STATE OF ART AND PERSPECTIVES AT INCDIE ICPE-CA IN THE FIELD OF MATERIALS FOR HYDROGEN STORAGE AND FUEL CELLS TECHNOLOGY

ROMANIA

EXPLORATORY WORKSHOP 2008

ENERGY

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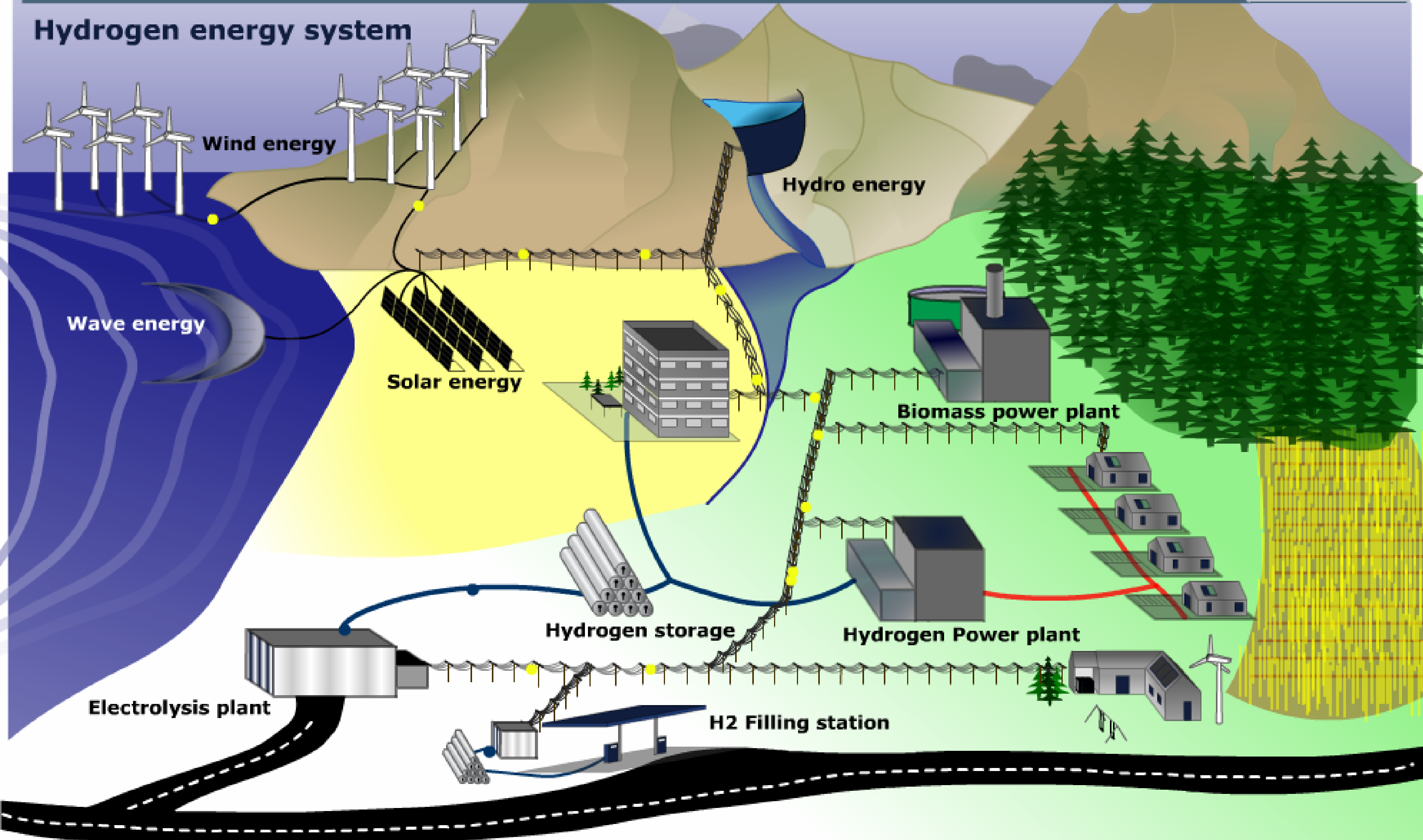
Hydrogen energy system



Fuel Cell Drivers

- **The treat of global warming**
- **Pollution legislation**
- **Demand for clean energy in the developing world**
- **Increasing awareness for energy security**
- **Fuel cells systems are able to achieve in small units (100 kW to 500 kW) electrical efficiencies approaching 50% while internal combustion only 30% to 40%**
- **Fuel cells are environmentally more benign than combustion engines with low toxic emissions, low noise level and clean waste-water**
- **Fuel flexibility: Fuel cells systems can operate on hydrogen, NG and biogas**

Fuel Cell Drivers

EUROPEAN PARLIAMENT – Written Declaration @ 12.02.2007

Calls upon the EU Institution to:

- **Pursue a 20% increase in energy efficiency by 2020**
- **Reduce greenhouse gas emmision by 30% by 2020 compared to 1990**
- **Produce 33% of electricity and 25% of overal energy from renewable energy sources by 2020**
- **Instutute hydrogen and fuel cell storage technology, and other storage technologies, for portable, stationary and transport uses by 2025**
- **Establishing a descentralised hydrogen infrastructure by 2025 in all EU Member States**
- **Make power grids smart and independent by 2025 so that the regions, cities, SMEs and citizens can produce and share energy**

ICPE-CA

Benefits of Fuel Cells

- **Modularity**
- **Dynamic response**
- **Reduced transmission losses**
- **Reduction of required grid capacity**

Cogeneration Applications

Domestic micro-CHP Systems up to 10 kW

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Currently Applications of Fuel Cells in the World

- **Power for portable electronic devices (5–50 W)**
- **Power for remote telecommunications applications (100W–1 kW)**
- **Power for construction and outdoor recreation uses (1–3kW)**
- **Auxiliary power units for cars and trucks, and motive power for scooters (3–5 kW)**
- **Stationary power generation (1 kW–50 MW)**
- **Automotive: electric passenger car, utility vehicle, and bus power systems (20 kW–250 kW)**

Barriers of Fuel Cells Development in Romania

- **Cost is the major market entry barrier**
- **Current distribution grids are not designed for large scale integration of distributed power generators**
- **Professional training of specialists**
- **Dissemination of new heat & power technologies**

How to overcome the barriers?

- **Long term development of the energy strategy framework in terms of distributed energy integration**
- **Materials research for reducing the costs**
- **Specialists training**

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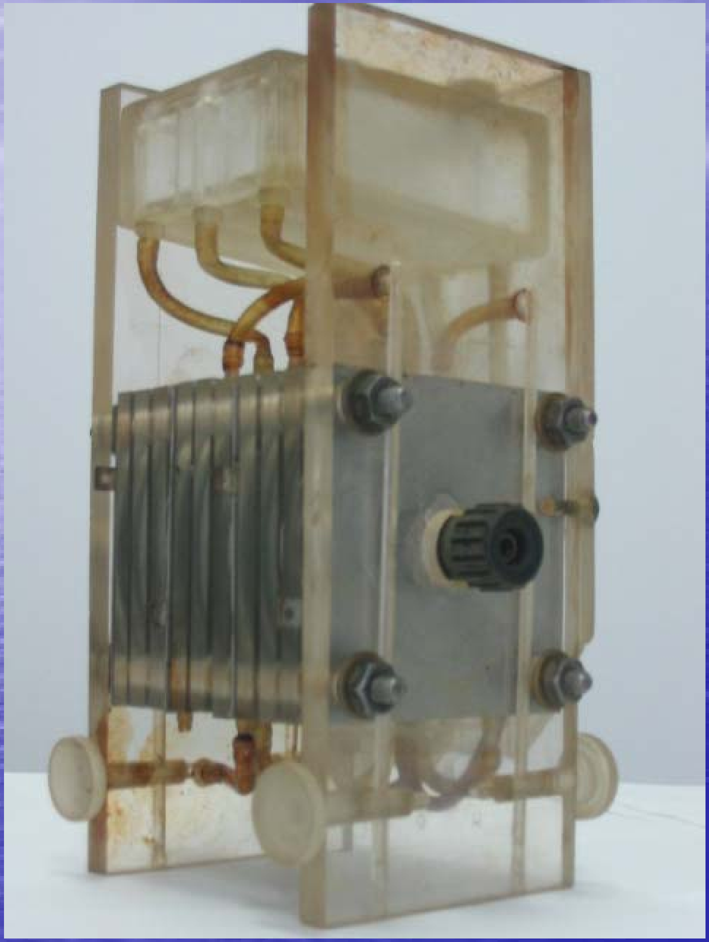
Romanian Perspectives for FC Tech – Research Trends

Membranes for PEMFCs & SOFCs	• Identify ionomers & fabricate membranes • Test and characterize membranes
Electrodes for PEMFCs & SOFCs	• Improve catalysts & catalyst supports • Optimize electrode design & assembly
MEAs for PEMFCs & SOFCs	• Integrate components & expand operating range • Test, analyze & characterize MEAs
GDLs for PEMFCs	• Improve GDL performance & durability • Develop testing protocols and characterization methods
Bipolar plates for PEMFCs	• Improve performance & durability • Decrease cost
Seals for PEMFCs & SOFCs	• Improve durability & performance
Fuel Cells Manufacturing, Investigation and Integration	• Mass production techniques; Develop testing protocols • Investigate impact of impurities on fuel cell performance • Controls & integration with conventional equipment

Romanian State of Art in the Fuel Cell Topic



First model of Zn/Air fuel cell ICPE (1970)

Authors:

Gheorghe Balasescu

Mihai Brehoi

Floarea Stavrica

Romanian State of Art in the Fuel Cell Topic

REPUBLICA SOCIALISTĂ ROMÂNIA
CONSILIUL NAŢIONAL PENTRU ŞTIINŢĂ ŞI TEHNOLOGIE
OFICIUL DE STAT PENTRU INVENŢII ŞI MĂRCI

Certificat de Inventator

Nr. 61918

acordat autorilor chim.GHEORGHE BALASESCU, MIHAI BREHOI şi FLOAREA STAVRICA din Bucureşti, Republica Socialistă România

pentru invenţia cu titlul "Pilă de combustie metal/aer"

conform descrierii şi desenelor alăturate, formind obiectul cererii de brevet de invenţie nr. 82524 din 12.06.1975, ora 14^{17}
cu prioritate de la 12.06.1975
pentru care s-a acordat titularului INSTITUTUL DE CERCETARI PENTRU INDUSTRIA ELECTROTEHNICA din Bucureşti, Republica Socialistă România
brevetul de invenţie nr. 61918 din 25.12.1975

Prin acordarea certificatului de inventator se recunoaşte inventatorului calitatea de autor al invenţiei cu toate drepturile ce decurg din această calitate, în baza legii nr. 62/1974.

DIRECTOR,

REPUBLICA SOCIALISTĂ ROMÂNIA
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brevetul de invenţie nr. 61878 din 25 decembrie 1975

Prin acordarea certificatului de inventator se recunoaşte inventatorului calitatea de autor al invenţiei cu toate drepturile ce decurg din această calitate, în baza legii nr. 62/1974.

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cu prioritate de la 12.06.1975
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brevetul de invenţie nr. 66376 din 25 decembrie 1975.

Prin acordarea certificatului de inventator se recunoaşte inventatorului calitatea de autor al invenţiei cu toate drepturile ce decurg din această calitate, în baza legii nr. 62/1974.

DIRECTOR,

“Pila de combustie metal/aer”

“Electrod anodic pentru pile de combustie Zn/aer”

“Electrod catodic de difuzie pentru pile de combustie metal/aer”

Romanian State of Art in the Fuel Cell Topic

Few of the present involved projects at INCDIE ICPE-CA in hydrogen and fuel cells related technologies are:

- **CEEX 88 / 2005 - Low cost alternative multifunctional materials for high temperature Polymer Electrolyte Fuel Cells; Project Director: G.A.Rimbu, 2005-2008, Value: 450000 EURO**
- **CEEX 195/2006 - PV/FC hybrid system for energetic autonomy; Project Director: G.A.Rimbu, 2006-2008, Value: 450000 EURO**
- **CEEX 760/2006 - Fuel cell system for direct bio-alcohol electrooxidation; Project Director: G.A.Rimbu, 2006-2008, Value: 450000 EURO;**
- **PNII-CNMP- 21-034/2007 - 5 kW Fuel Cells Integrated Energy System; Project Director: G.A.Rimbu, 2007 – 2010, Value: 600000 EURO**
- **PN 2 – C 71-116, Intelligent functional micro / nanomaterials; Project Director: M.Lucaci, 2007-2009, Value: 600000 EURO**

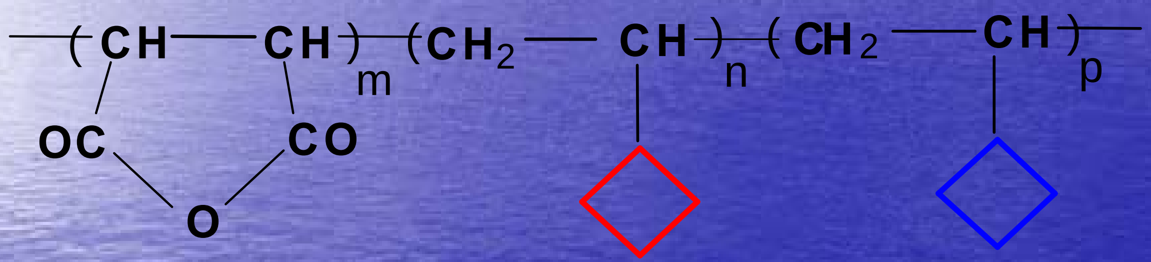
Romanian State of Art in the Fuel Cell Topic

- **PNII-CNCSIS – 222/2007 - New nanostructured Materials for Hydrogen Storage; Project Director: G.A.Rimbu, 2007 – 2010, Value: 275000 EURO;**
- **PN 06300201 - Components development for low temperature direct alcohol fuel cells (DAFC) and high temperature solide oxide fuel cells (SOFC), for applications in generating electrical power and didactic & demostrative kits; Project Director: G.A.Rimbu, 2006 – 2008, Value: 200000 EURO**
- **CEEX – 86 (4213)/2006 – Nanocristaline materials with high performance in hydrogen storage, Project Director: M.Lucaci, 2006 – 2008, Value: 450000 EURO**
- **CEEX 708-1 (7019)/2006 – Hydrogen storage materials to be used in ultraclean hydrogen thermal compressor, for fuel cells and hybride vehicles applications; Project Partner Coordinator: E.Enescu, Value: 60000 EURO**
- **PN II - 21-023 (7021)/2007 – Implementation clean energetic technologies by developing a hydrogen adsorbing metal alloys based thermal engine; Project Partner Coordinator: E.Enescu, Value: 80.000 EURO**
- **CEEX - 86/2006, High performant nanocristaline materials for hydrogen storage; Project Director: M.Lucaci, 2006-2008, Value: 450000 EURO**

DAFC & PEMFC TECHNOLOGY

Research status in FC Technology at INCDIE ICPE-CA

- **New thermal stable and low-cost alternative proton conducting electrolytes for "high temperature" (>180oC) PEMFC**



monomer activ hidrofil hidrofob

hydrophilic: vinyl acetate (VA)

hydrophobic: styrene (St), acrylonitrile (AN), metil metacrilate (MAM)

Copolymers of maleic anhydride for membrane in DAFC/PEMFC

Research status in FC Technology at INCDIE ICPE-CA

- **Alternative an low-cost catalysts:**
  - **high active area colloids: supported Pt and Pt alloys (Pt-Ru/Pt-Ru-Se)**
  - **non noble and alcohol tolerant catalysts : Ru-Se / Rh-Ru-Se**
  - **emerging ORR catalysts: Pt-Fe / Pt-Cr**

- **Low-cost alternative bipolar plates**
  - **graphite composites based bipolar plates**
  - **metallic bipolar plates**
  - **expanded graphite based bipolar plates**

- **Thermally and chemically stable polymer / carbon gaskets for "high temperature" (>180oC) PEMFC**
  - **Roseal type silicone ruber for 200oC**
  - **Roseal type politetrafluoretylen rubber for 200oC**
  - **Roseal type expanded politetrafluoretylen for 240oC**
  - **Roseal type expanded graphite for 300oC**

- **Optimized electrodes and gas diffusion layers**

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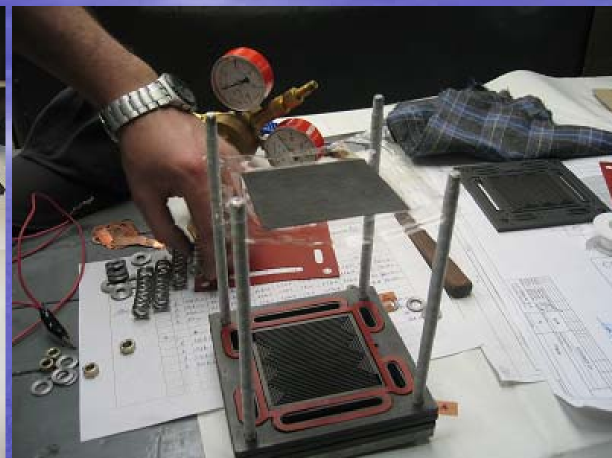
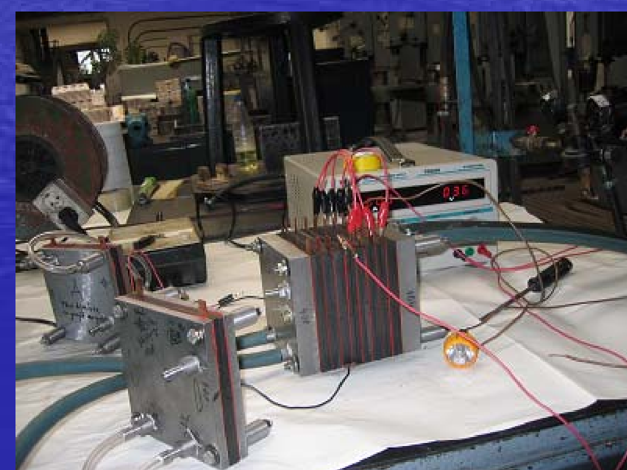
Research status in FC Technology at INCDIE ICPE-CA






Research Status at INCDIE ICPE-CA





SOFC TECHNOLOGY

Research status in FC Technology at INCDIE ICPE-CA

Ceramic Materials → Fuel Cell components → Fuel Cell Stack

Targeted activities

- **Developing SOFC components (electrolyte, electrodes, supports and interconnectors) starting from basic materials**
- **Prototyping and testing SOFC stack**

Research status in FC Technology at INCDIE ICPE-CA

SOLID ELECTROLIT MATERIALS - YSZ, Ba/Sr Cerats

- **High densification grade: Pa - max. 1%**
- **Stabilized phases structure**
- **Thermal expansion coefficient: $\alpha t = 9...11x10^{-6}/°C$**
- **Ionic / Protonic type electrical conductivity: σ (700-1000°C) = $0,2..2.10^{2-}$ S/cm**
- **Activation energy: Ea= 1,1-1,2 eV**
- **Chemical compatibility and good joint with cathode / anode**

ELECTRODE MATERIALS -

cathode: $LaMnO_3$- doped with Sr, Ca, Cr
anode: $LaCoO_3$- doped with Sr, Ca; ZrO_2/NiO

- **Apparent porosity: Pa = 10-25%**
- **Stabilized phases structure of perovskit / fluorite**
- **Thermal expansion coefficient: $\alpha_t = 10...11x10^{-6}/°C$**
- **Electronic type electrical conductivity: σ(700-1000°C) = 82...256 S/cm (cathode)**
  0.8...10 S/cm (anode)
- **Activation energy: Ea = 0,3...0,9eV**

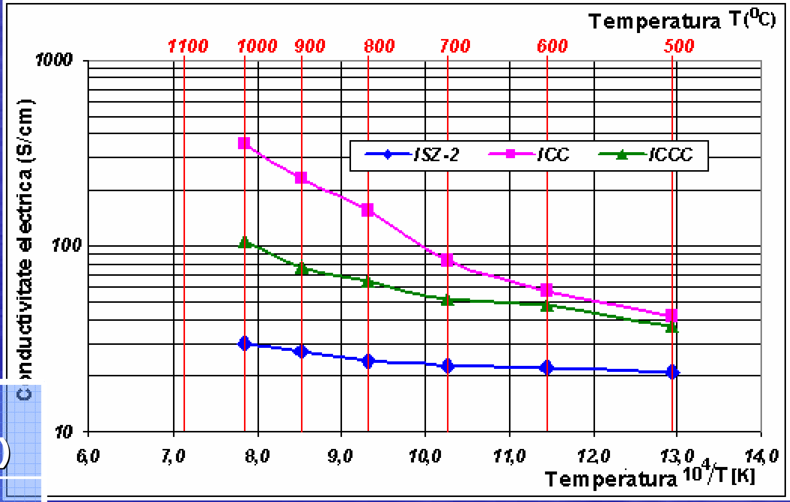
Research status in FC Technology at INCDIE ICPE-CA

INTERCONECTORS MATERIALS - $LaCrO_3$-doped cu Sr,Ca

- **Apparent porosity: *Pa = max. 1%***
- **Stabilized phases structure of *perovskit***
- **Electronic type electrical conductivity: *σ(700 -1000°C)=107..210 S/cm***
- **Activation energy Ea= 0.7 - 0.9 eV**
- **Chemical stability to doping with Sr and Zn**

Symbol Material	Electrical conductivity (S/cm)					
	500°C	600°C	700°C	800°C	900°C	1000° C
ISZ-2	21	22	22,7	23,9	26,8	30
ICC	42	57	83	155	229	357
ICCC	37	48	52	65	78	107

Material	Sintering shrinkage (%)	Apparent density (g/cm^3)	Apparent porosity (%)
ISZ-2	8,2	3,86	40,74
ICC	14,8	6,02	0,87
ICCC	17,3	6,17	0



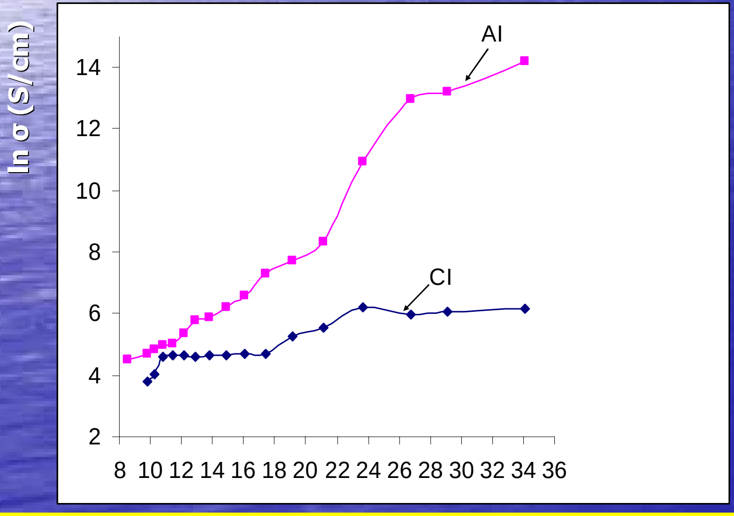
Conductivity vs. temperature for the investigated materials

Research status in FC Technology at INCDIE ICPE-CA

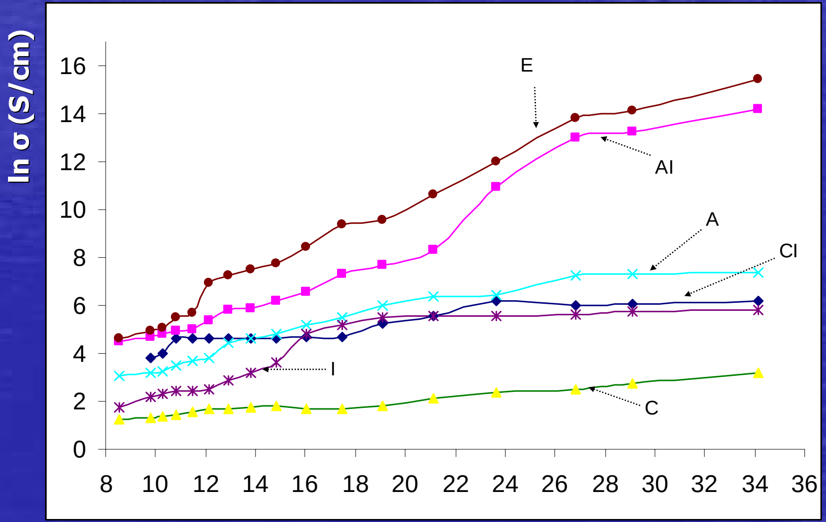
POROUS SUPPORT MATERIALS

- **anode support: 10% NiO, 60% stabilized ZrO2 in thernary system with 10 mol% CaO + 10 mol% CeO2 and 30% stabilized ZrO2 with 8 mol% Y2O3**
- **cathode support : CeO2 bazed material with 2 mol% Ta_2O_5**

- **Apparent porosity: Pa = 40-60%**
- **Electrical bulk rezistivity: ρv(20˚C)= 10^{13}Ωcm**
- **Chemical and thermal compatibility**



Conductivity vs. temperature for – support chatode material (CI) and support anode materials (AI)



Conductivity vs. temperature for all components investigated in SOFC model structure.

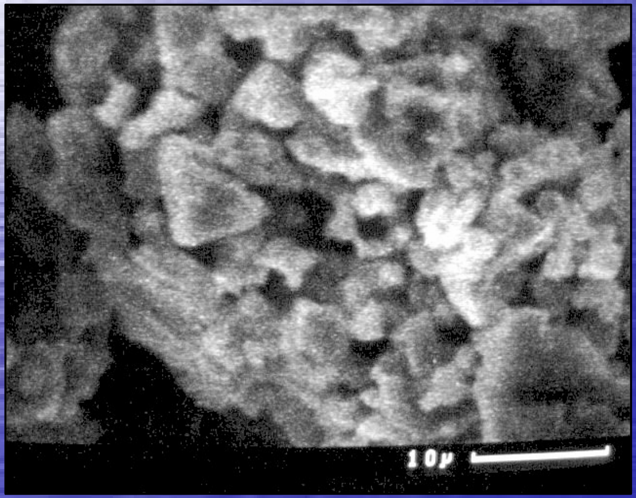
ICPE CA

HYDROGEN STORAGE

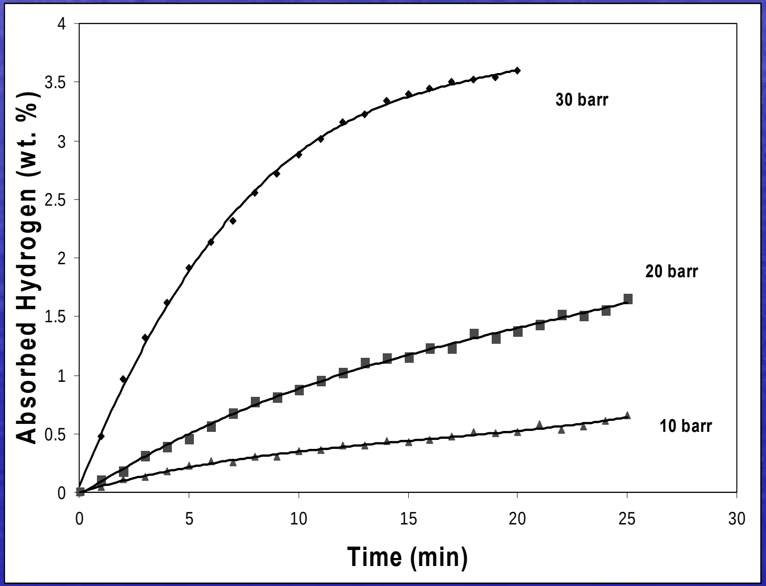
Research status in FC Technology at INCDIE ICPE-CA

Problems addressed: **advanced hydrogen storage materials with high hydrogen storage capacity and fast kinetics**

- **Fe-Ti and Zr-Ni based intermetallic compounds**
- **La, Mg and Al based intermetallic compounds**
- **Nanocristaline hydrides of intermetallic compounds**



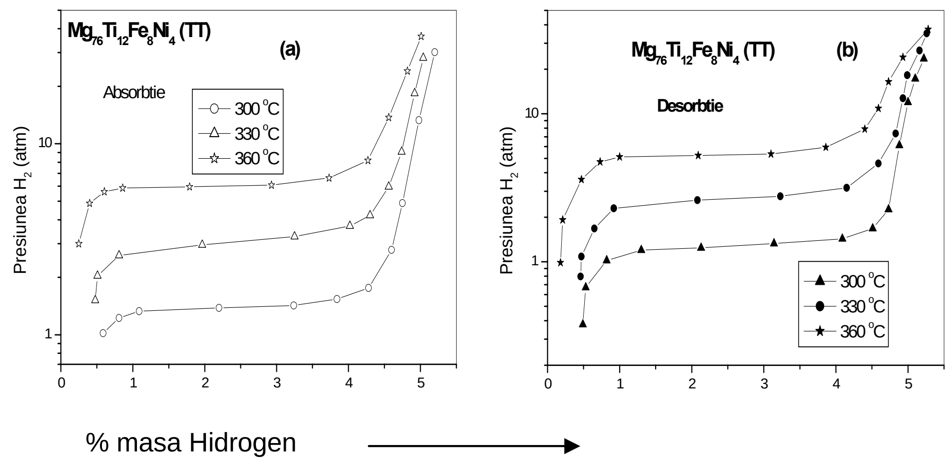
Mg_2Ni alloy



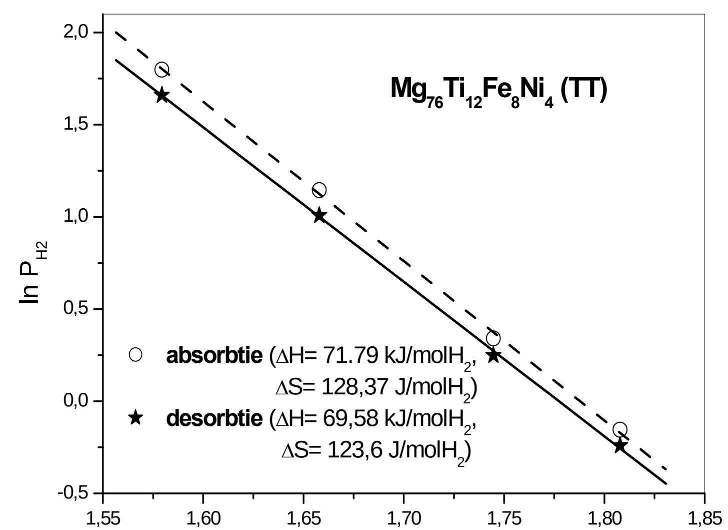
Hydrogen absorption at 250 °C and different H_2 pressure vs. time

REZULTATE RECENTE $Mg_{76}Ti_{12}Fe_{(12-x)}Ni_x$ x = 4, 8

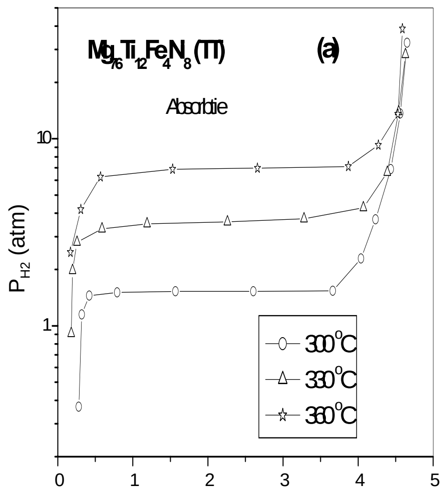
X= 4

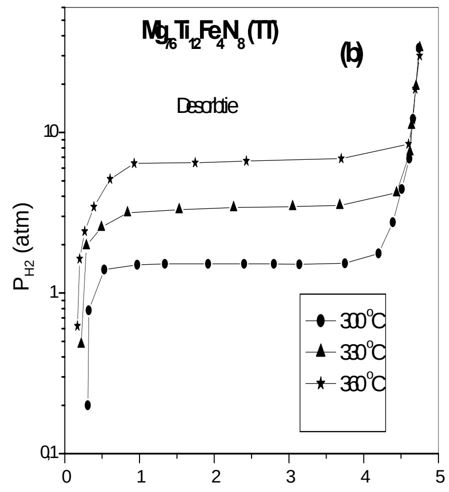


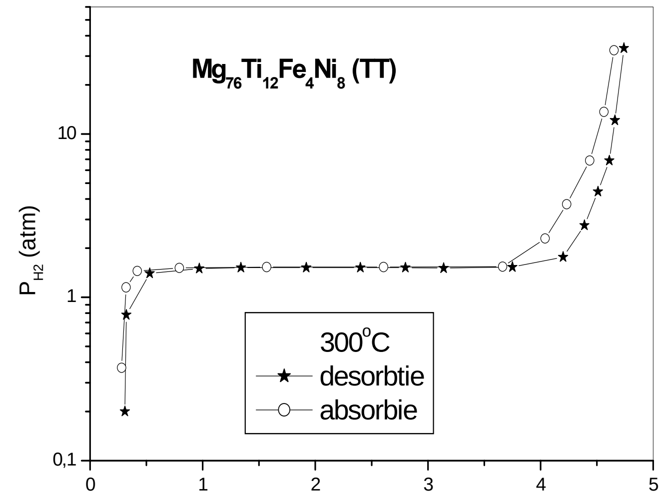
Curba	P_{H2} (atm)	Δ P_{H2} (atm)	Δ %H	$t_{1/2}$(s)
absorbtie	5.6	1.2	4.33	66
desorbtie	0,67	0.67	3	270

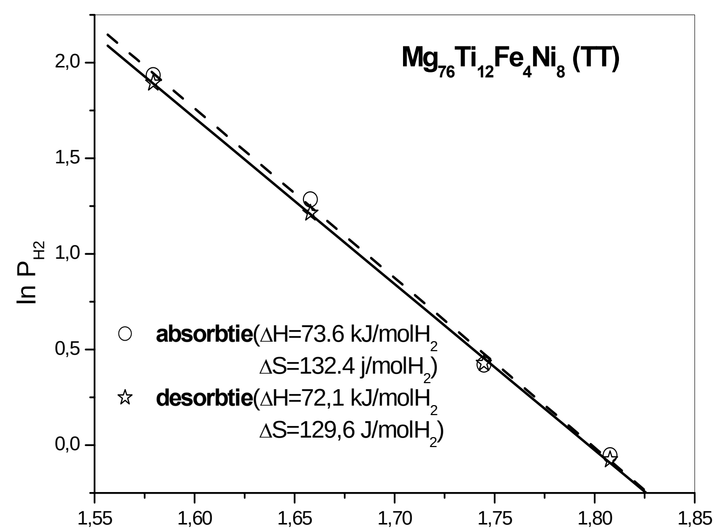


X= 8







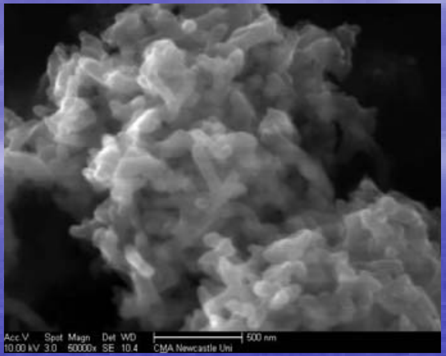


Procesul	T (ºC)	Δ P_{H2} (atm)	Δ %H	$t_{1/2}$ (s)	<$t_{1/2}$> (s)
Absorbtie	300	2.84	1.05	45	54
	330	2.83	1.01	48	
	360	3.28	1.1	71	
Desorbtie	300	0.73	0.26	90	74
	330	1.3	0.48	82	
	360	3.25	1.43	50	

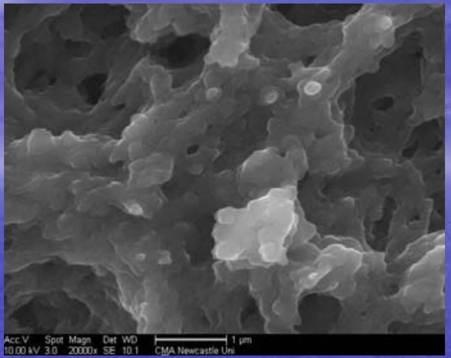
Material	T, ^{o}C	P, atm	H_2 ,%masa	V, min
$Mg_{76}Ti_{12}Fe_4Ni_8$	300 - 360	1,2 - 6	4,75	1,36 6,15
$Mg_{76}Ti_{12}Fe_8Ni_4$	300 - 360	1,3 – 5,7	5,33	1,1 3
Mg-5%Ni	230-370	1,4 - 4	6	90

Research status in FC Technology at INCDIE ICPE-CA

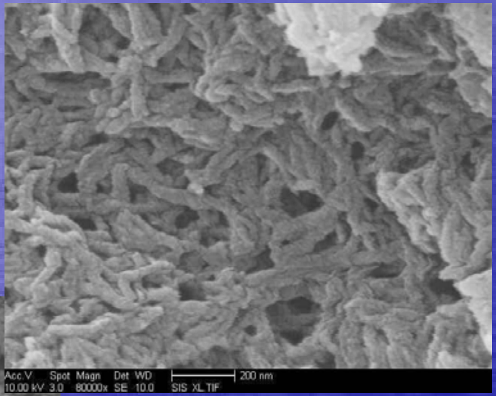
Investigation of hydrogen storage in high surface area carbons and organic conducting polymers in their semiconducting and metallic forms



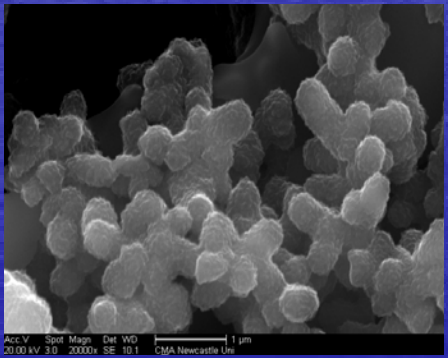
Self Assembly Polymerization



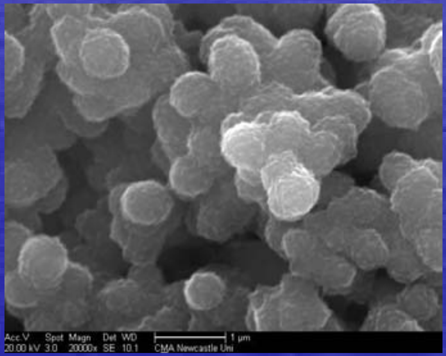
CV Deposition



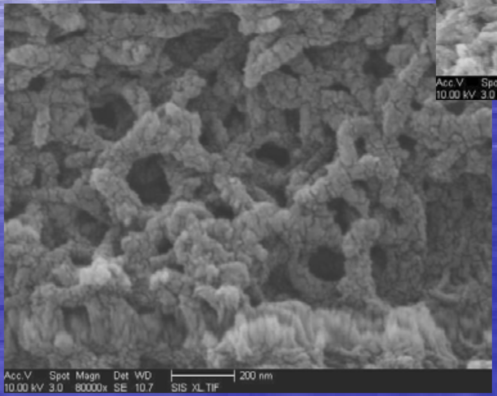
Polymer based nanofibrous network



Pulse Galvanostatic Deposition



Galvanostatic Deposition



Carbon based nanofibrous network

Fuel Cell Technology Standardization

The Institute for Energy (IE) of the European Commission's Joint Research Centre (JRC) in Petten, the Netherlands has designed and built a state-of-the-art fuel cell testing facility to support and facilitate the development and harmonisation of fuel cell testing procedures in transport and stationary applications in the EU

(1) Baseline Performance Characterisation

- **Fuel cell leak-tight testing for operational safety investigations**
- **Operating fuel cells on various simulated hydrogen fuels (with deliberate controlled additions of fuel impurities)**
- **Operating fuel cells on various fuel/ oxidant relative humidity**
- **Dynamic changes in anode/cathode stoichiometry and system pressure caused by ambient pressure variations (simulating stack altitude testing)**
- **Compositional and emissions analysis of the in- and outlets of the fuel, oxidant, and water streams**

Fuel Cell Technology Standardization

(2) Efficiency Characterisation

- **Fuel cell testing in load-following mode for performance characterisation in terms of power density, electrical and thermal efficiency**
- **Performance testing of fuel cell power systems in a grid-connected configuration**
- **Evaluating heat-recovery capabilities of fuel cell systems under various thermal load scenarios in steady-state and transient conditions**

Fuel Cell Technology Standardization

(3) Characterisation of performance under simulated environments

- Testing fuel cell systems under simulated environmental conditions including temperature (-40 to 60 ºC) and relative humidity (up to 95 %)

- Simulating shock and vibration with six degrees of freedom at frequencies up to 250 Hz, and on-line evaluation of their effects on fuel cell performance

Fuel Cell Technology Standardization

(4) Expansion possibilities

- Application of *in-situ* AC electrical loads to identify and analyse cell performance degradation (impedance measurements) in an on-line grid connected configuration

- On-line evaluation of fuel processor performance in terms of fuel conversion efficiency and emissions

- Continuous monitoring of thermodynamic balances of an entire energy conversion chain consisting of reformer, fuel cell and grid inverter

Fuel Cell Technology Standardization

IEC/TS 62282-1 Ed. / 2005-03-22
Fuel cell technologies - Part 1: Terminology

IEC 62282-2 Ed. 1.1 / 2007-03-29
Fuel cell technologies - Part 2: Fuel cell modules

IEC 62282-3-1 Ed. / 2007-04-24
Fuel cell technologies - Part 3-1: Stationary fuel cell power systems – Safety

IEC 62282-3-2 Ed. / 2006-03-21
Fuel cell technologies - Part 3-2: Stationary fuel cell power systems - Performance test methods

IEC 62282-5-1 Ed. / 2007-02-23
Fuel cell technologies - Part 5-1: Portable fuel cell power systems - Safety

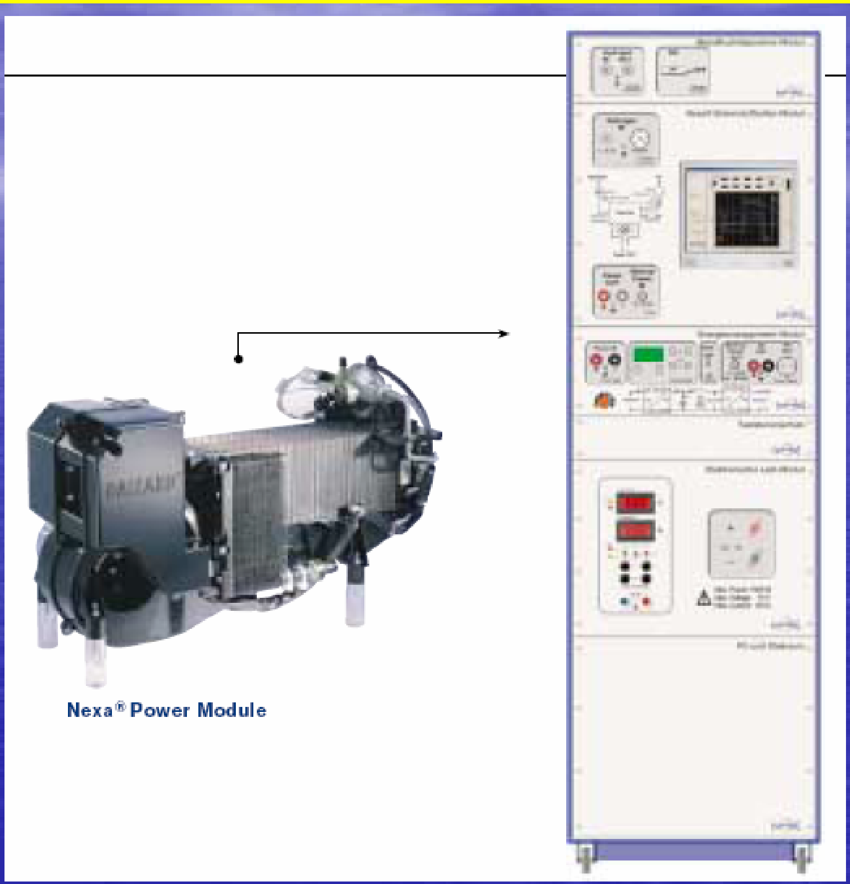
IEC/PAS 62282-6-1 / 2006-02-23
Fuel cell technologies - Part 6-1: Micro fuel cell power systems – Safety

IEC/PAS 62282-6-1 / 2007-04-18
Corrigendum 1 - Fuel cell technologies - Part 6-1: Micro fuel cell power systems - Safety

Research facilities at INCDIE ICPE-CA

MTS 150 Manual Fuel Cell Test Station

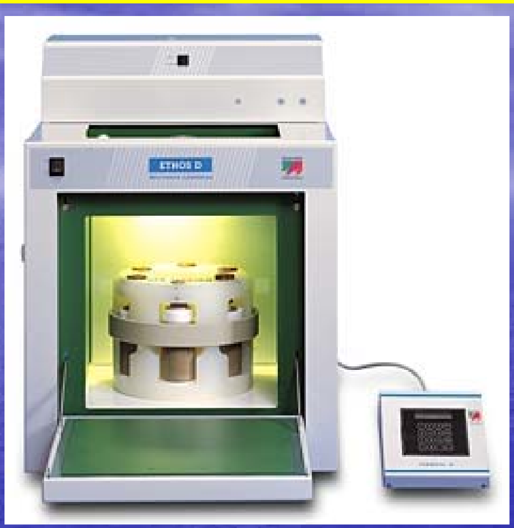
VoltaLab Potentiostat / Galvanostat



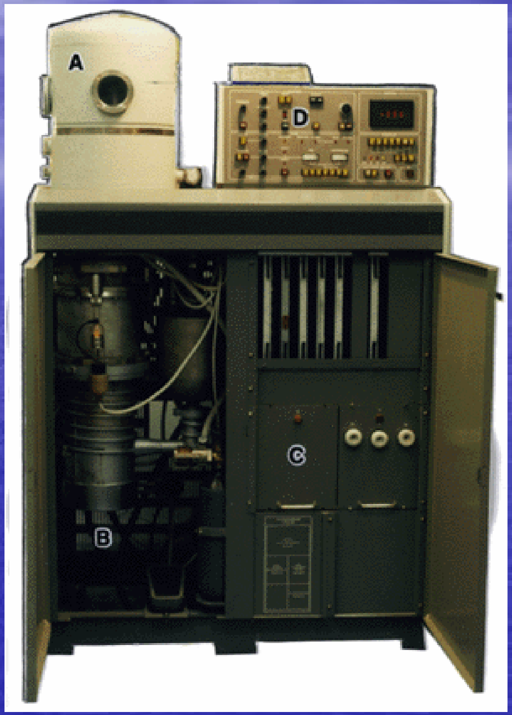
1.2 kW Fuel Cell Nexa Power System

Research facilities at INCDIE ICPE-CA

Analytical X ray Difractometer
type D8 Advance



Atomic Absorbtion Spectrometer
type SOLAAR S4



Thin layer deposition by sputtering technique

UV-VIS Spectrophotometer

Atomic Force Microscope
Type CPII VEECO

Research facilities at INCDIE ICPE-CA

- ✓ **Thermogravimetry (TG or TGA)**
- ✓ **Derivative thermogravimetry (DTG)**
- ✓ **Differential thermal analysis (DTA)**
- ✓ **Differential scanning calorimetry (DSC)**
- ✓ **Dilatometry (DIL) and dynamic mechanical analysis (DMA)**

Coupled Thermal analysis:

TG - DTA - DSC - FTIR

DSC 204 F1 Phonix

Dilatometer DIL 402 PC/4

ICPECA

CONCLUSIONS

- **The research at INCDIE ICPE-CA is very active and has a high interest in the EU / FP7 priority area including the area of Fuel Cell & Hydrogen Storage Technologies.**

- **In the above presented context, the institute has the competence and the authority to address the electrical engineering community and has the full support of the Romanian Research Authority.**

- **New interested partners for participating together in national and international research consortia regarding the Fuel Cell & Hydrogen Technologies are very welcomed.**