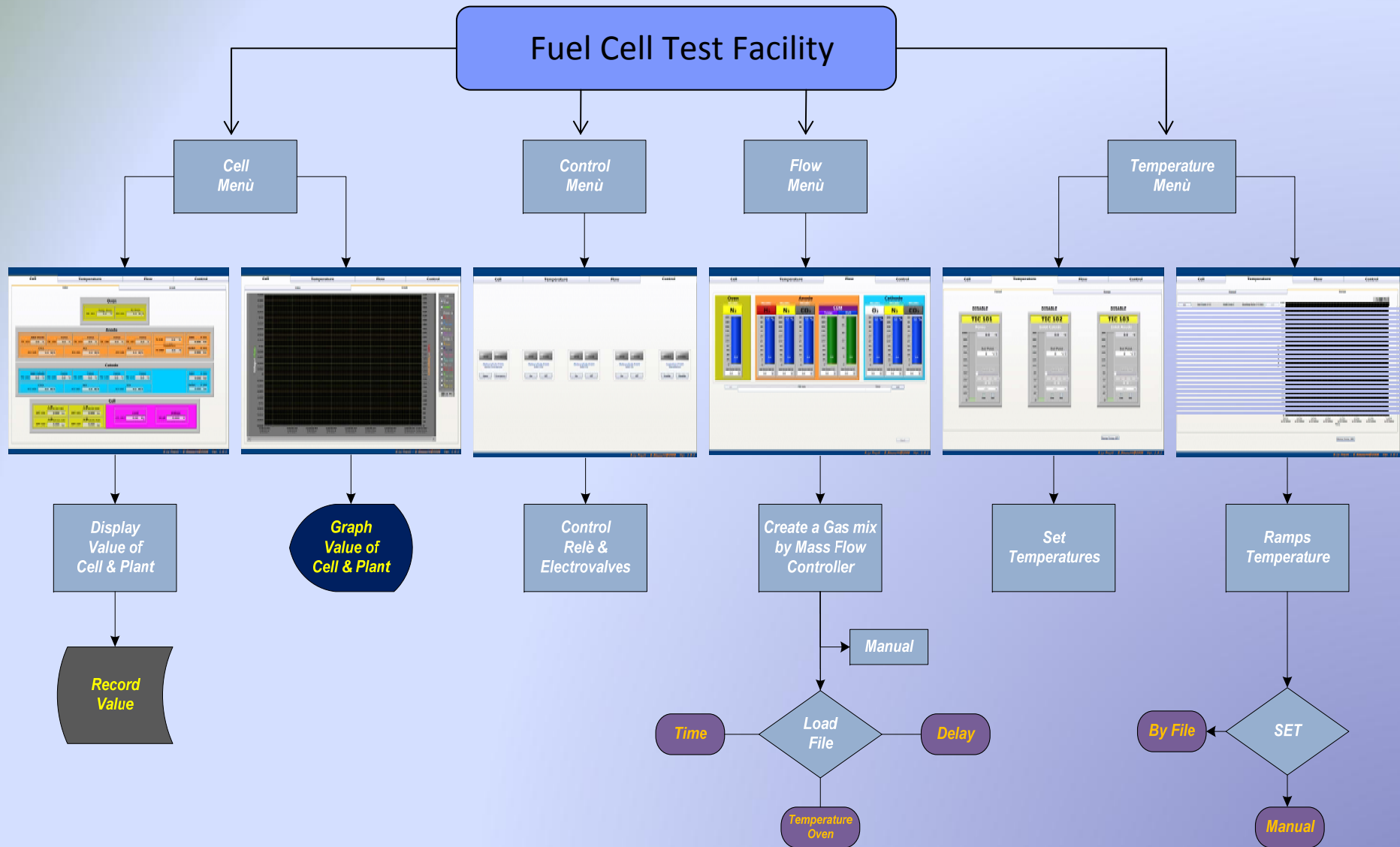
The **FC-TF** Software was compiled in ENEA to manage the MCFC Test Plants.

**FC-TF** Software, by a 34980 Agilent data logger, interfaces with the test facility acquiring voltage (thermocouples, mass flow controllers, relè...).

By **FC-TF** it's possible to:

- ✓ Set an anodic humidity by Controlled Evaporator Mixer (CEM)
- ✓ Set the anodic and cathodic gas composition by Mass Flow Controller (MFC)
- ✓ Apply a temperature ramp
- ✓ Record all parameters in a visual and in a textual way
- ✓ An alarm system points out irregular working

# FC-TF (Fuel Cell Test Facility)



# Fuel Cell-Electrochemical Check

The **FC-EC** Software was compiled in ENEA to carry out the Electrochemical Measures

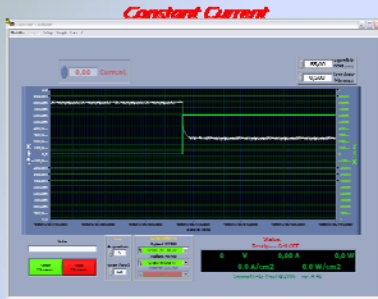
The **FC-EC** software, by the electronic load Agilent N3300, carries out different types of electrochemical measurements:

- ✓It draws a fixed current from the fuel cell and measures the corresponding output voltage;
- ✓It applies to the cell several current steps as a function of time and of the cell response (polarization curves);
- ✓It imposes or withdrawn at time  $t=0$  a current to the cell and the voltage resulting time dependent approach to steady state is measured.
- ✓Keep the cell polarized between two measures.
- ✓Protect the cell from a dangerous low voltage.
- ✓Repeat the same measure several times
- ✓All parameters are immediatly recorded both in a visual and in textual way.

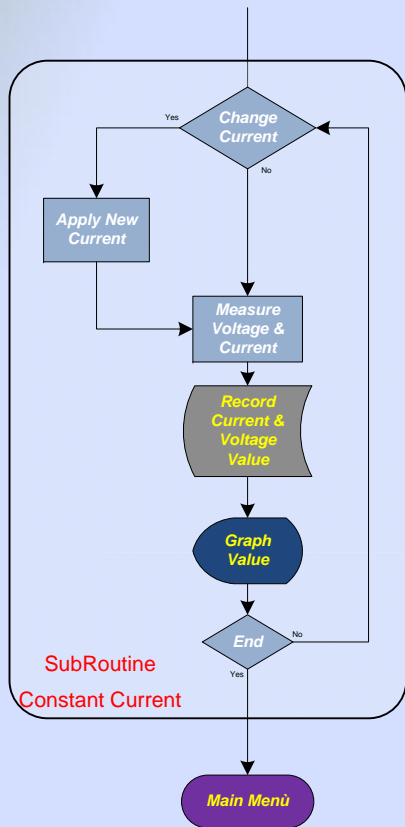


# Fuel Cell-Electrochemical Check

## Constant Current Polarization



The software applies a constant current, recording voltage continuously. The cell is polarized for many hours in order to increase performance (carbonates distribution, oxidation and lithiation process) and check stability.



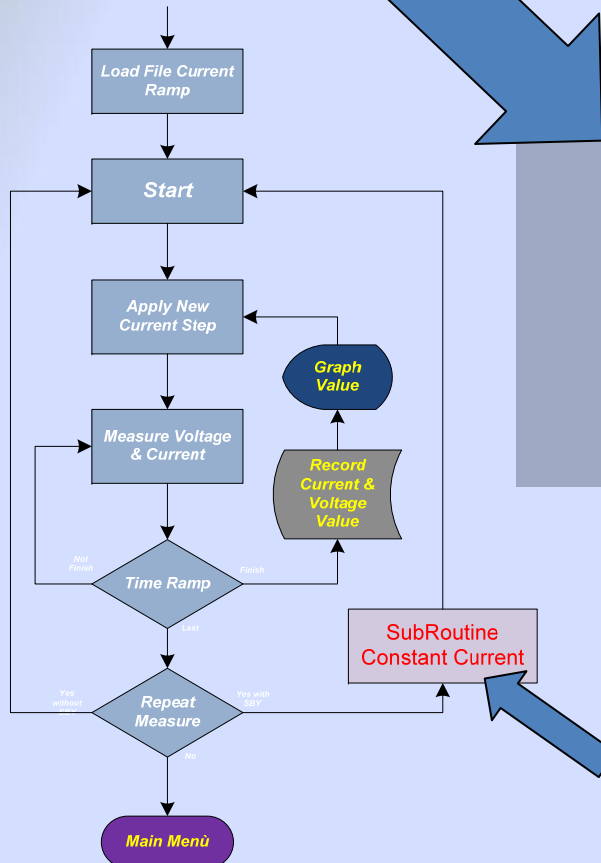
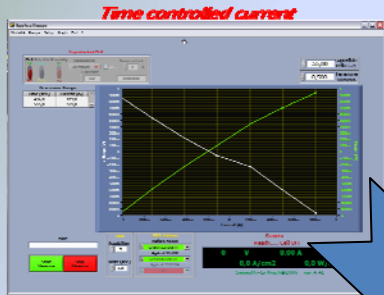
This subroutine can be applied when a constant current is required between two measures.



# Fuel Cell-Electrochemical Check

## Polarization Curves vs Time

The software applies a current stepwise. The current step duration is fixed by time.



The screenshot shows a software window with a table titled "Descrizione Rampa". The table has two columns: "Time (sec.)" and "Current (A.)". The data rows are: 200.0, 5.5; 250.0, 7.0; 250.0, 8.0; and 120.0, 9.0. The table is overlaid on a background showing a graph of current vs time.

Time (sec.)	Current (A.)
200.0	5.5
250.0	7.0
250.0	8.0
120.0	9.0

The operator can create a list of current steps with different length.

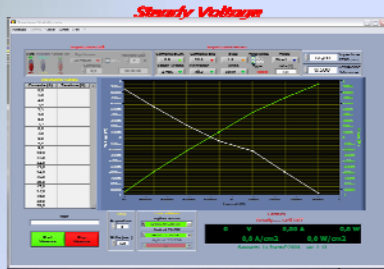
The same measure can be automatically carried out several times

This subroutine can keep polarized the cell between a measure and the following

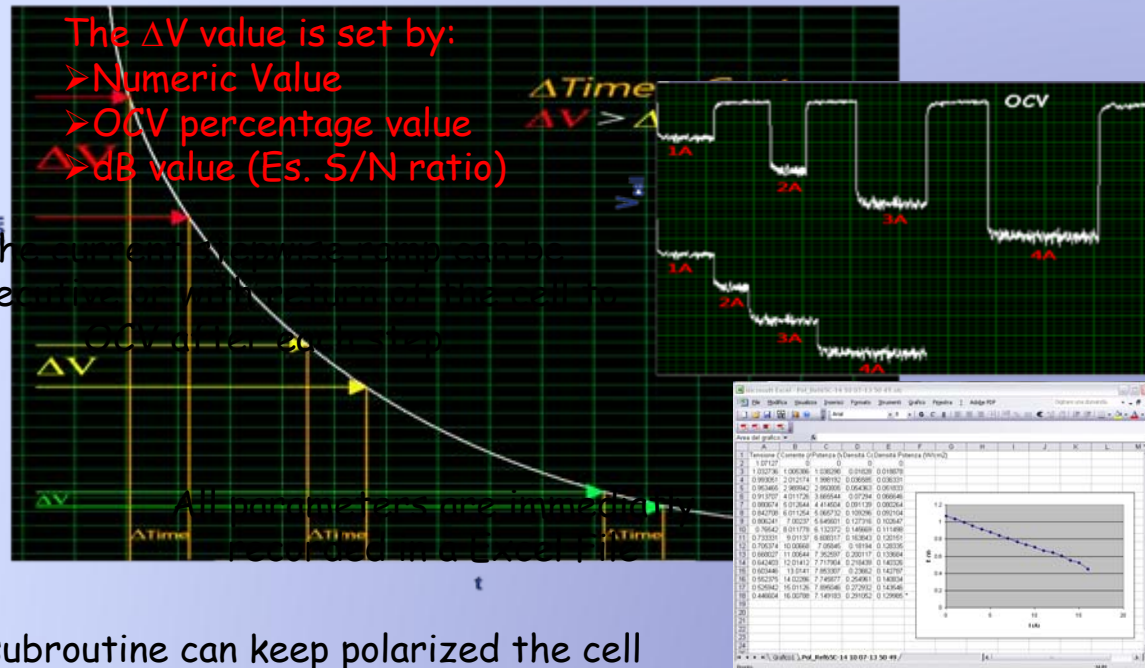
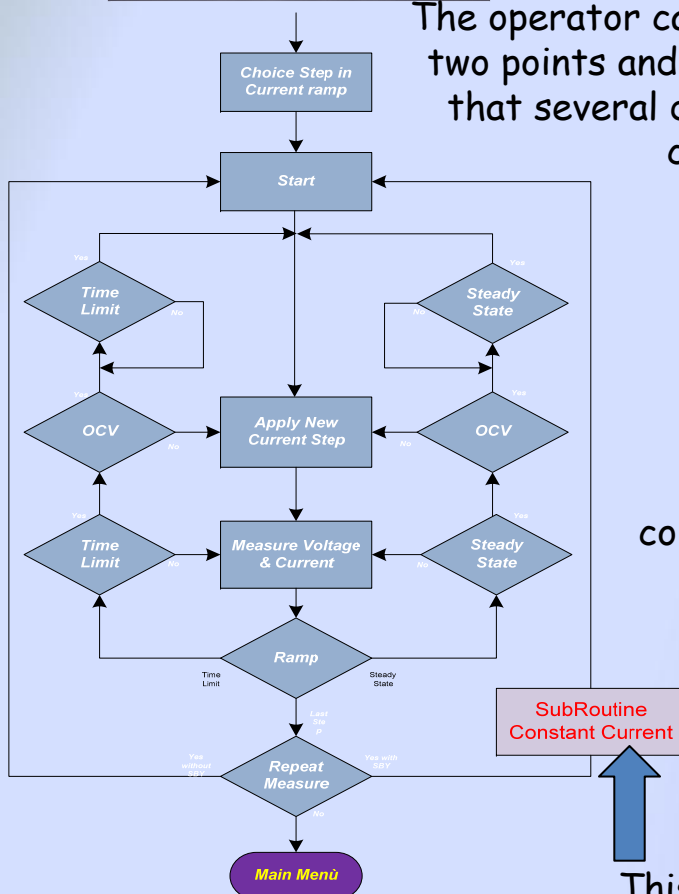
# Fuel Cell-Electrochemical Check

## Polarization Curves vs Steady State

The software applies a current stepwise. For each current step, steady state is defined by the keeping of a fixed  $\Delta V$  for a fixed time. The software continuously acquires a cell voltage value. At each instant it calculates the difference between the last value and a previous one ( $\Delta V$ )



The operator can set the interval width between the two points and can set the keeping time ( $\Delta Time$ ) so that several degrees of stability and acceptance criteria can be imposed.

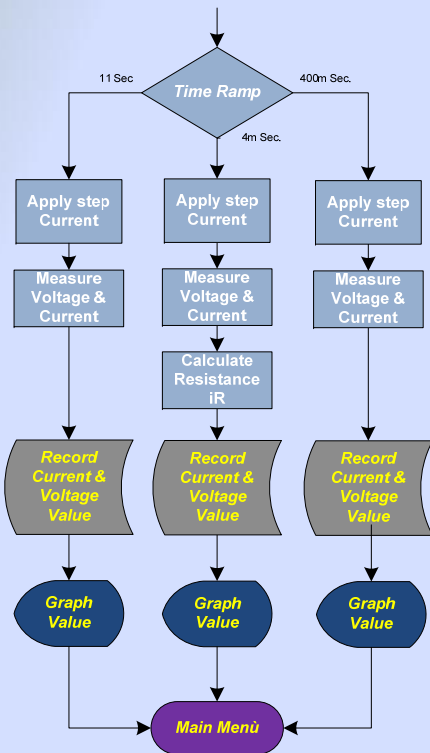
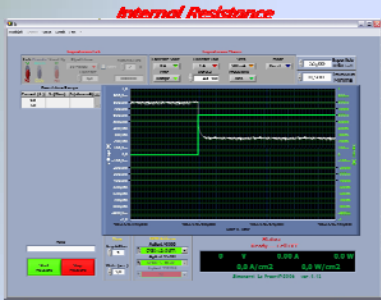
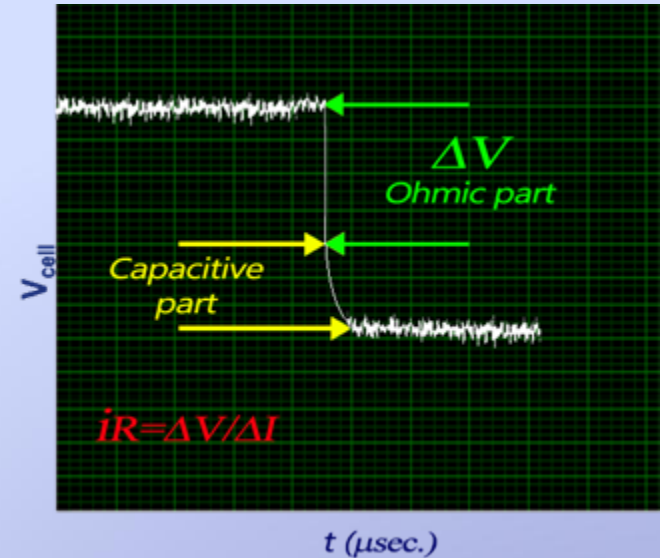


This subroutine can keep polarized the cell between a measure and the following.

# Fuel Cell-Electrochemical Check

## Internal Resistance Measurements (Ir)

The software measures internal cell resistance by "current interruption" method, that separate the contributions to fuel cell performance into ohmic and non-ohmic losses.



When a constant current load is abruptly ( $\mu\text{sec.}$ ) interrupted the resulting time dependent voltage response is representative of the resistive and capacitive behaviors of the cell components.

The voltage drop across the resistor is immediate while the voltage drop across the RC/Walburg element is time dependent.

# Fuel Cell-Electrochemical Check

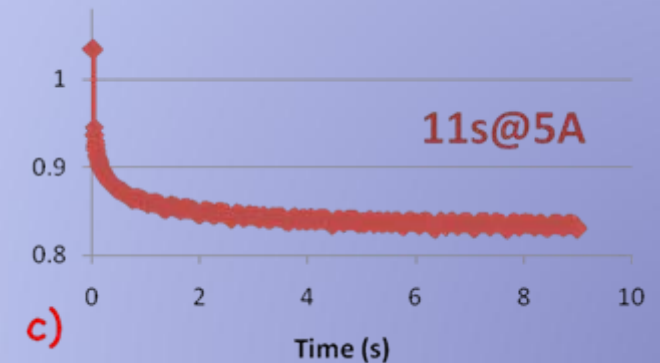
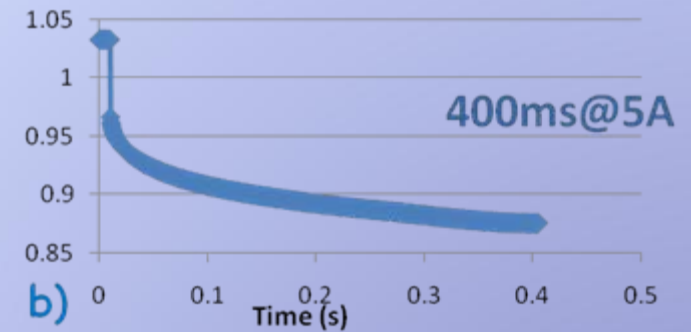
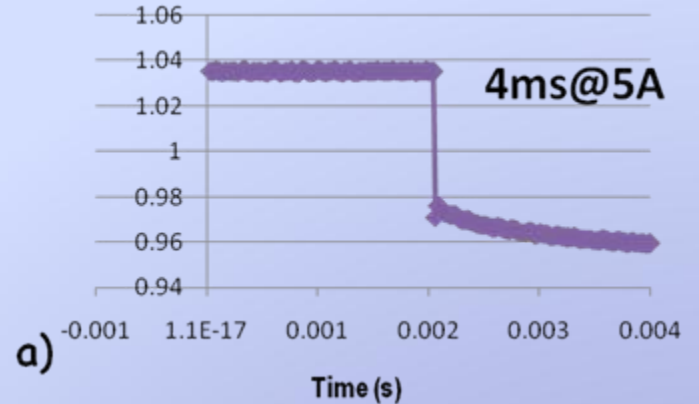
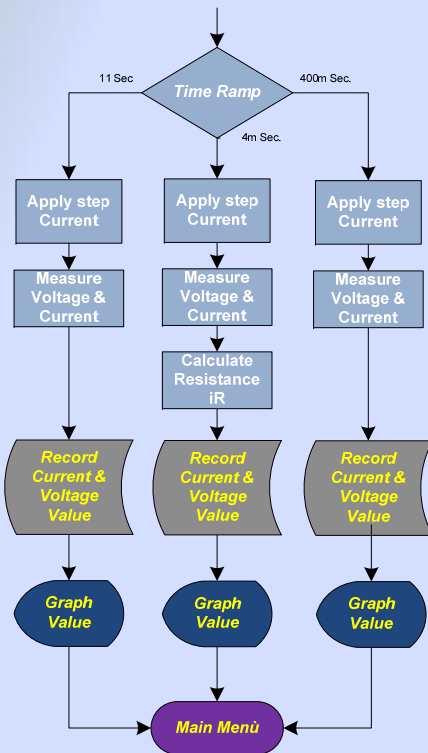
## Internal Resistance Measurements (Ir)

It's possible to carry on the measures with three different time ranges :

a) 4m s.

b) 400m s.

c) 11 s.



The voltage output of a fuel cell under current load, is less than thermodynamically predicted voltage output due to irreversible losses. More current is demanded to the cell, greater are the losses.

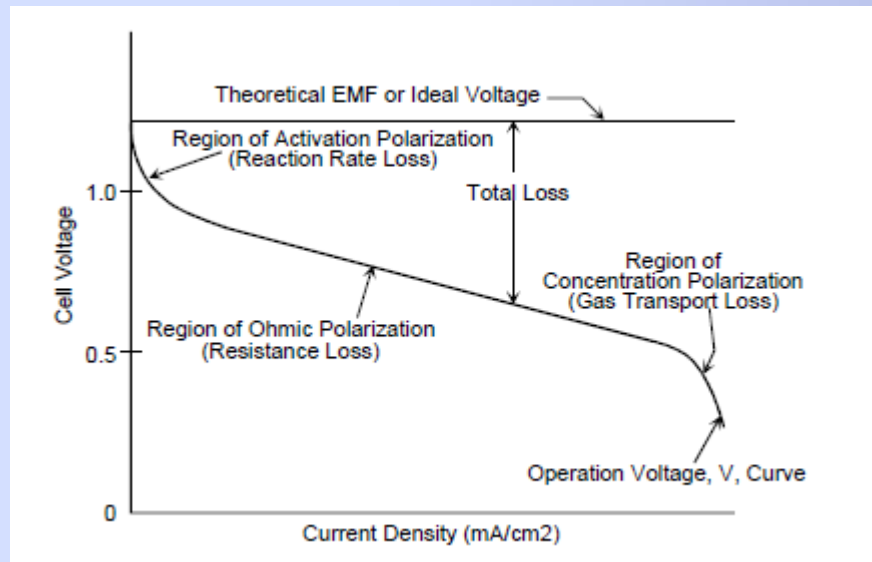
There are three major types of fuel cell losses:

- **Activation losses ( $\eta_{act}$  losses due to electrochemical reaction)**
- **Ohmic losses ( $\eta_{iR}$  losses due to ionic and electronic conduction)**
- **Concentration losses ( $\eta_{Nernst}$  losses due to mass transport).**

The real voltage output for a fuel cell ( $V_{out}$ ) can thus be written by starting with the thermodynamically predicted voltage output ( $E_{OCV}$ ) and then subtracting the voltage drops due to the various losses:

$$V_{out} = E_{OCV} - \eta_{iR} - \eta_{act} - \eta_{Nernst}$$

The  $\eta_{iR}$  is attributed to the ohmic resistance through the cell components. The  $\eta_{act}$  is due to the charge and mass transfer resistance of electrode reactions. The  $\eta_{Nernst}$  results from the Nernst potential difference between gas inlet and outlet positions during current load.

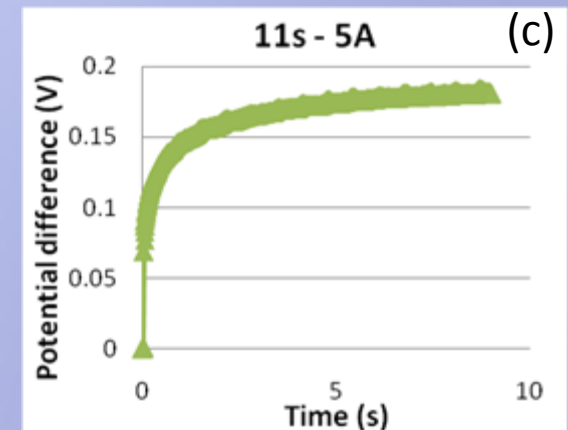
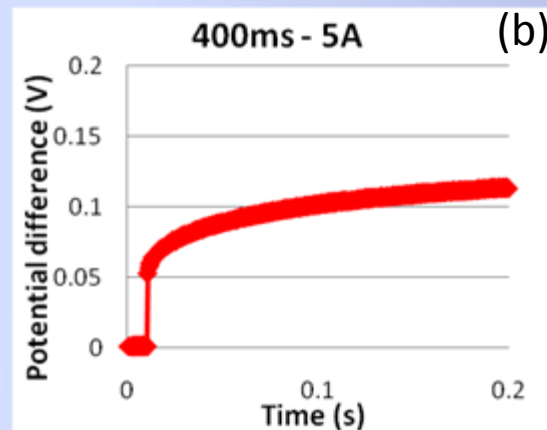
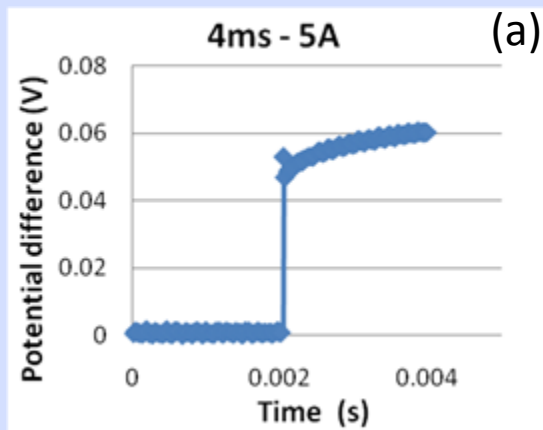


## Ideal and Actual Fuel Cell Voltage/Current Characteristic

## Three different relaxation patterns

Potential differences between open circuit cell voltage and cell voltage under current load, as a function of three different time ranges :

- the shortest time region (less than 4 ms) is due to the ohmic loss ( $\eta_{iR}$ ) and the internal resistance is obtained dividing the potential jump by the current load.
- an intermediate time region (up to 400 ms) is due to the electrode overpotential ( $\eta_{act}$ ) related to charge and mass-transfer resistance of the electrodic reactions.
- the third time region is due to the Nernst loss ( $\eta_{Nernst}$ ) related to the potential difference between gas inlet and outlet during current load.

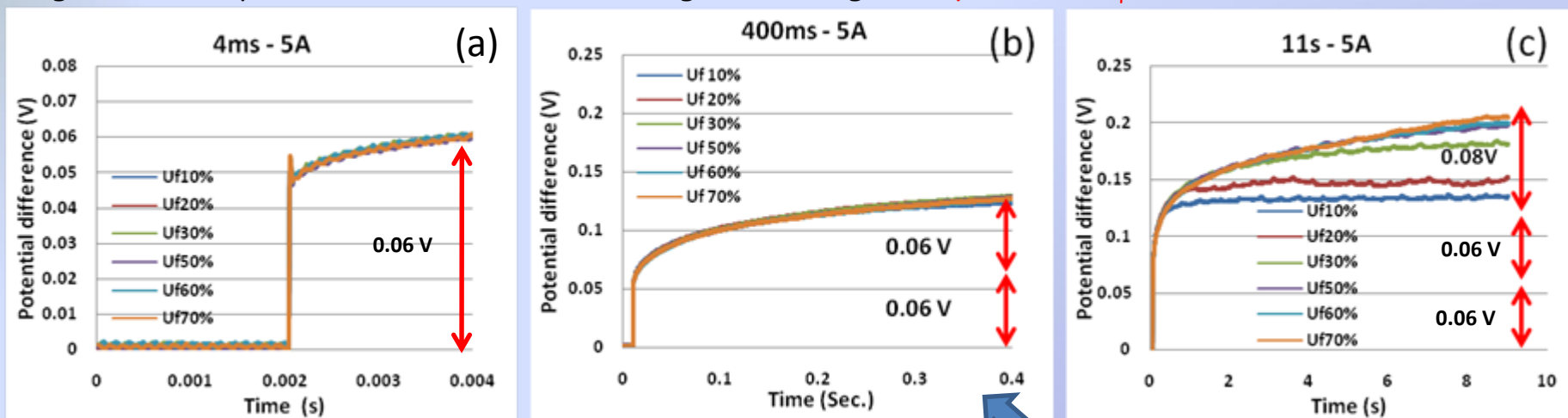


## Three different relaxation patterns as a function of different time ranges and different levels of anodic gas utilizations ( $U_f$ from 10% to 70%).

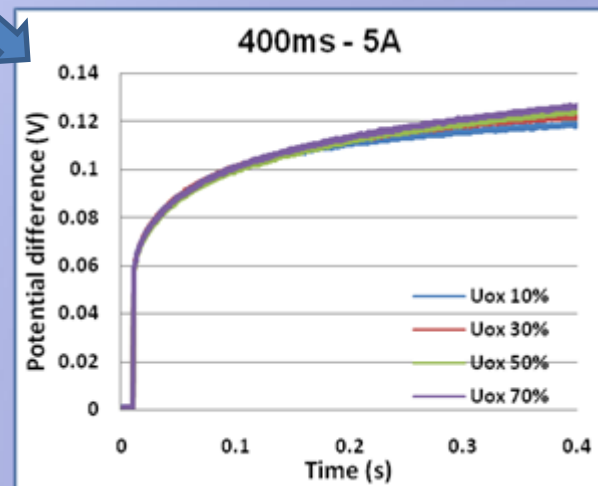
Figure (a) shows a rapid potential jump due to the ohmic loss which is independent from fuel utilization.

Figure (b) shows the intermediate time region where the potential relaxation is again not affected by fuel utilization.

Figure (c) the potential relaxation in the longer time region depends on  $U_f$ .



To understand the physical chemical phenomena related to the intermediate region, current interruption measurements were carried out keeping constant fuel gas utilization (20%) and changing oxidant gas utilization ( $U_{ox}$  10% - 70%). A comparison between plots at 400ms points out the dependency of middle region from cathodic gas composition. The potential change in this case is due to polarization at the cathodic side and the anodic contribution is very little because of the fast hydrogen oxidation kinetic.

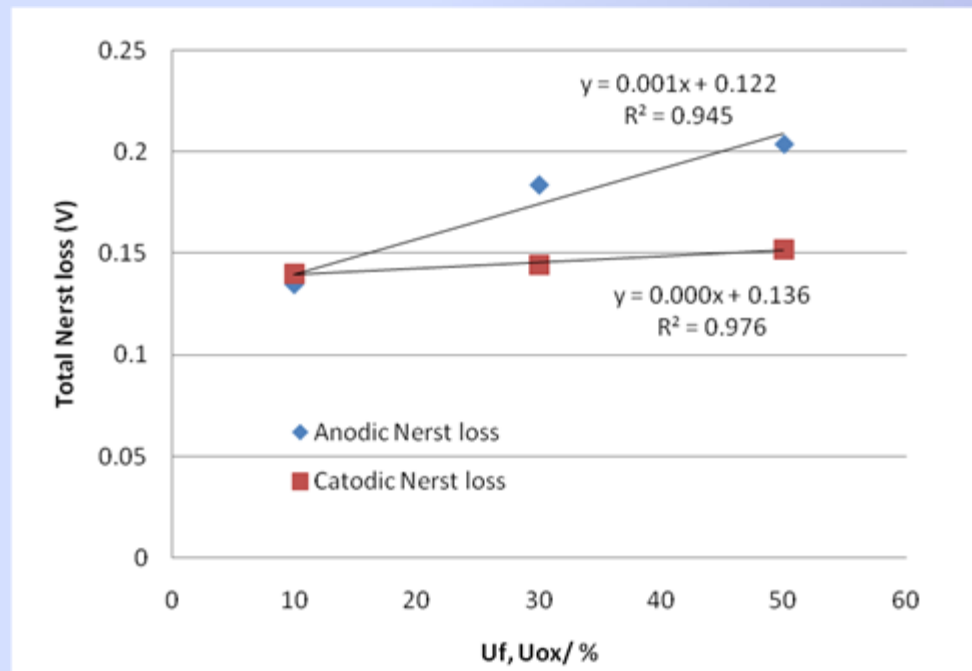


## Experimental determination of cathodic and anodic Nernst losses by current interruption measurements.

The potential difference changes at 11 s, were plotted against the anode gas utilization keeping constant cathode gas utilization and viceversa.

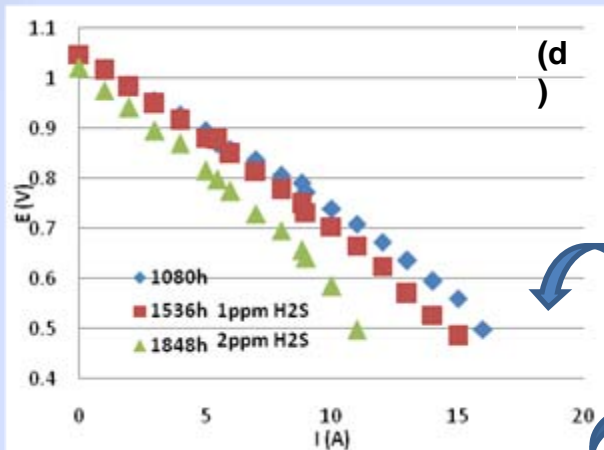
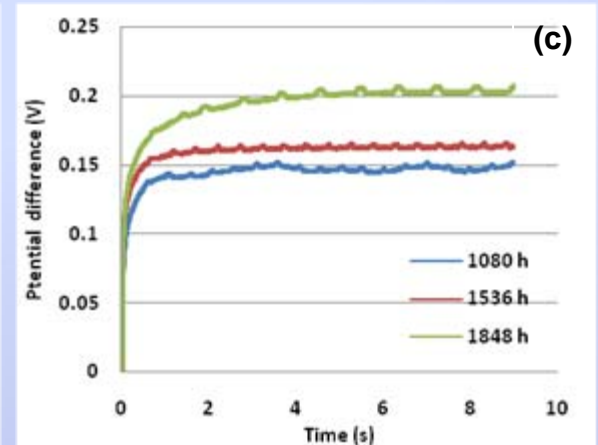
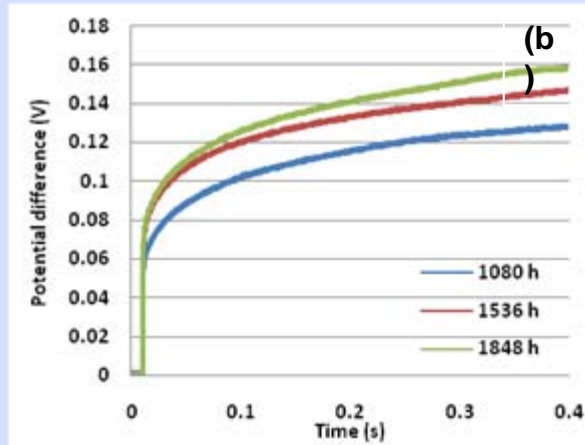
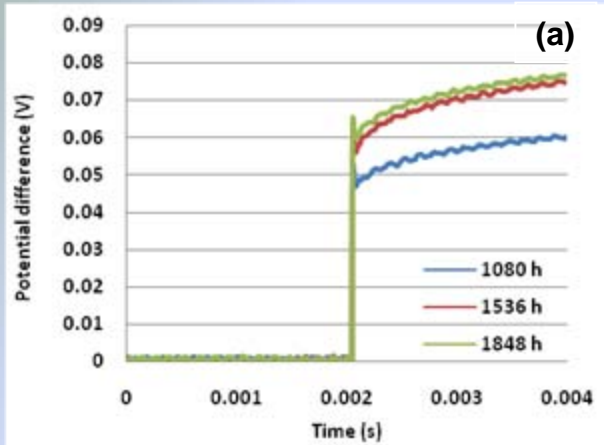
The extrapolated values to zero utilization gives an approximated value of anodic and cathodic Nernst losses.

By this plot is possible to separately establish the anodic and cathodic contribution to the total fuel cell Nernst loss. For the cell under test the values of anodic and cathodic Nernst losses are respectively 0.122 and 0.136 volts.





Traces of current interruption measurements for different time ranges at constant anodic, cathodic gas utilization at different cell lifetime and H<sub>2</sub>S poisoning: a) 4ms, b) 400 ms, c) 11 s, d) polarization curves at the same cell lifetime.



Data analysis of measurements (a,b,c) carried out at different cell lifetime give useful information on each contribution to the cell voltage losses. The  $iR$  measurements (a) carried out at 1080, 1536 (1ppm H<sub>2</sub>S) and 1848 (2ppm H<sub>2</sub>S) hours from the cell start up are shown.

The corresponding polarization curves (d) put in evidence a decrease of cell performance during the time as a consequence of H<sub>2</sub>S poisoning.

In the table the values of each voltage loss, calculated from figure a, b, c curves, were written.

$U_f, U_{ox} = \text{constant}$	1080h	1536h (1ppm H <sub>2</sub> S)	1848h (2ppm H <sub>2</sub> S)
$\eta_{iR}$	60 mV	76 mV	76 mV
$\eta_{act}$	67 mV (127-60)	70 mV (146-76)	80 mV (156-76)
$\eta_{Nernst}$	21 mV (148-67-60)	17 mV (163-70-76)	47 mV (203-80-76)

The cell voltage loss due to Nernst overpotential at 1848 h is very high and probably is the main cause of cell performance decrease.

# Conclusions

1

- The current interruption / potential relaxation method was applied to a Molten Carbonate Fuel Cell (MCFC) as a suitable technique to understand cell voltage losses.

2

- The single cell showed three different relaxation patterns of time regions during the potential relaxation from open circuit to steady state polarization conditions;
- ohmic losses ( $\eta_{iR}$ ) due to ionic and electronic conduction, activation losses ( $\eta_{act}$ ) due to electrochemical reaction and concentration losses ( $\eta_{Nernst}$ ) due to mass transport, were separated and determined.

3

- Two different software were compiled by LABVIEW language, in ENEA laboratories:
- **FC-TF** (Fuel Cell Test Facility) to manage the MCFC facility,
- **FC-EC** (Fuel Cell Electrochemical Check) to carry out electrochemical measurements.

4

- Current interruption measurements were automatically carried out on a single 100 cm<sup>2</sup> cell during 2000 hours of cell lifetime. The ohmic losses, activation loss ( $\eta_{act}$ ) and concentration loss ( $\eta_{Nernst}$ ) were separated and determined in three different cell lifetimes before and after anode poisoning with 1 and 2 ppm of H<sub>2</sub>S. Nernst loss was identified as the major responsible of cell performance decay.

## Biography

- [1] J. Larminie and A. Dicks, *Fuel cell systems explained*, John Wiley & Sons Ltd., Chichester (2000)]
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Thank You  
for your  
attention