Centro di Ricerca
HYDRO-ECO
Idrogeno e Energie Alternative

Hydrogen, Fuel Cells & Batteries
Energy Storage & Conversion
Ecology

Hydrogen and Fuel Cells related activities at Sapienza University of Rome

Prof. Stefania Panero
Director of the Research Center HYDRO-ECO
Sapienza University of Rome, Department of Chemistry,

stefania.panero@uniroma1.it

5th International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) H2igher Educational Rounds
Rome, December 1st 2014

Description of the organisation SAPIENZA University of Rome

Sapienza University of Rome, founded in 1303 by Pope Boniface VIII, is one of theoldest universities in the world and a high performer among the largest universities in international rankings.

Since its founding over 700 years ago, Sapienza has played an important role in italian history and has been directly involved in key changes and developments in society, economics and politics.

It has contributed to the development of Italian and European science and culture in all areas of knowledge.

Sapienza offers a vast array of courses including degree programmes, PhD courses, Specialization Schools in many disciplines, run by 63 Departments and 11 Faculties.

Description of the organisation HYDRO-ECO

- **HYDRO-ECO** is a highly interdisciplinary Research Center of Sapienza University of Rome, involving four Departments from the Faculty of Science and from the Faculty of Engineering.

- Moreover, **HYDRO-ECO** has established formal agreements with the University of Camerino, University of Chieti and with the Istituto dei Sistemi Complessi (ISC) ofl CNR for the development of common research activities.

- Its mission is to develop scientific and technological activities, focused on the study of materials and processes for the energy storage, conversion and utilization, possibly from renewable sources.

- The research activities are mainly carried out in the fields of:
  - ✓ high efficiency batteries, including lithium-ion and metal hydride batteries;
  - ✓ materials for the solid state hydrogen storage and purification;
  - ✓ PEM and biologic fuel cells.

- Particular attention is also devoted to new procedures for the synthesis on a nanoscale of electrodes and electrolyte materials and of hydrogen absorbing hybrid systems.

Description of the organisation HYDRO-ECO: the equipmets

The equipment and facilities belonging to the Departments and groups involved are the sum of the equipment and laboratories required to conduct research of common interest.

Sieverts apparatus

TGA-DSC-MS

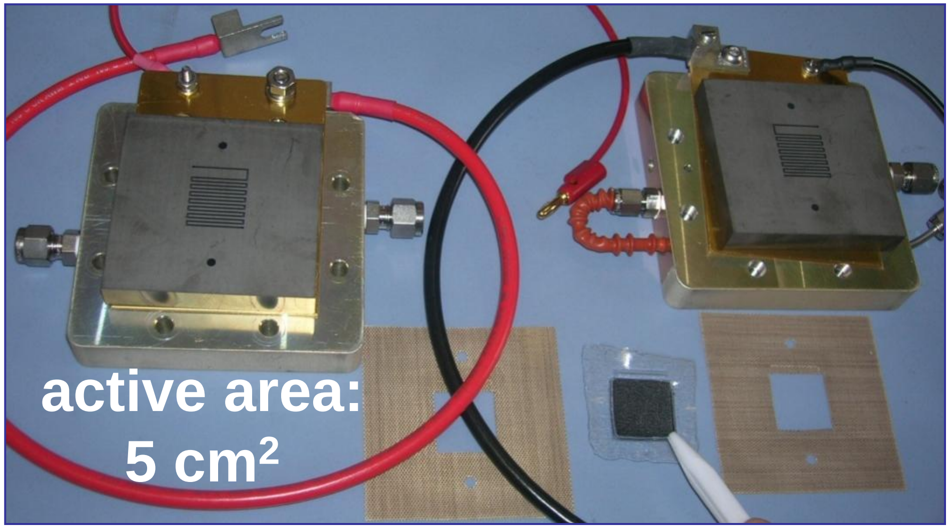
Multipurpose X-ray diffraction system

Dynamic Mechanical Analysis

Anelastic spectroscopy

Infrared spectroscopy

Description of the organisation HYDRO-ECO: the equipmets



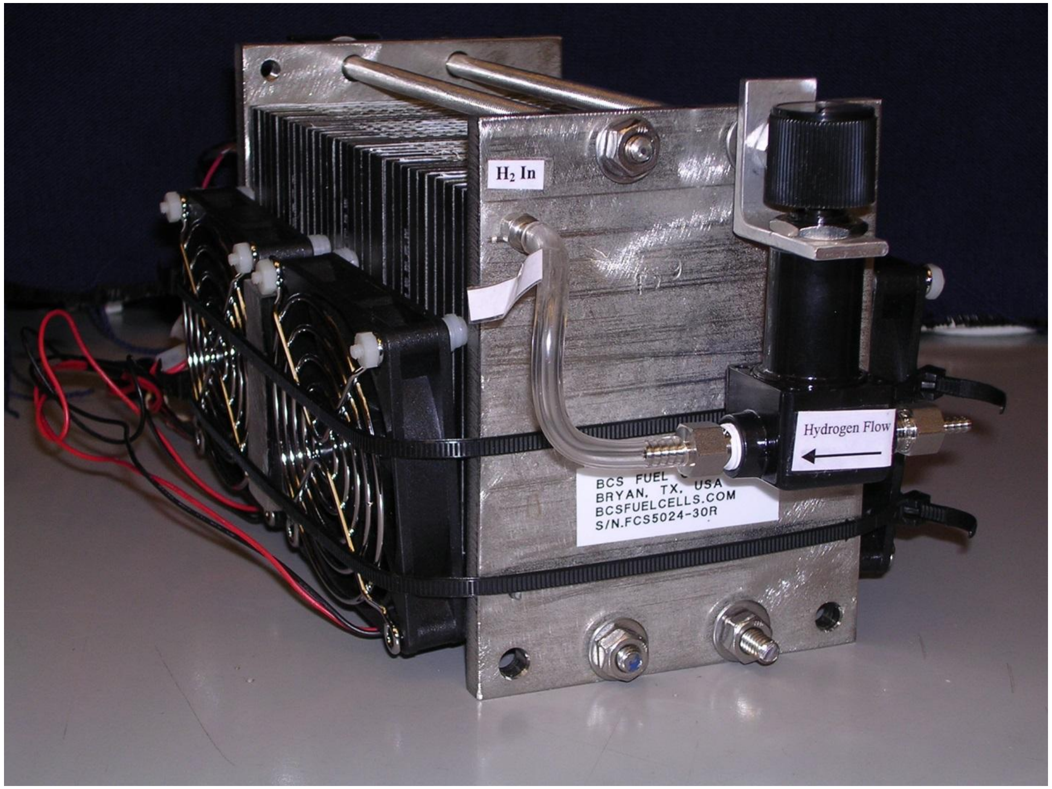
Fuel cell test unit

Additional components:

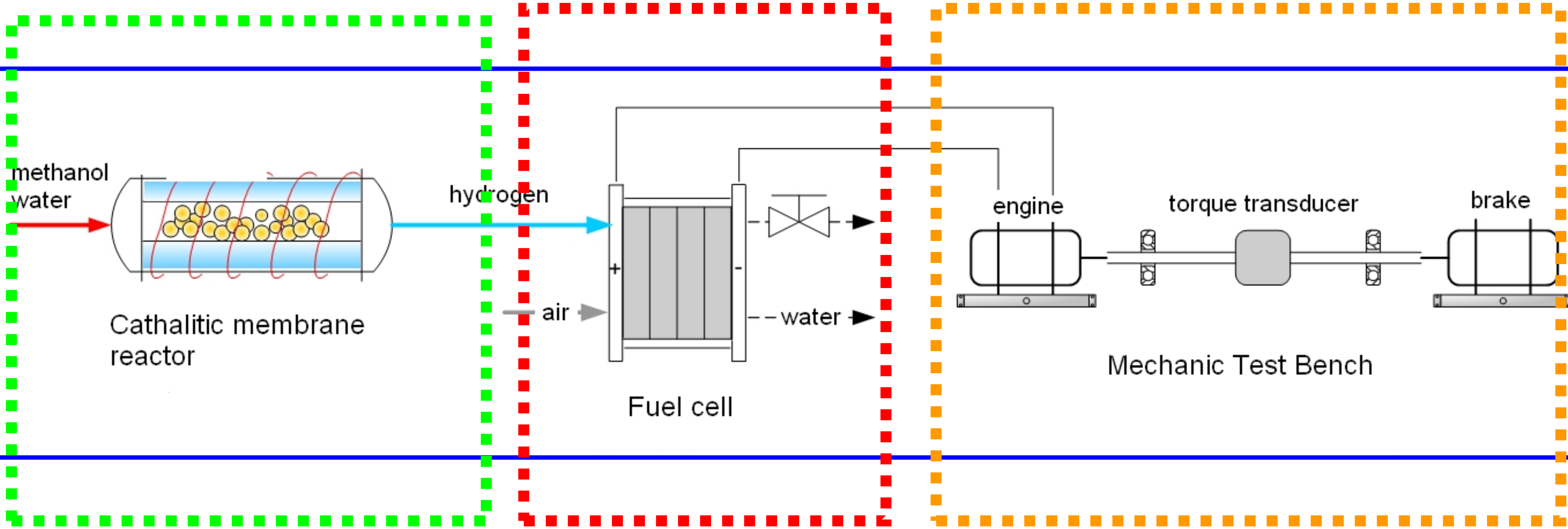
-Integrated Potentiostat
-In-plane Conductivity Cell

Fuel Cell Stack

Power 150 W @ 15 V
n° cells: 24
PH_2 = 0,1÷0,2 bar



Realisation of a bench for measuring the performance of an engine based on fuel cells, with production of H_2 "on board" through the a catalytic metal-membrane reactor



The efficiency of an automotive engine based on a “self-breathing” and “self-humidified” proton exchange membrane fuel cell stack (PEM FC) connected to a dc brushless electrical motor was measured under variable power load conditions.

National Project FIRB 2001 cod. RBAU01K4HJ

Topics of interest in the hydrogen storage field: HYDROSTORE project

INDUSTRIA 2015

Industria 2015
Energy Efficiency Call

September 2011 – February 2016

HYDROSTORE Project aims to develop innovative systems for solid state hydrogen storage.

The Consortium consists of qualified Companies and Research Institutions well established in the field of materials and devices for energy applications.

Objectives

- \- to realize the first and unique chain of national production of "traditional" metallic hydrides (AB_5 and AB_2 alloys and Mg-based) for hydrogen storage, operative from the research stage up to the pilot and preindustrial scale.

- \- to validate such hydrides at pilot and preindustrial scales.

- \- to explore the concrete possibilities offered by materials suitable for hydrogen storage alternative to the previous ones, having more advanced innovative characteristics.

- \- to realize, at the pilot and preindustrial scales, working prototypes of hydrogen tanks finalized to specific applications: stationary, transport by sea or lagoon.

- \- to study the integration and optimisation of developed prototypes with systems of hydrogen production by means of water electrolysis (realizing to this purpose an innovative device) with renewable source energy (photovoltaic and solar) and of its utilization in co-generative systems.

Investigate the physical properties and the hydrogenation/dehydrogenation processes of innovative promising materials:

- C_{60} / LiH-NaH
- Nanoconfined $NaAlH_4$
- NH_3BH_3
- $Ca(BH_4)_2$

Moreover, a detailed study of a complex alloy based on MgH_2 was accomplished.

C_{60} /LiH-NaH

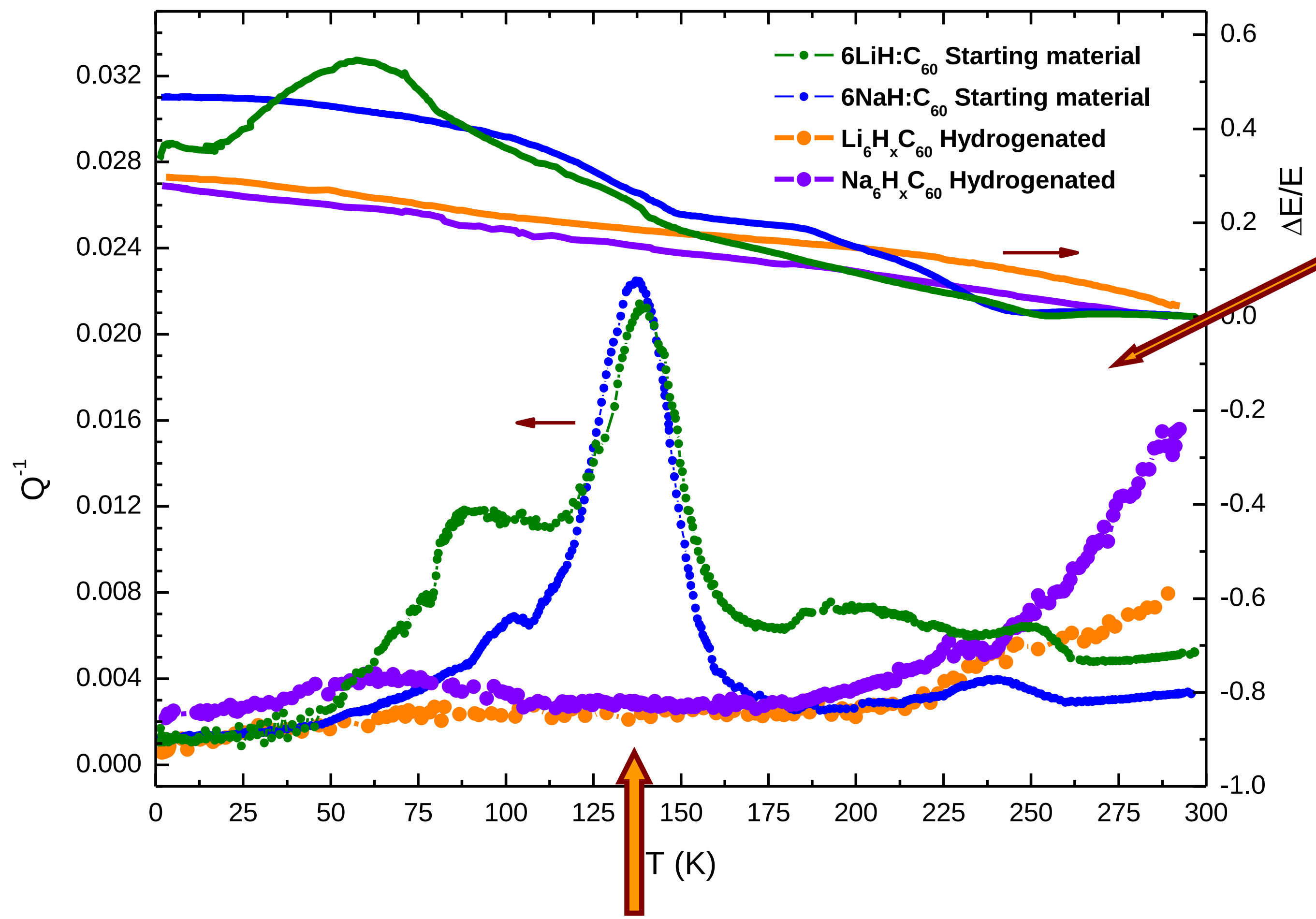
LiH/NaH and C_{60} were dissoved in THF or toluene in a molar ratio 6:1.

The solid materials obtained after evaporation of the solvents can reversibly store about 4.9 ($Li_6H_xC_{60}$) and 2.5 ($Na_6H_xC_{60}$) wt% hydrogen.

C_{60} /LiH-NaH desorbs hydrogen at much lower temperature than C_{60} and LiH or NaH, respectively

Moreover only pure H_2 evolves.

Anelastic spectroscopy measurements on C_{60} /LiH-NaH



No phase transition after rehydrogenation → The crystal structure is deeply modified.

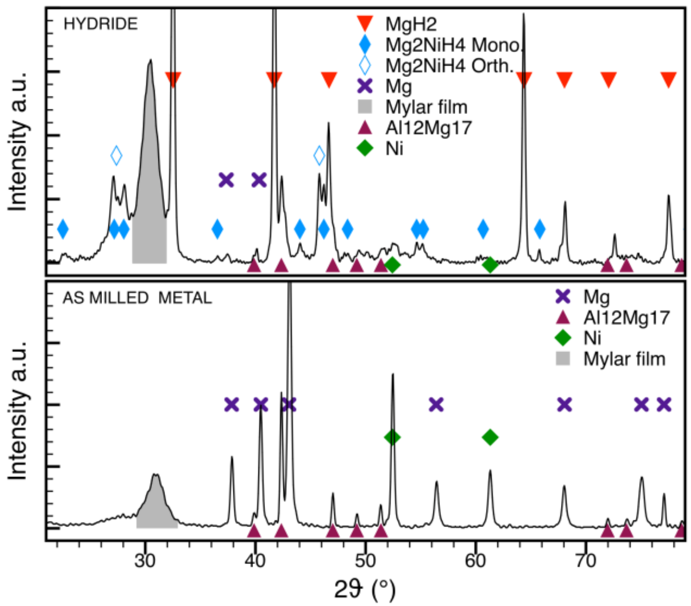
No more dynamic rotations of C_{60} → structure has changed. Local polymerization

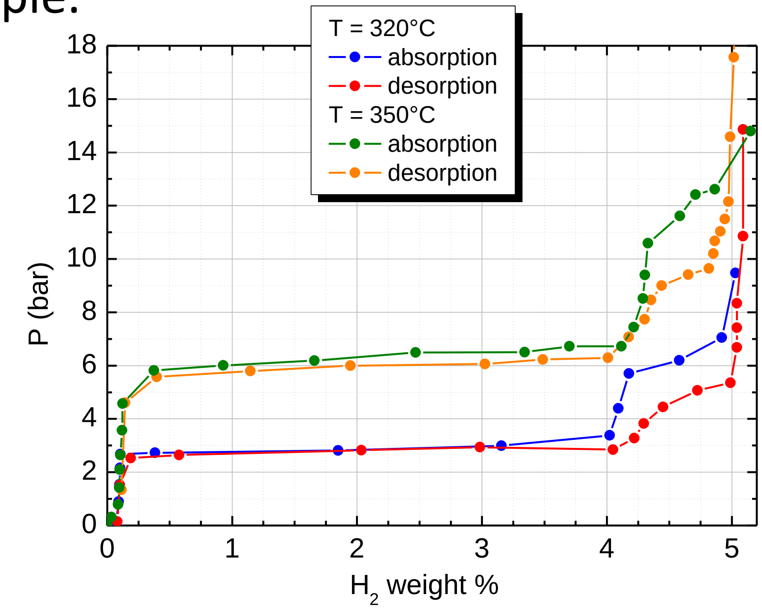
MgH_2+Ni+Al

The hydrogenation/dehydrogenation properties of a sample composed by a mixture of a ball milled phase Mg 79.5% Ni 14% C 5% TiO_2 1.5% in weight have been measured.

The hydrogenation of the Mg-Ni compound occurs in two steps and is compatible with the formation of MgH_2 and Mg_2NiH_4.

The activation energy for the dehydrogenation of MgH_2 is strongly decreased with respect with the bulk uncatalyzed sample.





ADVANCED, NANO-COMPOSITE ELECTRODE AND ELECTROLYTE MATERIALS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

National and International Projects support the activities

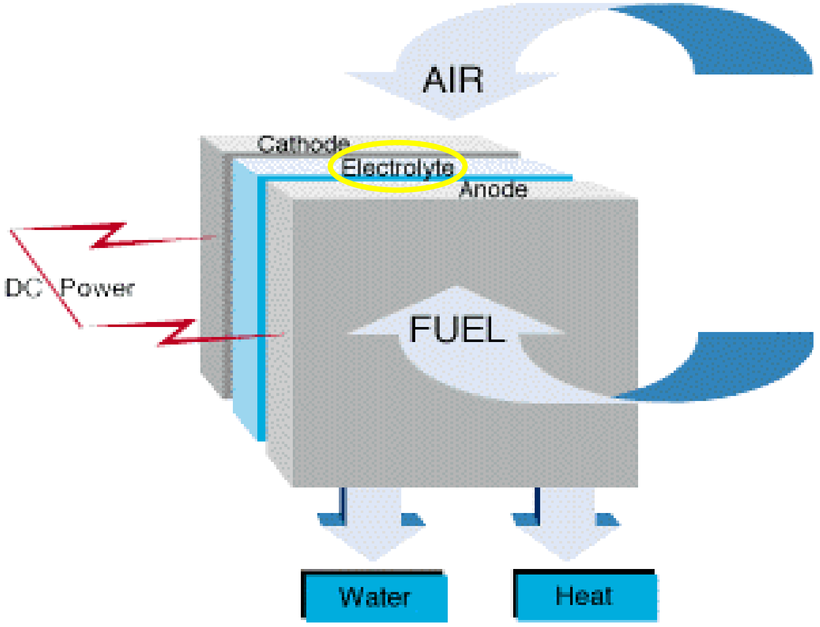
Topics of interest in the Fuel Cell field

Main topics of interest in the Fuel Cell field:

development of low-relative humidity, high-temperature proton conducting polymer membranes

development of new low-Pt content catalysts for hydrogen oxidation and oxygen reduction

for PEMFCs



THE GOAL:

Improvement of
the proton conducting membrane

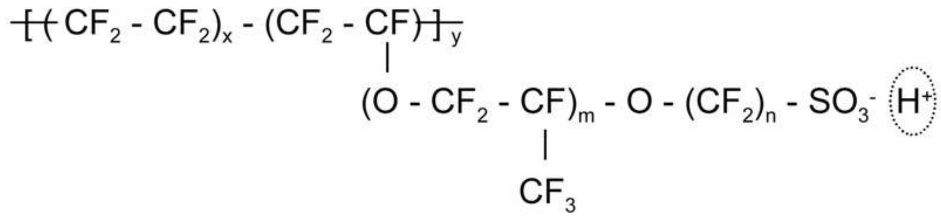
- lower relative humidity (<100%)
- higher temperature (70°C<T<120°C)

THE STRATEGIES:

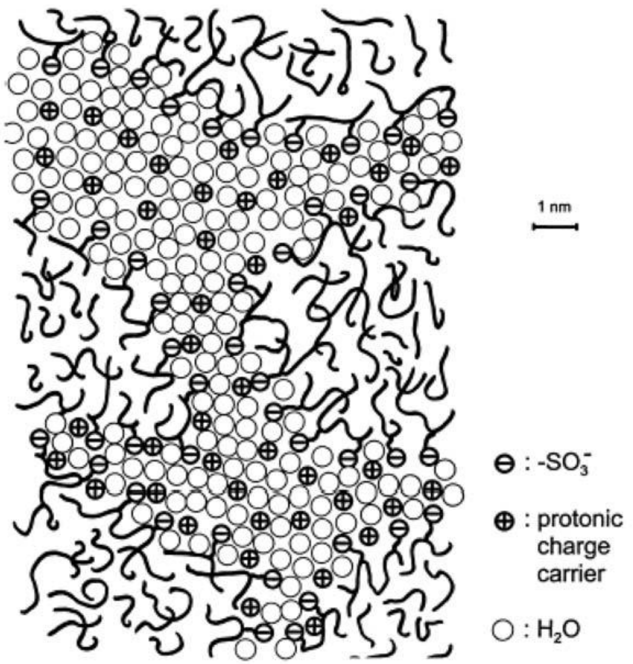
✓ alternative new polymer systems

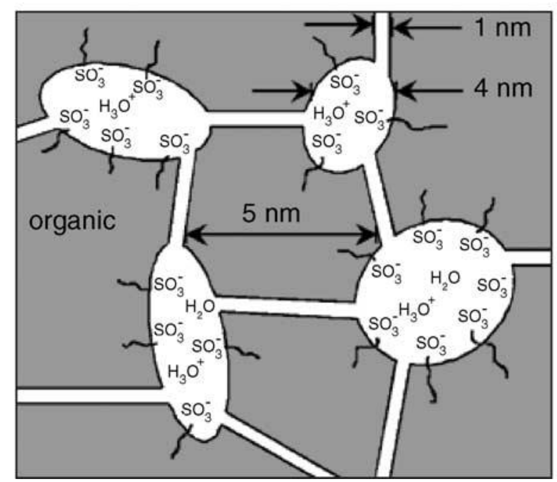
✓ modification of the conventional perfluorosulfonic-based polymer system (i.e., Nafion membranes)

Nafion-membrane structure: the “random network model”



Nafion: m = 1-3, n = 2, x = 5-13, y = 1000-1200
Others: m = 0, n = 1-5, x = 1-14, y = 800-1200





K.D. Kreuer, J. Membrane Sci., 185 (2001) 2
K. Mauritz, R. Moore, Chem. Rev., 104 (2004) 4535

B. Smitha et al., J. Membrane Sci., 259 (2005) 10
S.M. Haile, Acta Materialia, 51 (2004) 5981

The strategy

NANOCOMPOSITE MEMBRANES:

incorporation of various hygroscopic inorganic particles in the host polymer

Malhotra and Datta first proposed the addition of INORGANIC SOLID ACIDS in conventional membranes such as Nafion.

S. Malhotra, R. Datta, J. Electrochem. Soc., 144 (1997) 23

Why?

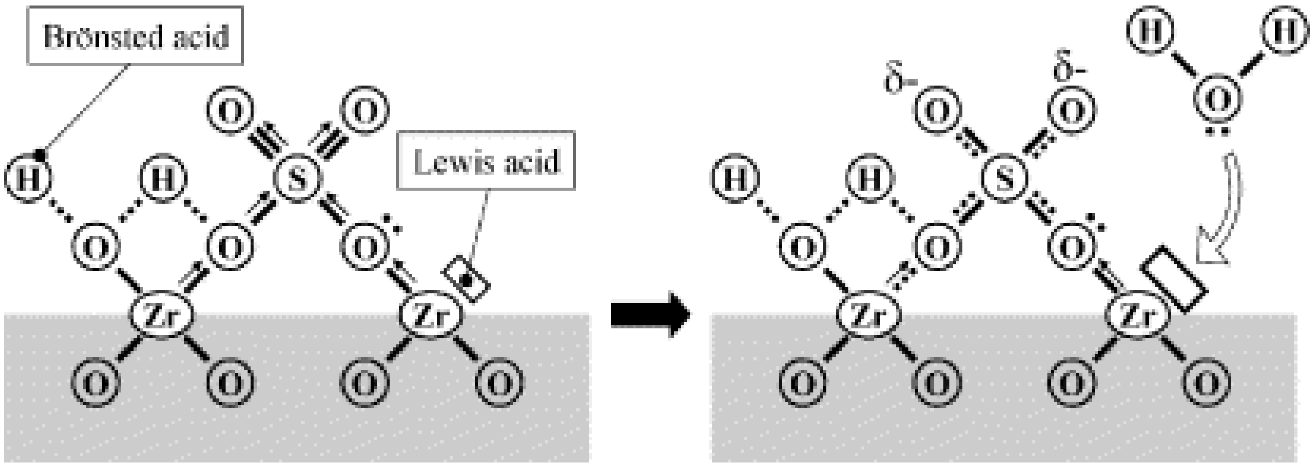
IMPROVING WATER RETENTION

PROVIDING ADDITIONAL ACID SITES

Our choice:

Superacidic sulfated metal oxide

Activities



S. Hara, M. Miyayama, Sol. State Ionics, 168 (2004) 111

It is recognized as one of the strongest acid among all those known solid with its Hammet acid strength of -16!

Current Activities

Starting from the study of sulfated ZrO2, investigate the properties of other sulfated metal oxides and their effect as additives by comparing the behavior of various composite SMO_2-added Nafion membranes with that of additive-free Nafion systems.

Preparation of the membranes

Nafion solution

N,N-dimethylacetamide (DMAc)

Inorganic compound

magnetic stirring

casting

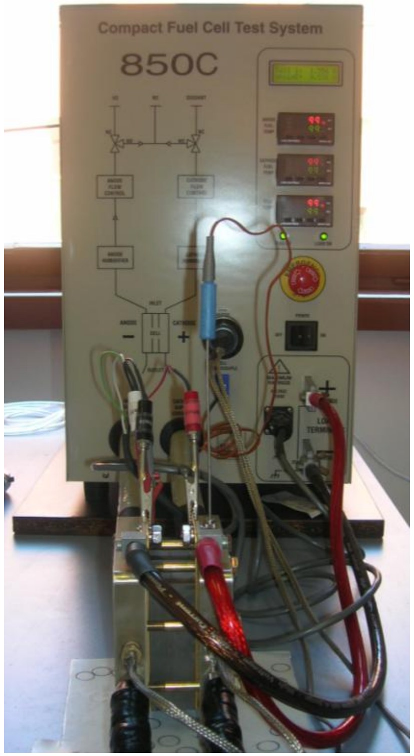
thermal treatment (100°C over night)

hot-pressing

activation procedure (H_2O_2, H_2SO_4, H_2O)

Sample name	*Nafion [wt.%]*	*SZr [wt.%]*	*Thickness [μm]*
Nafion	100	-	85
Nafion/SZr	95	5	100

Fuel Cell tests



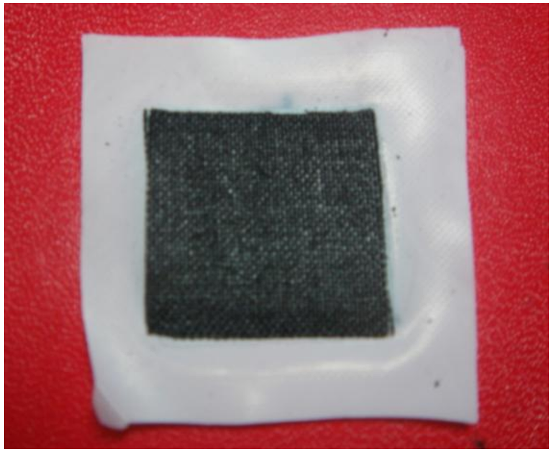
H_2 -(Pt) / membrane / (Pt)- Air

- Commercial electrodes: 0,5 mg Pt/cm^2
- Cell fixture: 5cm^2 active area
- Current-controlled mass flow rates of the feed gas:
  - 1.4 times stoichiometric flow for H_2
  - 3.3 times stoichiometric flow for Air

P(H_2-air) = 1 atm!

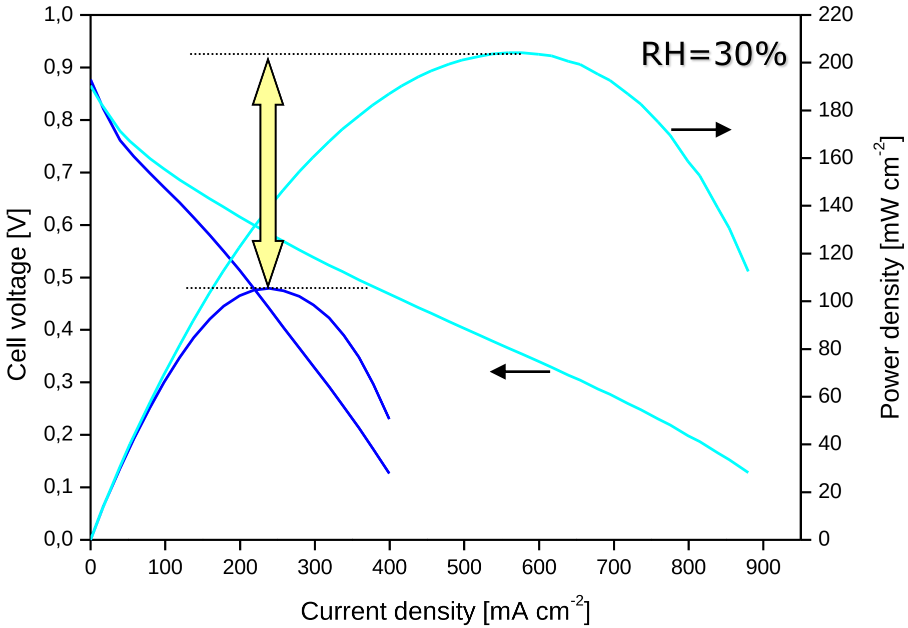
Membrane-electrode assembly (**MEA**) hot-pressing conditions:

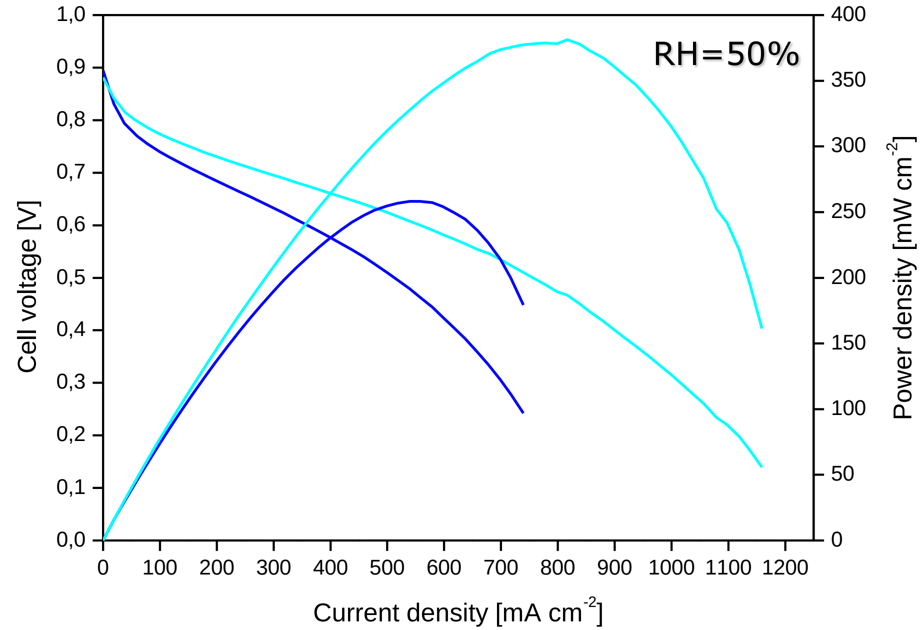
120°C – 2 atm – 7 min

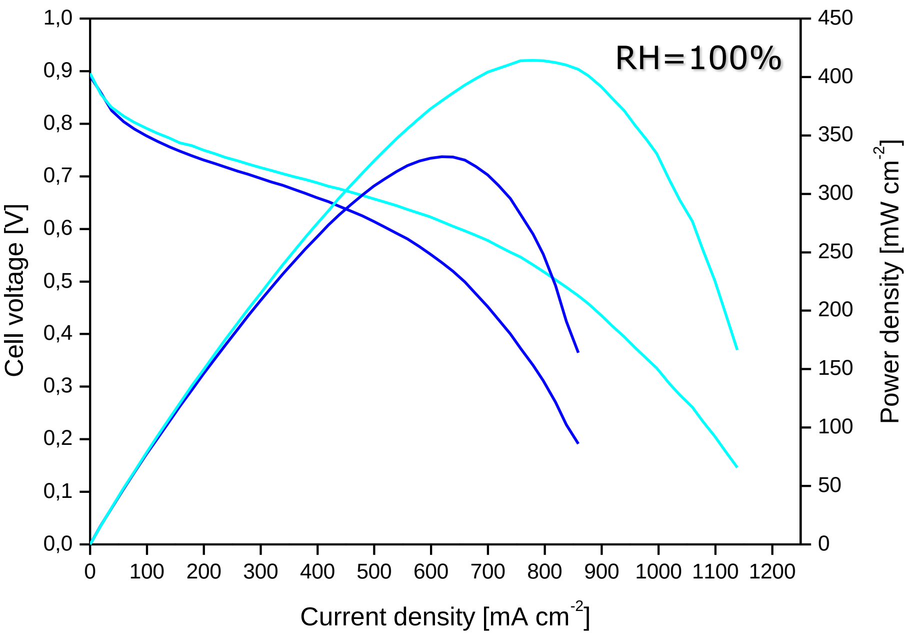


S-ZrO_2 nano-composite, hybrid Nafion membranes

T(cell)=70°C



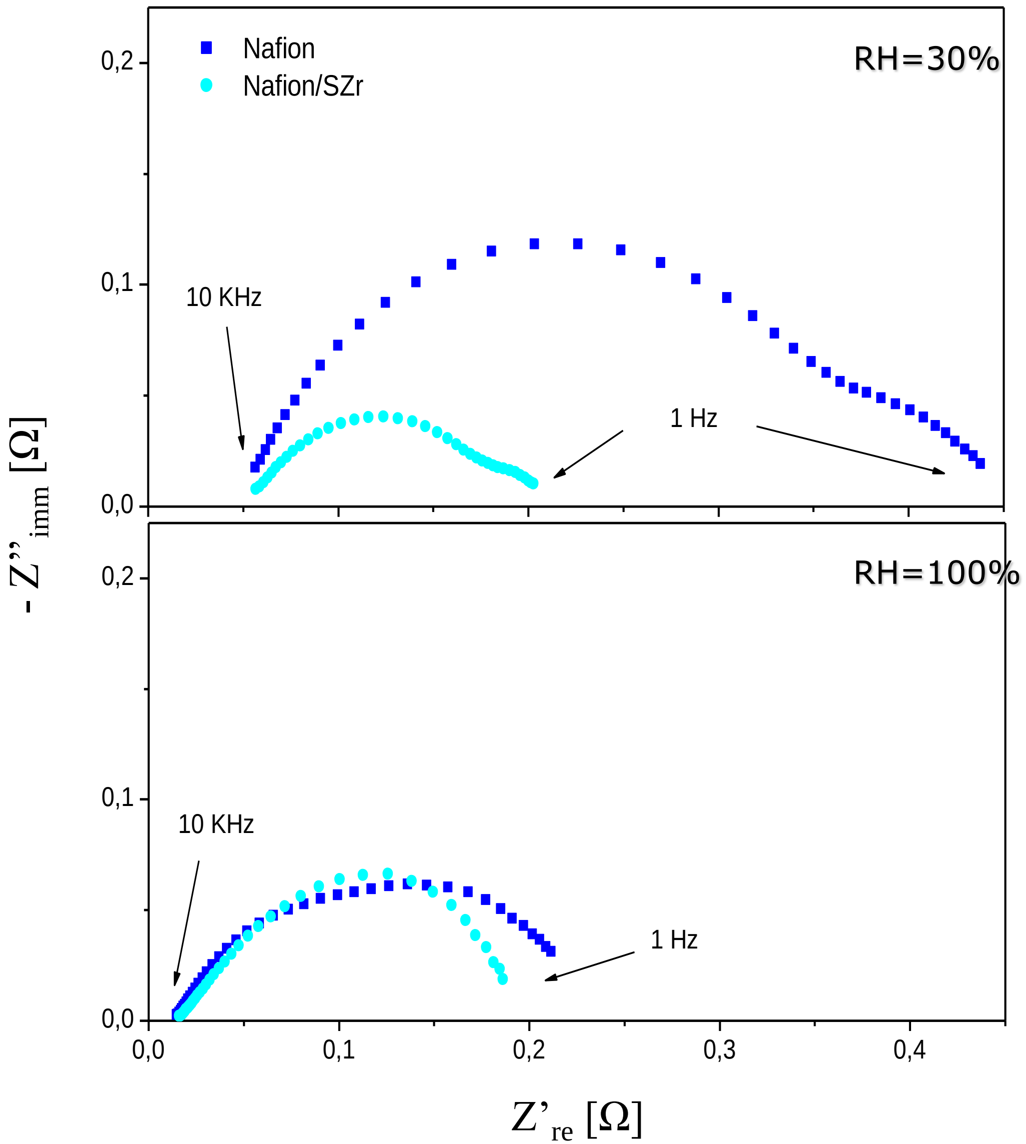




— Nafion — Nafion/SZr

RH [%]	Δi [%]	Δp [%]
30	135	93
50	46	47
100	26	25

T(cell)=70°C



In situ impedance measurements at cell voltage = 0,5 V

Sulfated metal oxide additives

$S\text{-}SnO_2$

S. Brutti, R. Scipioni, M.A. Navarra, S. Panero, V. Allodi, M. Gia

International J. Nanotechnology (2014), in press:

"*SnO_2-Nafion® nanocomposite polymer electrolytes for fuel cell*

R. Scipioni, D. Gazzoli, F. Teocoli, O. Palumbo, A. Paolone, N. Ibris, S

Membranes (2014), volume 4, pp 123-142:

"*Preparation and characterization of nanocomposite polymer membranes cont*

additives"

$S\text{-}TiO_2$

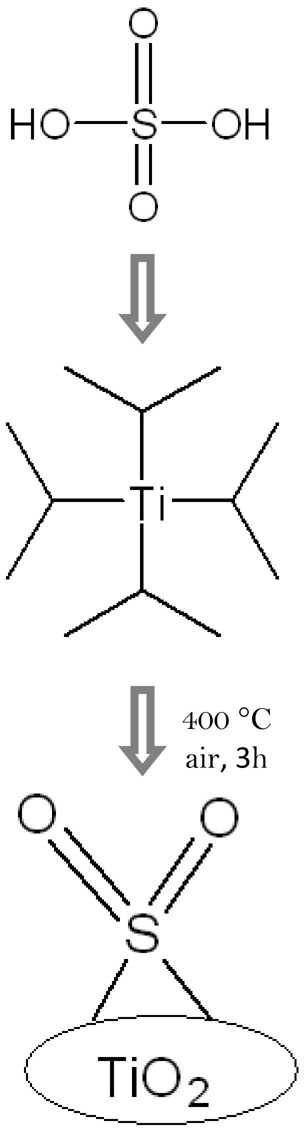
M. Sgambetterra, S. Panero, J. Hassoun, M.A. Navarra,

Ionics, (2013), volume 19, pp 1203-1206:

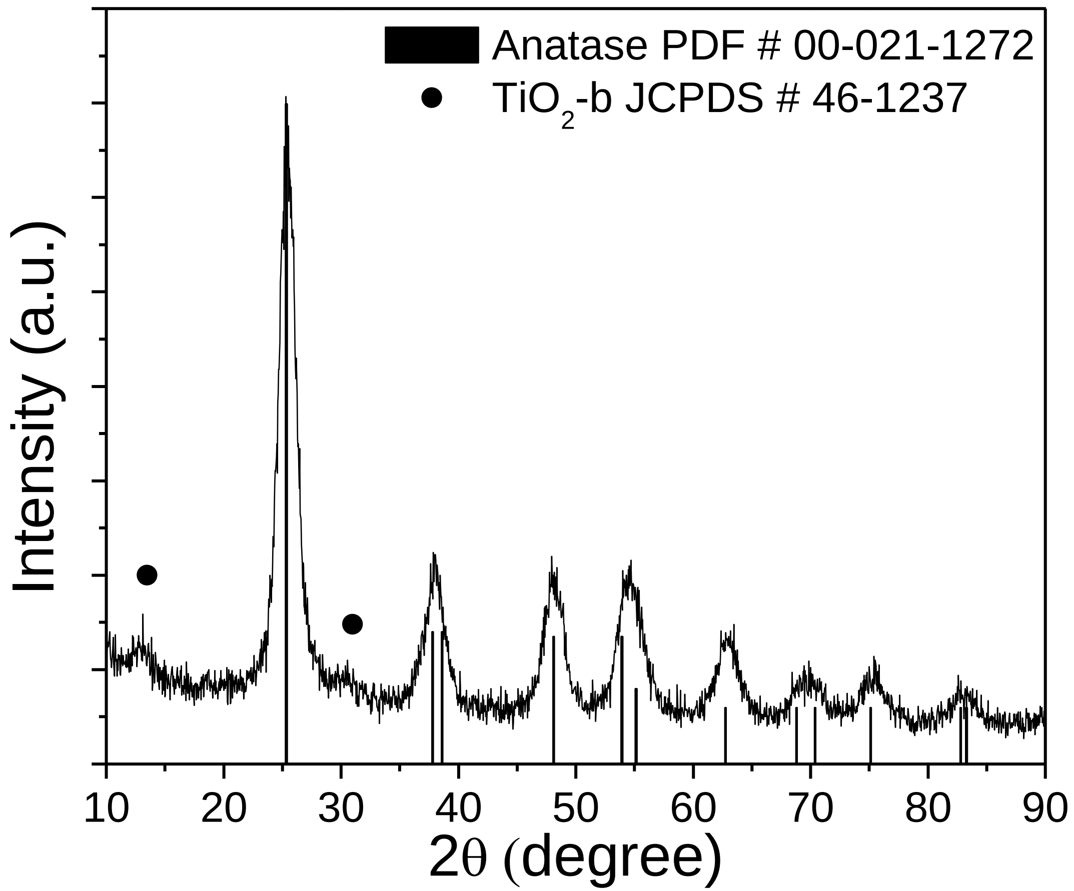
"*Hybrid membranes based on sulfated titania nanoparticles as low cost proton conductors*"

S-TiO_2

1-step sol-gel synthesis



XRD



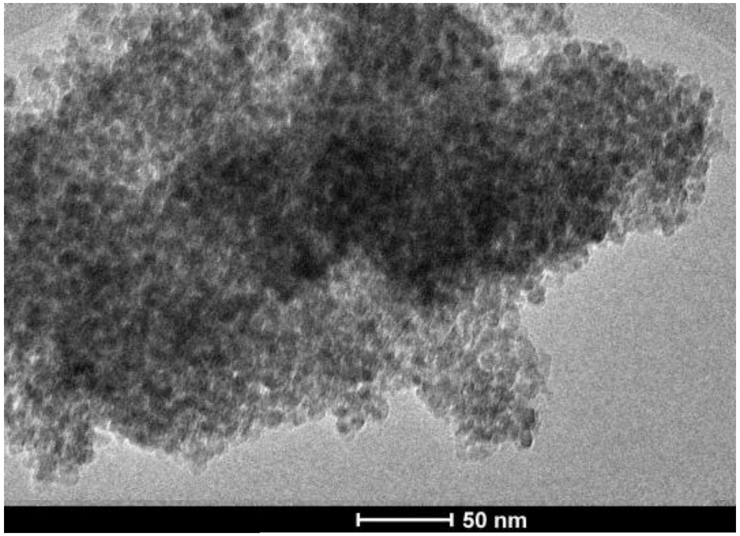
Crystallite size 10.1 ± 0.6 nm

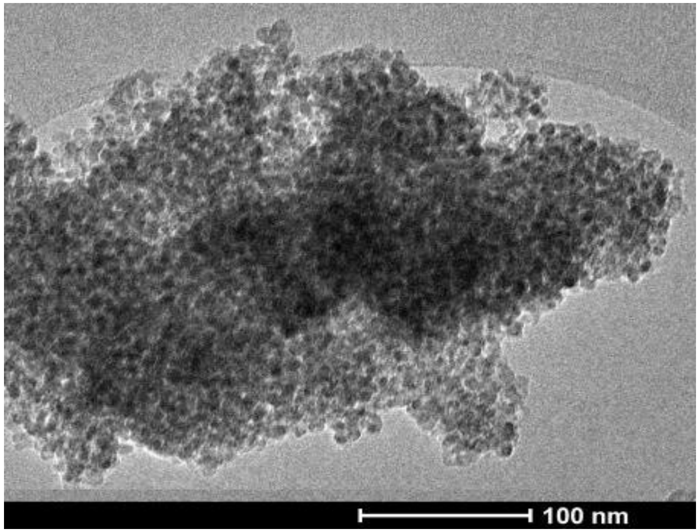
BET **S**pecific surface area 150 m^2/g

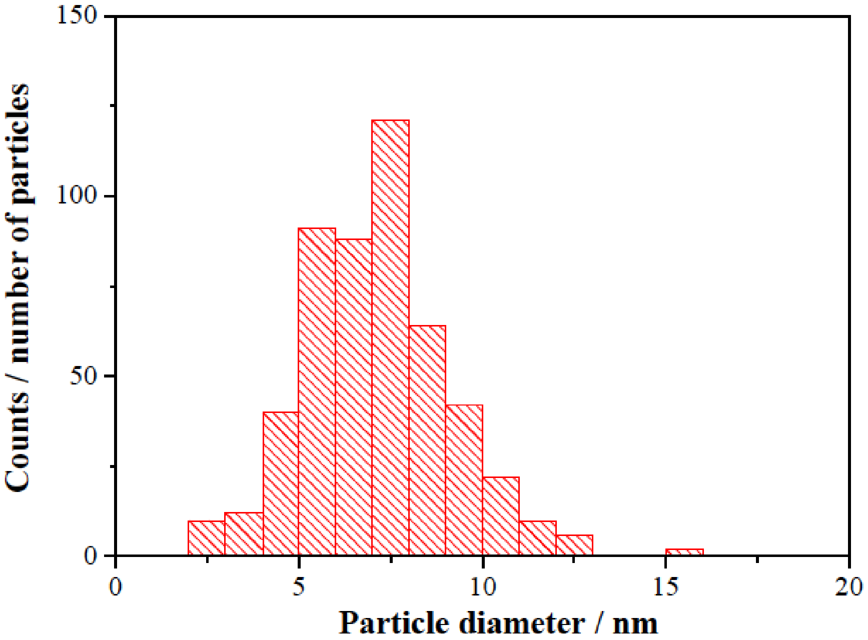
Krishnakumar B, Velmurugan R, Swaminathan M, *Catal. Commun* **2011**, 12, 375

S-TiO_2

TEM

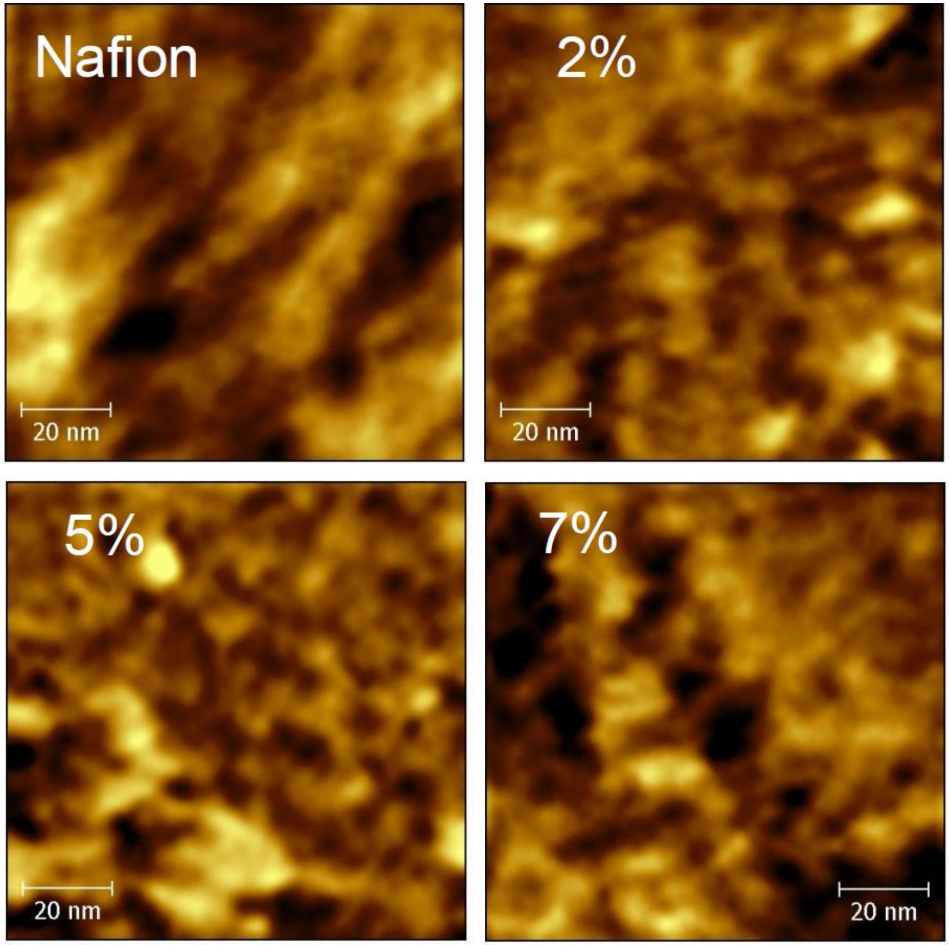

50 nm


100 nm

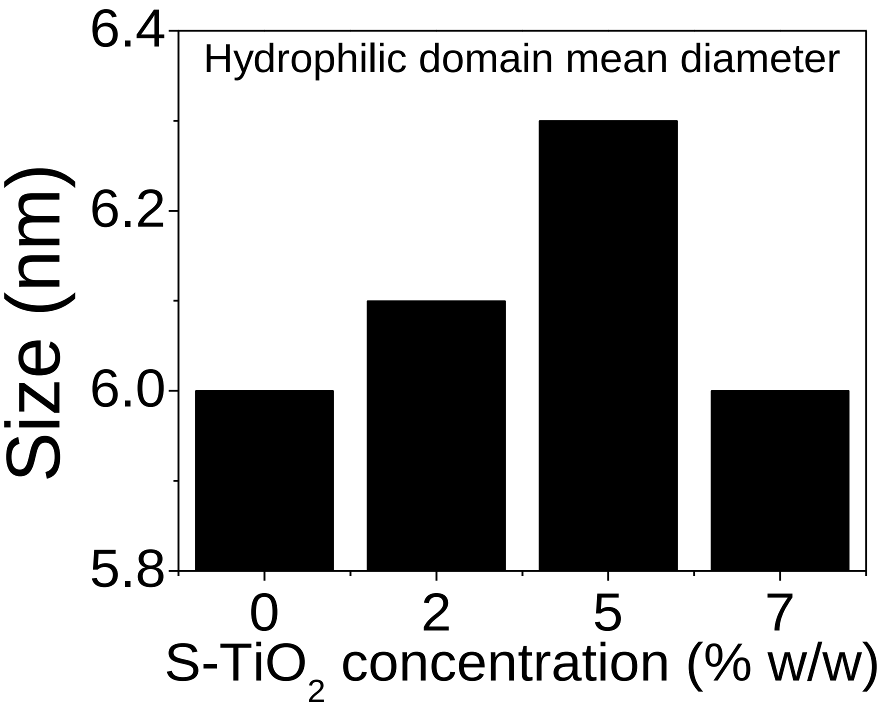

Counts / number of particles
Particle diameter / nm
0
50
100
150
0
5
10
15
20

$S\text{-}TiO_2$ / Nafion composite membranes

AFM phase images, RH=33%



Alternation of light and dark areas corresponds to the transition between hydrophobic and hydrophilic domains, respectively.



AFM images have been analyzed by the ImageJ software in order to study the evolution of the size of the hydrophobic and hydrophilic domains.

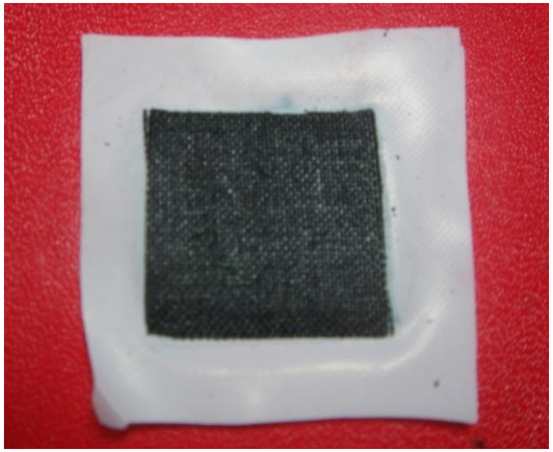
S-TiO_2 / Nafion composite membranes – FC tests

H_2 – Pt / membrane / Pt - Air

- Commercial electrodes: 0,5 mg Pt/cm^2
- Cell fixture: 5cm^2 active area
- Current-controlled mass flow rates of the feed gas:
  - 1.4 times stoichiometric flow for H_2
  - 3.3 times stoichiometric flow for Air
- P_{gases} = 2 atm

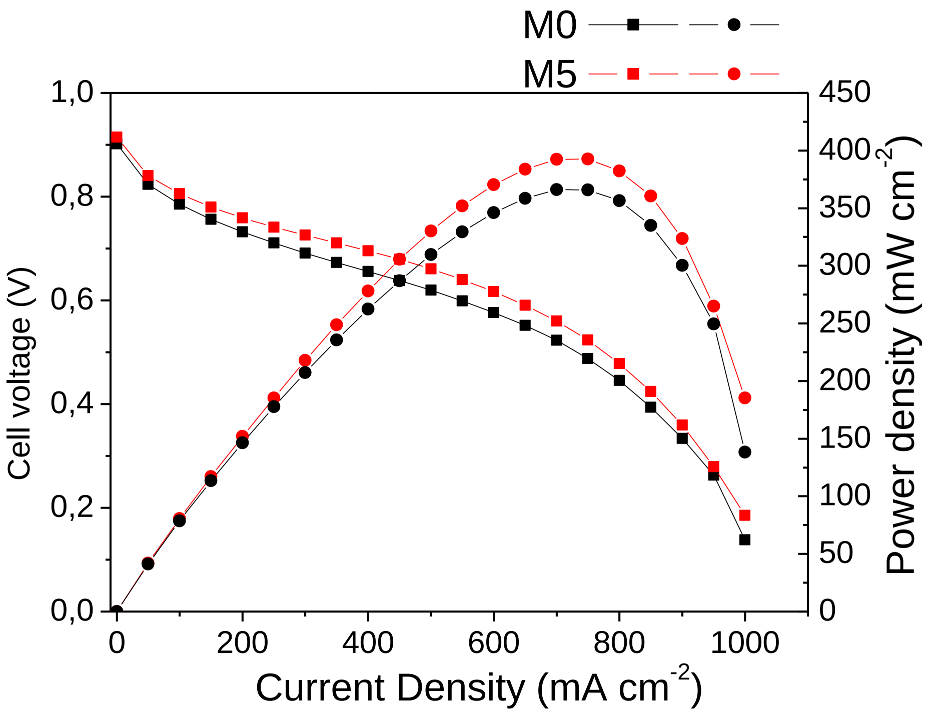
Membrane-electrode assembly (**MEA**)
hot-pressing conditions:

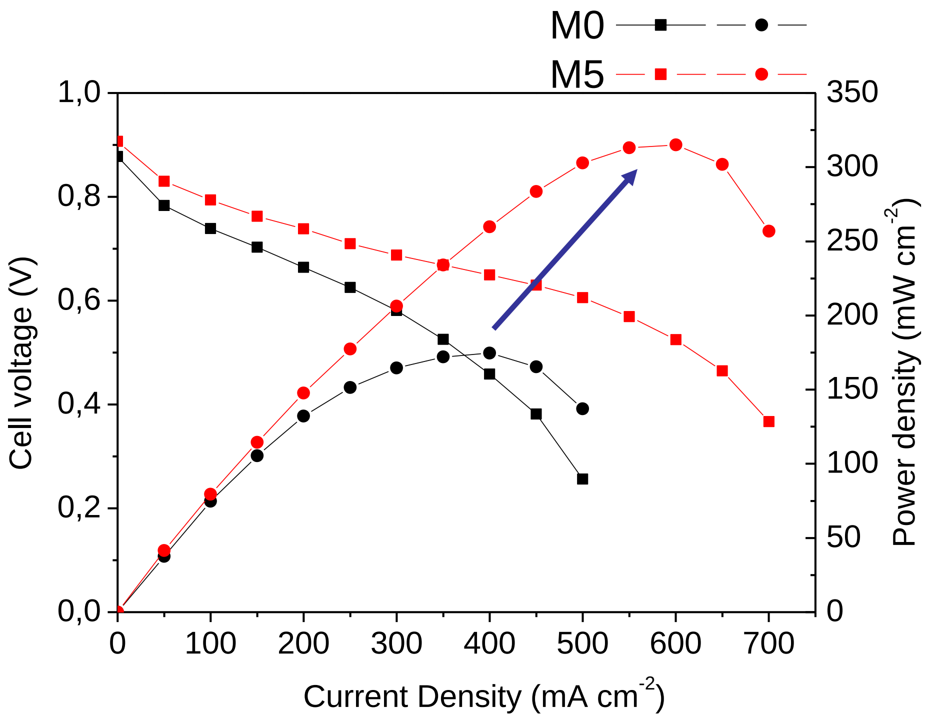
120°C – 2 atm – 7 min



S-TiO_2 / Nafion composite membranes – FC tests

RH = 30%



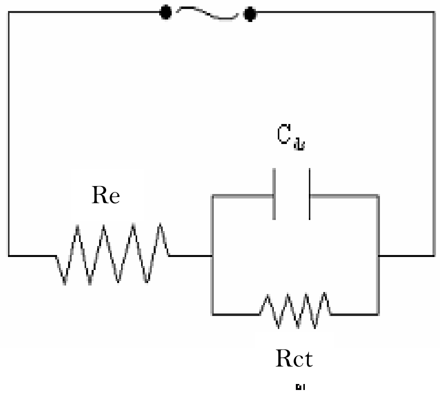


T_{cell} = 70 °C

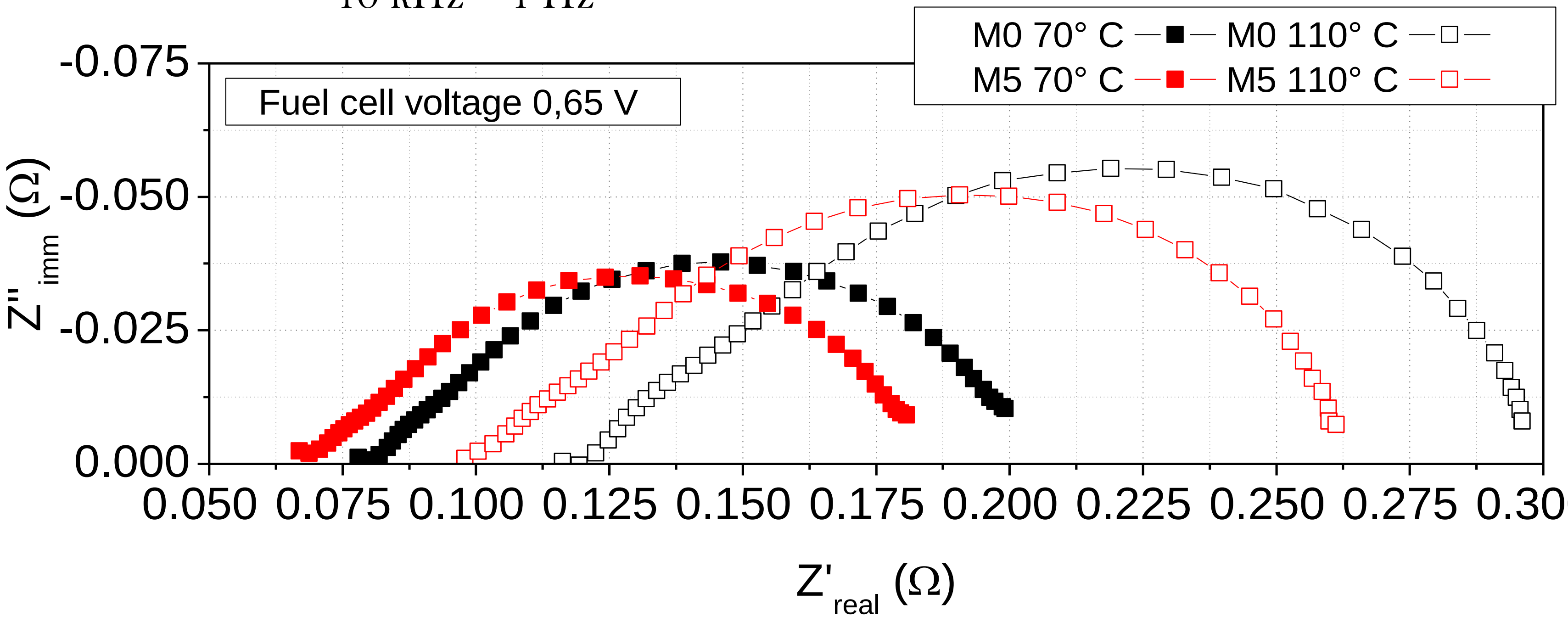
T_{cell} = 110 °C

S-TiO$_2$ / Nafion composite membranes – *in situ* EIS

RH = 30%, T_{cell} = 70°C ⟶ 110 °C



10 kHz – 1 Hz



Conclusions

Nano-metric sulfated titania particles, with highly homogeneous morphology, have been obtained by a fast, 1-step synthesis.

As in the case of sulfated zirconia, it has been demonstrated the role of the acidic filler in:

- promoting higher hydration level
- reducing electrolyte resistance
- improving membrane-electrode interface contact

Fuel Cell performances are generally positively affected by the presence of the inorganic compound.

In particular, the use of a superacidic solid oxide allows to work in more drastic conditions, i.e. low relative humidity and higher temperature.

Recent activities: SPE for electrolyzer applications

Int. J. Electrochem. Sci., 7 **(2012)** 1532 - 1542

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Investigation of Composite Nafion/Sulfated Zirconia Membrane for Solid Polymer Electrolyte Electrolyzer Applications

S. Siracusano[1,*], *V. Baglio*[1], *M.A. Navarra*[2], *S. Panero*[2], *V. Antonucci*[1], *A. S. Aricò*[1]

A composite Nafion-Sulfated Zirconia (SZrO2) membrane was prepared and investigated in a solid polymer electrolyte (SPE) water electrolyzer at different temperatures.

The superior performance of the composite electrolyte was due to the strong acidity and water affinity of sulfated zirconia nanoparticles used as filler.

Funding projects of the HYDRO-ECO group in the PEMFC field:

-Coordination group of the NUME Project (Development of composite proton membranes and of innovative electrode configurations for polymer electrolyte membrane fuel cells), supported by the Italian Ministry of University and Research. February 2005-October 2008.

- Member of the CARISMA network, a 2-year European Coordination Action on High Temperature MEAs. January 2007.-December 2008

-Member of the FIRB Project (Innovative electrochemical technologies for energy storage from renewable sources), sponsored by the Italian Ministry of University and Research. July 2007-July 2010.

-Coordination group of the PRIN 2011 Project (Advanced nanocomposite membranes and -innovative electrocatalysts for durable polymer electrolyte membrane fuel cells) funded by the Italian Ministry of Education and Research. February 2013- January 2016

ACKNOWLEDGMENTS

Thanks to

People (Researchers, PhD students, master students)
from the Departments of Sapienza University of Rome
as well as from the CNR Research group
involved in HYDRO-ECO activities

All of you for your kind attention