Nanoscience
Nanotechnology
Innovative Instrumentation

Nanostructured Materials for Health, Environment and Energy

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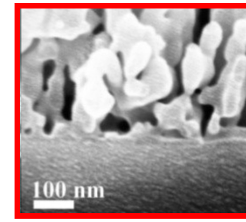
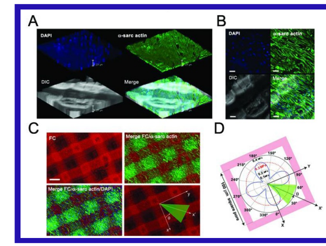
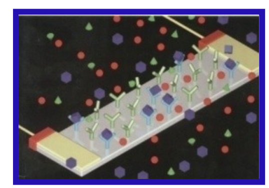
Our Present Research Fields

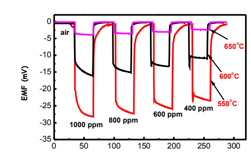


- **Energy**
  - Polymer electrolyte membrane fuel cells (PEMs)
- Solid oxide fuel cells (SOFCs)



- **Health**
  - Tissue engineering
  - Composite synthetic and biological polymers
  - Drug delivery
  - Nanomechanics





- **Environment**
  - Gas sensors for on-board diagnostics
  - Gas sensors for environmental monitoring

Energy:Solid Oxide Fuel Cells (SOFCs)

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Main limit: high operating temperature needed by YSZ electrolyte

(1000 °C)

Advantages

- High thermodynamic efficiency
- Low environmental impact
- Internal reforming of fuel

Disadvantages

- Elevated material costs
- Stress on components stability
- Slow start-up

IT-SOFC

Intermediate Temperature Solide Oxide Fuel Cells

(T < 700°C)

Increased life time of all components

Use of lower cost materials

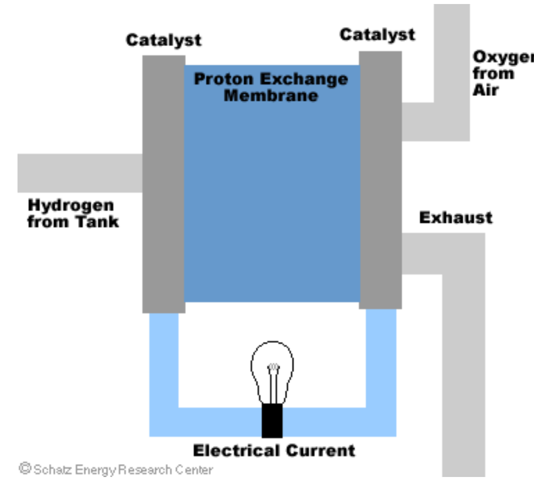
Faster start up and shut down procedures

Overall lower cost, improved reliability → Better performance

Polymeric electrolytes in PEMFCs

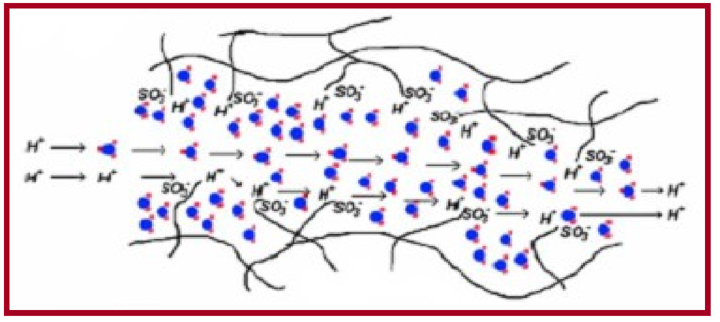
What do we want:

- high conductivity ($\sigma \geq 10^{-2}$ S/cm) @ T ≥ 100 °C
- high chemical, thermal and mechanical stability
- low methanol permeability
- hydrolytic stability
- low cost
- durability



What can we tune:

- composition, backbone, and acid groups characteristics
- water domain, size, shape, interface, water transport properties, water uptake, reactant permeability
- ion exchange capacity, proton conductivity
- processing
- stabilization of morphology



Create alternative routes for H^+ to move through the electrolyte

Our goals:

rise the T in PEMFCs

lower the T in SOFCs

Develop new chemical strategies to prepare nanostructured materials

Design specific synthetic procedures to control materials structure/function

Controlled synthetic and processing procedures can reduce the grain size (nm)

Chemical routes often versatile and cheaper than physical methodologies

It is possible to control the porosity of ordered and mesoporous structures.

Not only the grain size can be controlled but also empty spaces

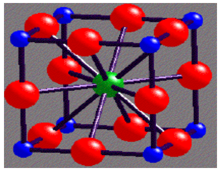
Our strategies for SOFCs

use of solid electrolytes alternative to YSZ: *e.g.* doped-ceria, lanthanum gallate, bismuth oxide

reduction of the electrolyte thickness to reduce ohmic resistance

use of high T proton conductors oxides (HTPC)

SOFCs using HTPC as electrolyte conductor produce water at the cathode, while the use of an oxygen-ion conductor leads to water generation at the fuel-side electrode.



The dilution of the fuel in water reduces the cell efficiency.

Proton conduction can be thermally activated at rather low T because of the low Ea (0.3-0.6 eV)

Lowering the T, the electrolyte/electrode interface overpotential increases

REDUCE CATHODE OVERPOTENTIAL

Development of composite cathodes

Used of mixed oxygen ion/electron conductors (MIECs) cathode materials

HTPC (400-700°C)

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Main families

Cerates: $SrCe_{1-x}M_xO_{3-d}$, $BaCe_{1-x}M_xO_{3-d}$

Zirconates: $CaZr_{1-x}M_xO_{3-d}$, $BaZr_{1-x}M_xO_{3-d}$ M = Y, Yb, In, Gd

Cerates:
- ✓high proton conductivity
- ✓poor chemical stability in CO_2

Zirconates:
- ✓lower proton conductivity
- ✓good chemical stability

Zr-substituted Y-doped barium cerate may have both high protonic conductivity and good chemical stability

$BaCe_{0.8-x}Zr_xY_{0.2}O_{3-\delta}$ ($0 \leq x \leq 0.8$)

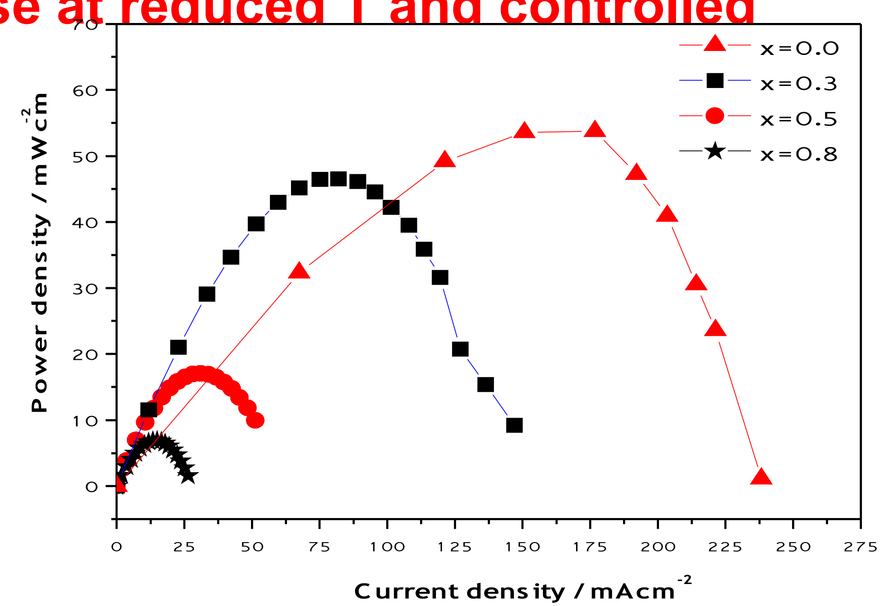
Optimization of the synthetic procedure: sol-gel methods to achieve powders with a stable single phase at reduced T and controlled chemical structure

Stability under CO_2 atmosphere

Sintering behavior

FC test

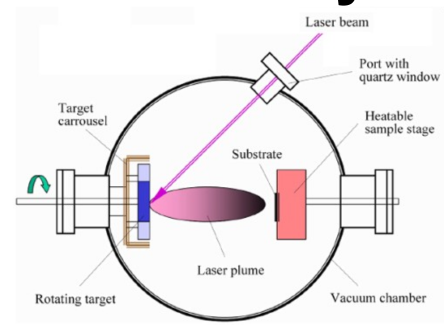
X = 0.5 best compromise



Electrolyte thickness 0.6 mm T = 700°C

Possible improvement: bilayer electrolyte

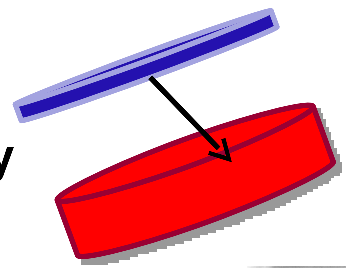
sintered Y-doped barium cerate pellet protected with PLD deposited Y-doped barium zirconate layer



Pulsed Laser Deposition (PLD)

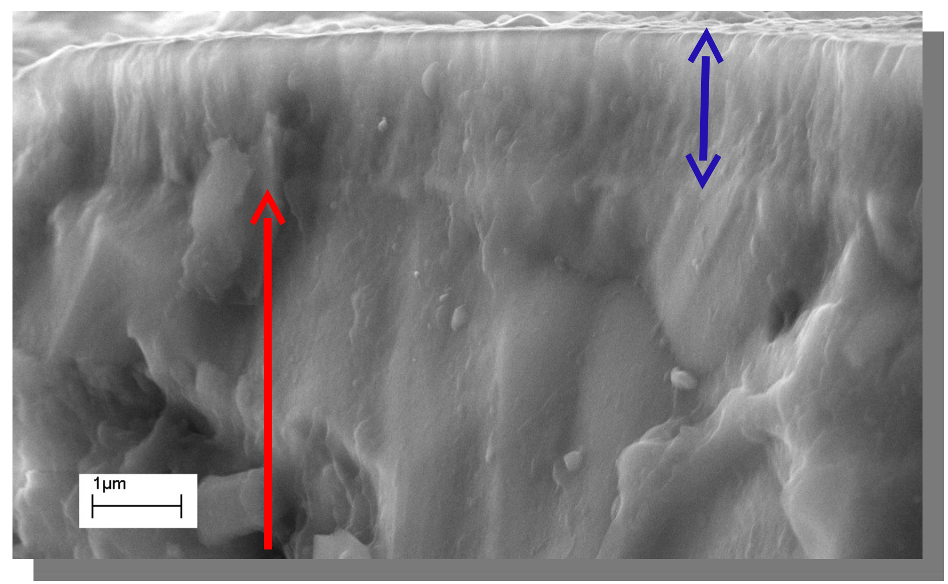
✓Stoichiometric reproduction of the target
✓Control of crystal structures
✓ High control in film microstructure

$BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY)
protecting layer
✓high chemical stability



$BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (BCY)
pellet substrate
✓high proton conductivity

BZY layer:
dense and homogeneously deposited on BCY pellet substrate

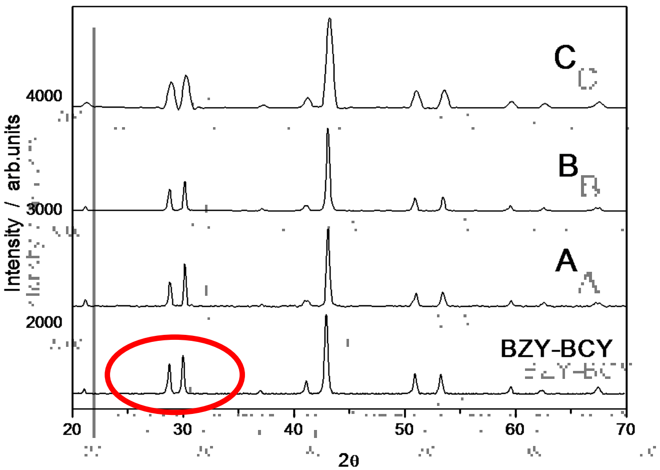


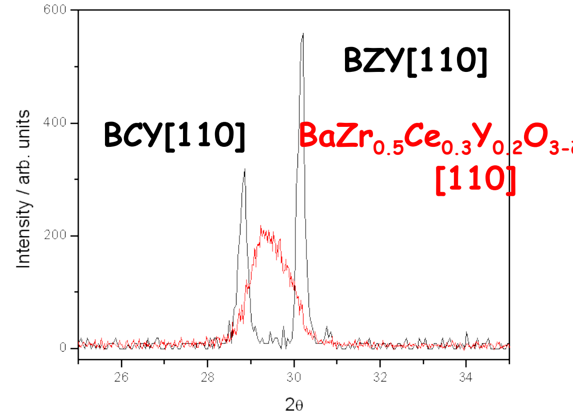
Bilayer interface:
well defined and sharp

SEM & XRD analysis →
epitaxial grain by grain growth of the BZY layer on the BCY substrate

Chemical stability & Electrochemistry

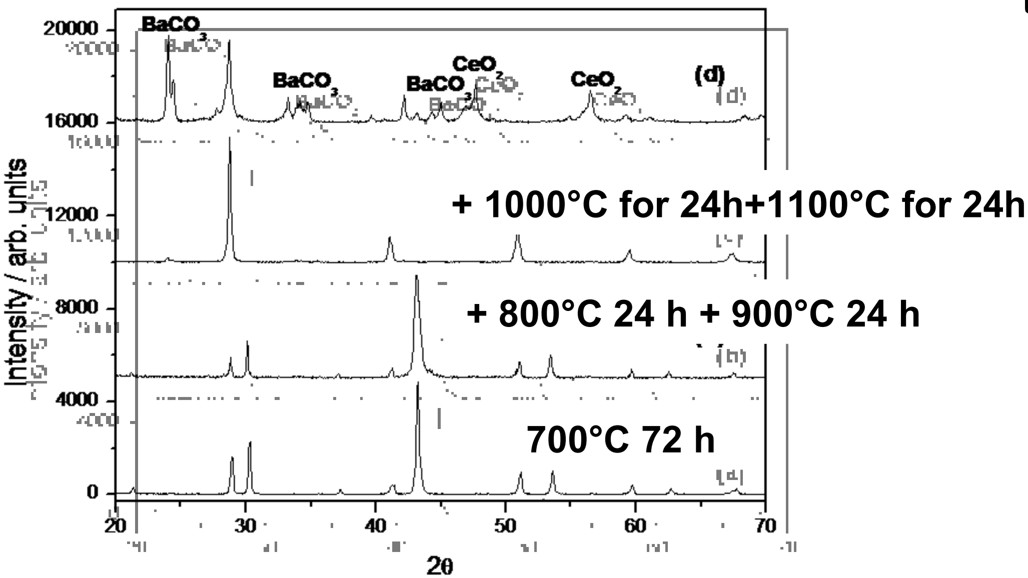
Interdiffusion & exposure to CO_2

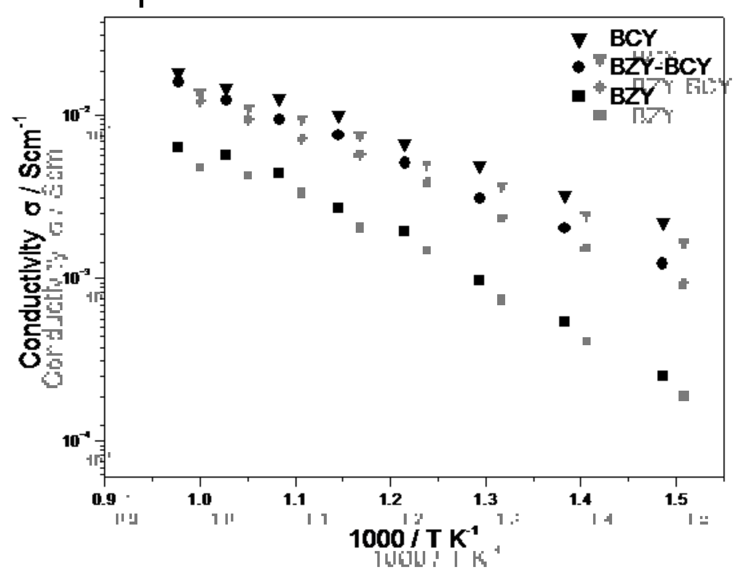




The [110] reflection of the BZY-BCY solid solution compounds falls between the [110] reflections of BCY and BZY

→in the case of thermally activated interdiffusion between BCY and BZY the presence of the characteristic peaks of solid solution compounds would be expected in the XRD plot

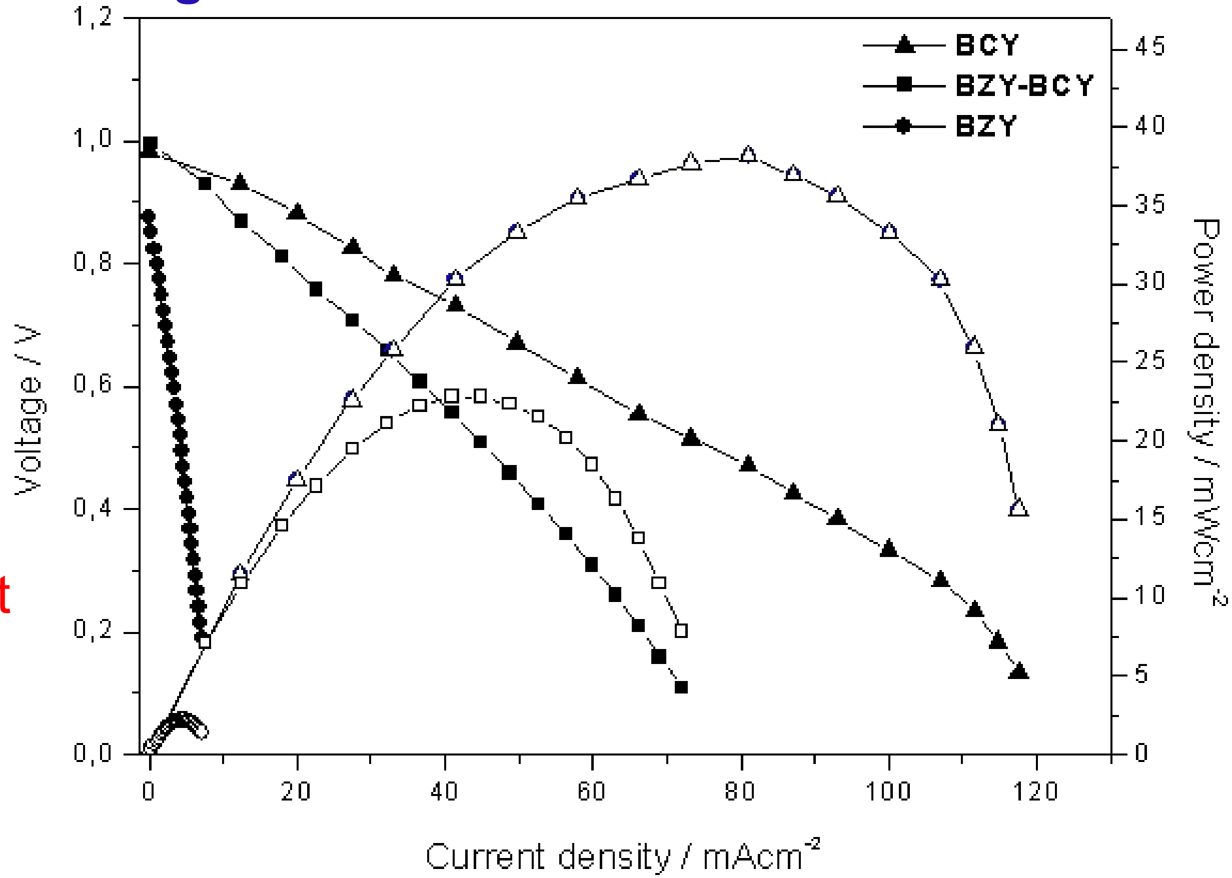




FC tests

Power density for the bilayer electrolyte over one order of magnitude higher than BZY

The cathode-reaction resistance (BZY side) significantly lowered the bilayer fuel cell performances rather than the electrolyte resistance with respect to the BCY electrolyte

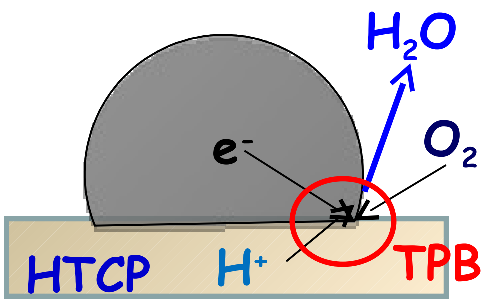


•Pt electrodes

Polarization curves and power output in humidified H_2 and air at 700°C of BZY-BCY bilayer, BCY and BZY electrolytes.

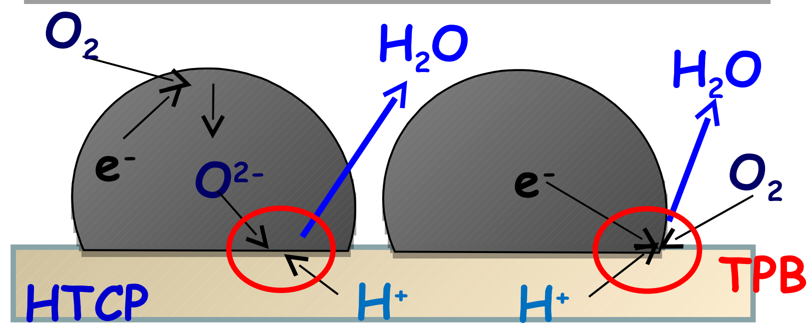
Cathodes for HTPC electrolytes

Electronic conductor cathode



Cathode reaction occurs only at the triple phase boundary (TPB)

Mixed O^{2-}/e⁻ conductor cathode

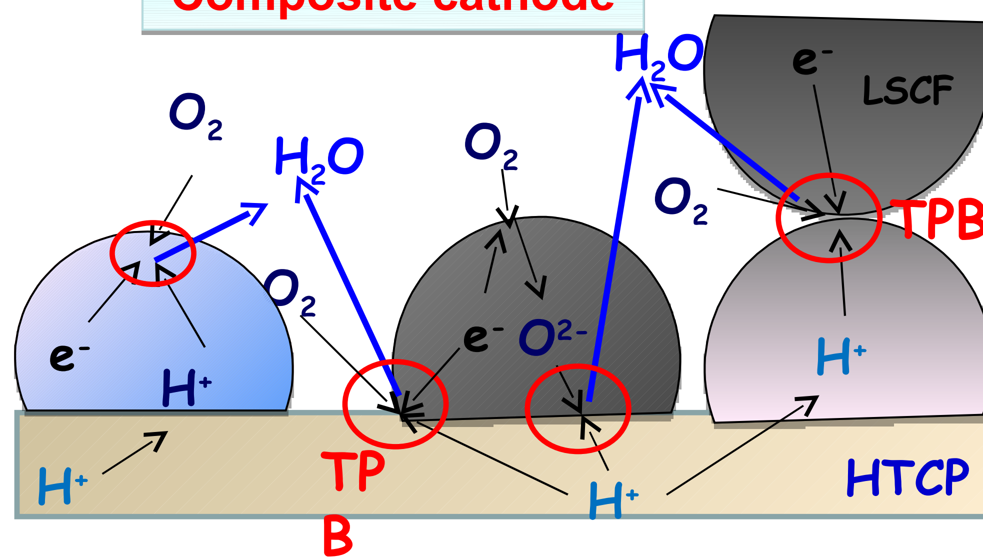


Cathode reaction occurs only at the electrode/electrolyte interface

Composite cathode

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF, mixed O^{2-}/e⁻ conductor)/ $BaCe_{0.9}Yb_{0.1}O_{3-\delta}$ (10YbBC, mixed H^+/e⁻ conductors) composite cathode:

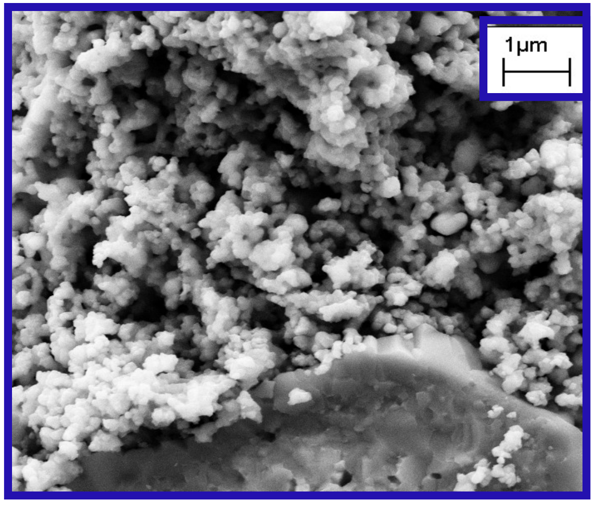
cathode reaction is extended to the whole cathode surface



Electrodes Optimization

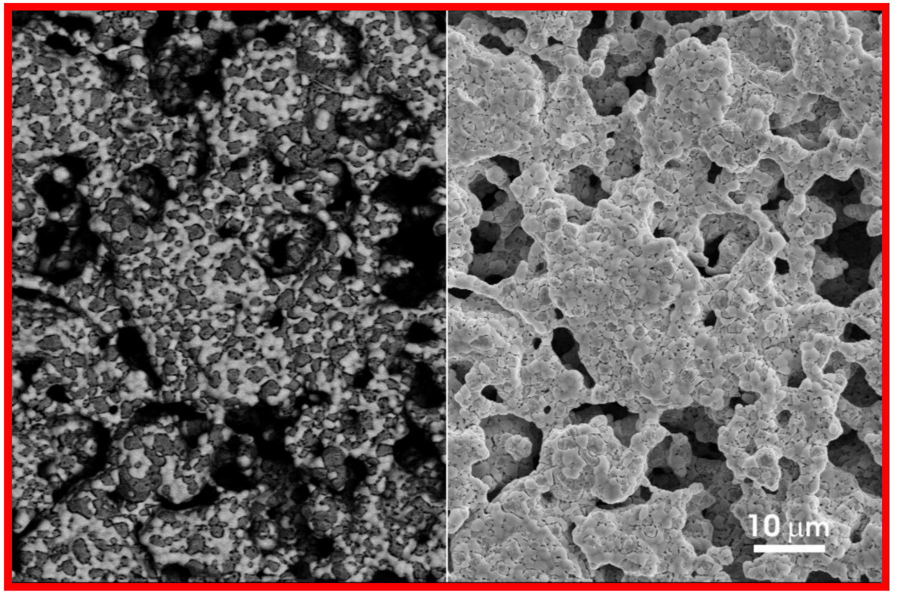
Composite cathode: LSCF/10YbBC

- Composition: 10YbBC (10-50 nm) - LSCF (0.3-0.4 μm)
- Chemical Stability: no chemical reactions up to 1100˚C
- Microstructure: proper porosity
- Lower ASR than single phase Pt electrode: enhanced cathode reaction site, better contact with the electrolyte



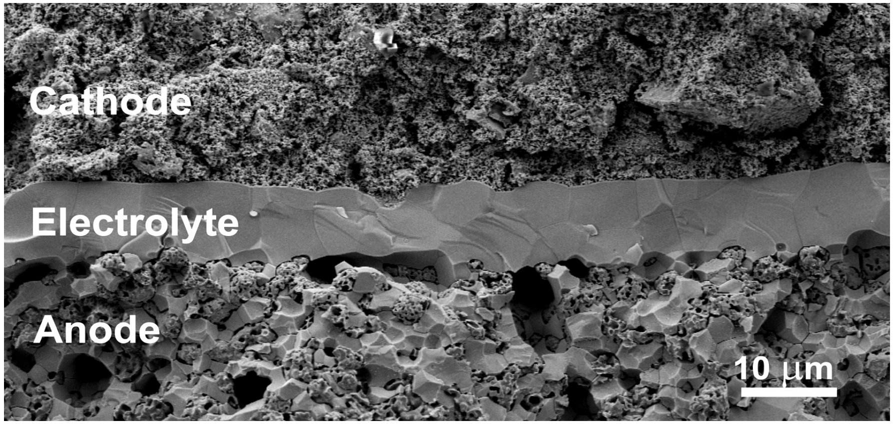
- Good connectivity
- Homogeneous dispersion
- Open porosity
- Micro porosity
- ASR=1.7-0.6 W cm2 @ 500-700°C

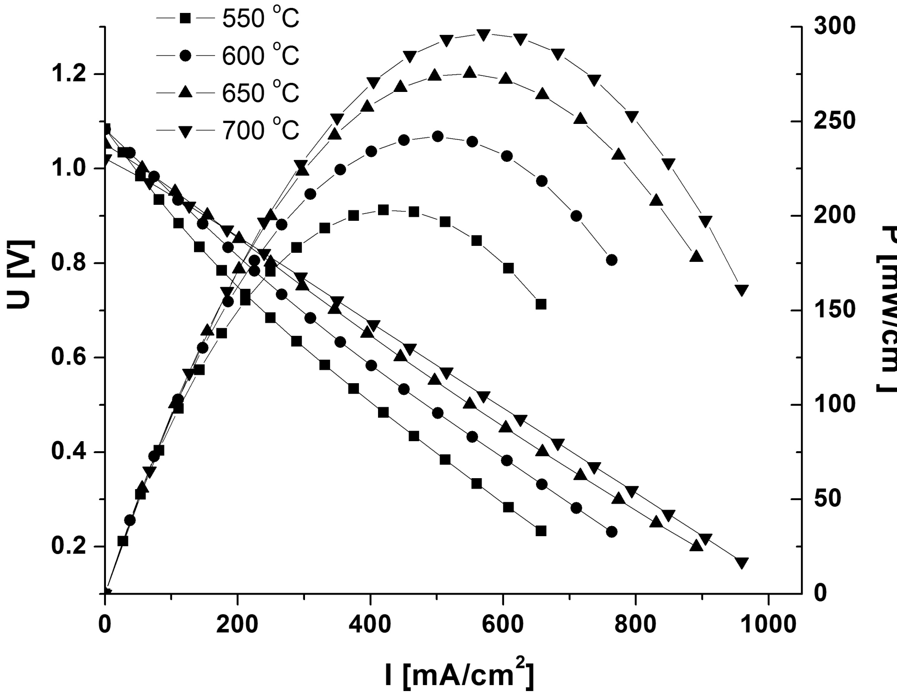
Anode: Ni-BCY 10



Our complete cell

Ni-BCY10/BCY10/LSCF-10YbBC



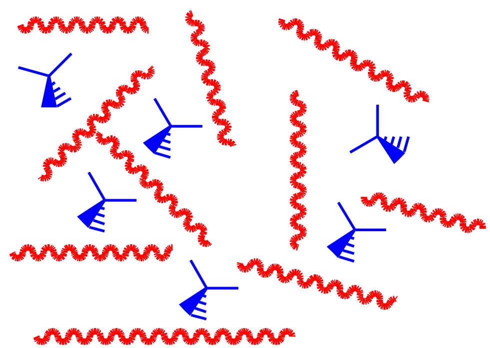


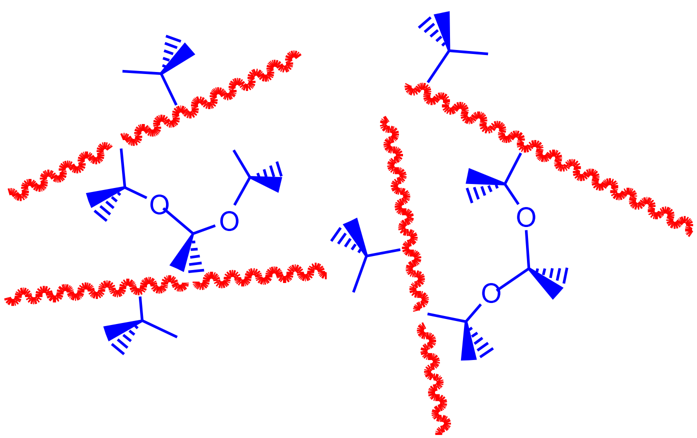
Anode supported cells by ElectroPhoretic Deposition (EPD) of electrolyte

our strategies for PEMFCs

develop innovative synthetic procedures to form hybrid electrolytes

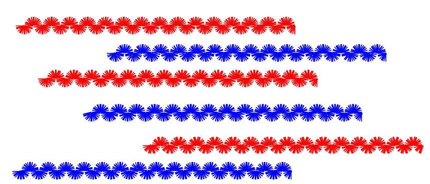
O/I weak interactions,
nanocomposites



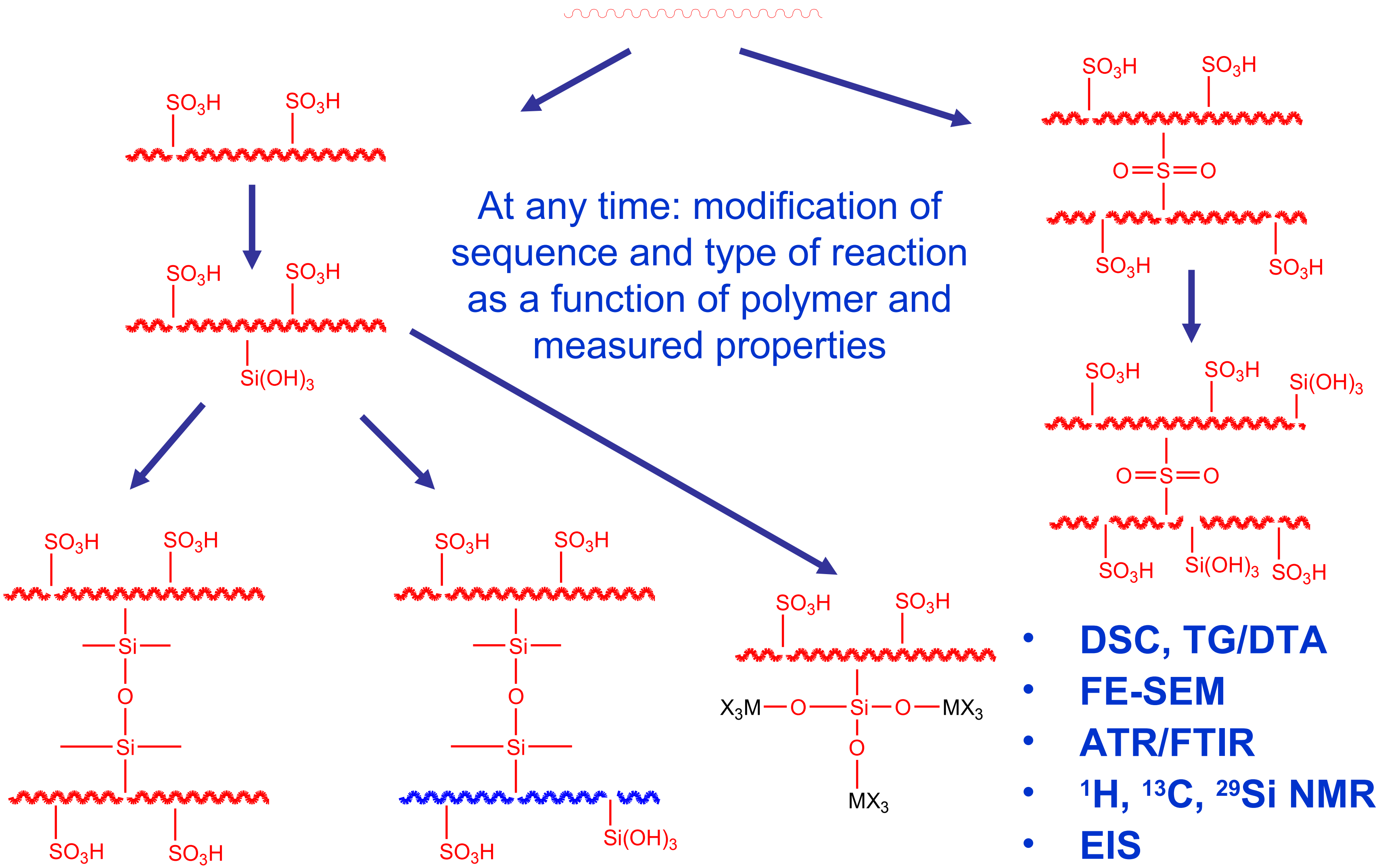


O/I covalent interactions

polymer blends



Hybrids: synthetic strategies



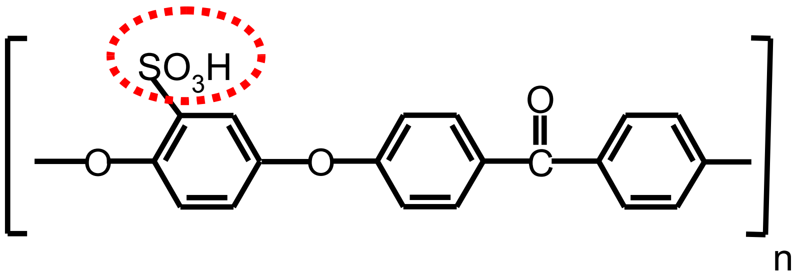
At any time: modification of sequence and type of reaction as a function of polymer and measured properties

- **DSC, TG/DTA**
- **FE-SEM**
- **ATR/FTIR**
- **^{1}H, ^{13}C, ^{29}Si NMR**
- **EIS**
- **FUEL CROSSOVER**

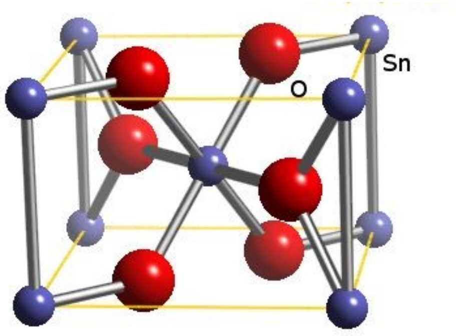
All data used in loops to implement synthetic procedures or design new ones

Organic/Inorganic Composites

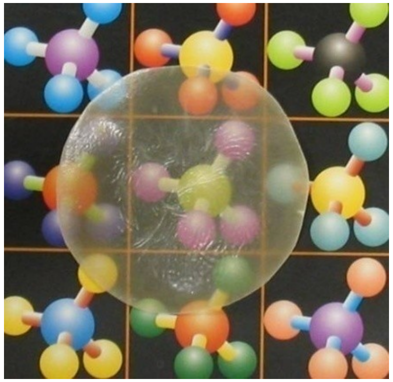
DISPERSION IN THE POLYMERIC MATRIX OF FILLERS WITH CONTROLLED FUNCTIONALITIES, DIMENSION AND MORPHOLOGY



Polymer:
SPEEK



Inorganic filler:
$SnO_2 nH_2O$

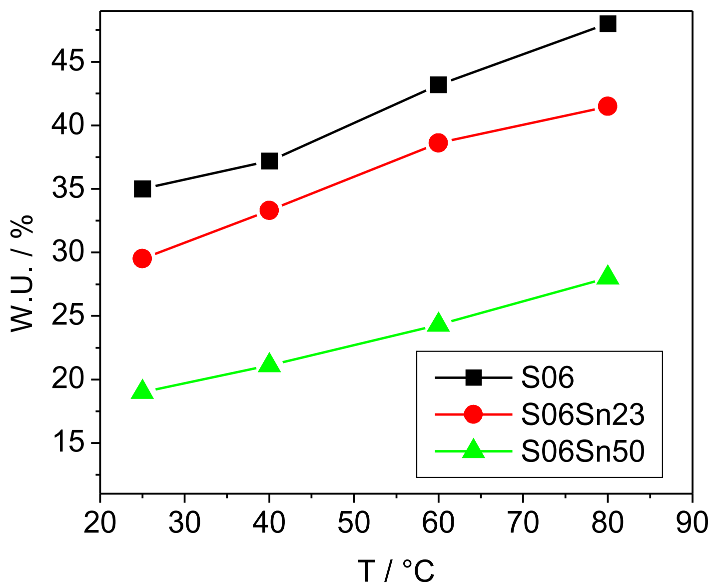


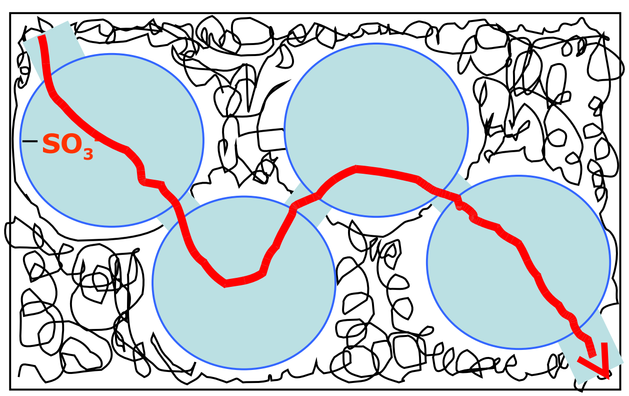
Composite membrane

INCORPORATION OF FILLER PARTICLES ALTERS TRANSPORT PROPERTIES AND MIGHT DECREASE FUEL PERMEABILITY

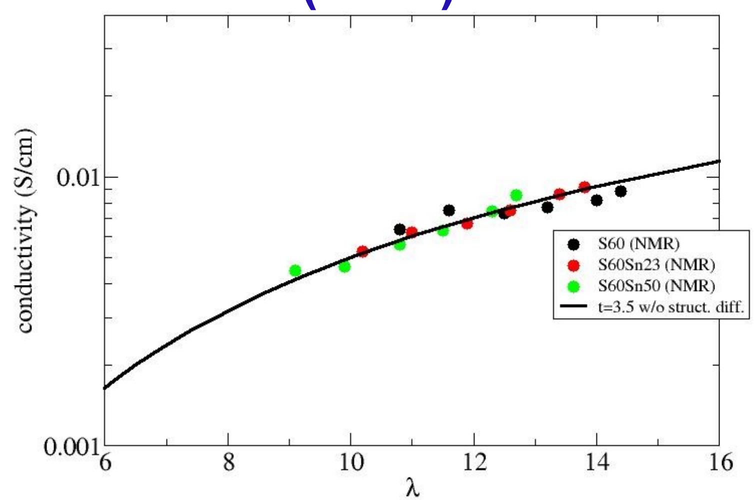
SPEEK/SnO$_2$ • n H$_2$O

Water uptake





Modeling analysis of experimental water diffusivity (NMR)

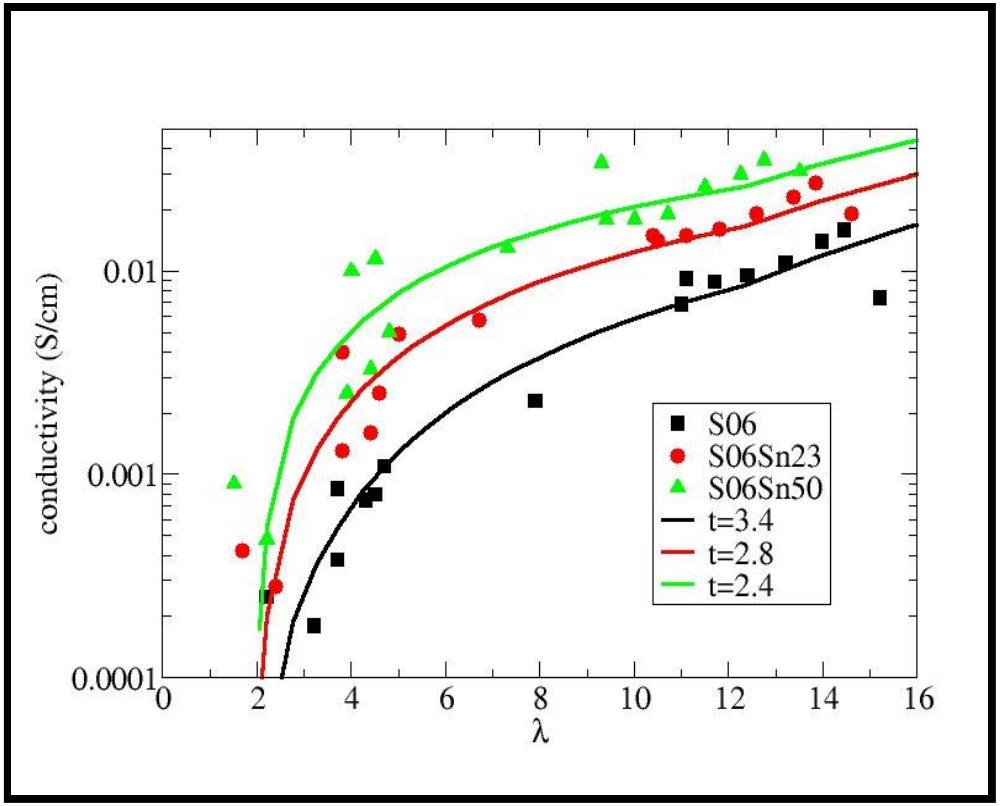


Sample	t (H$_2$O)
S06	3.5
S06Sn23	3.5
S06Sn50	3.5

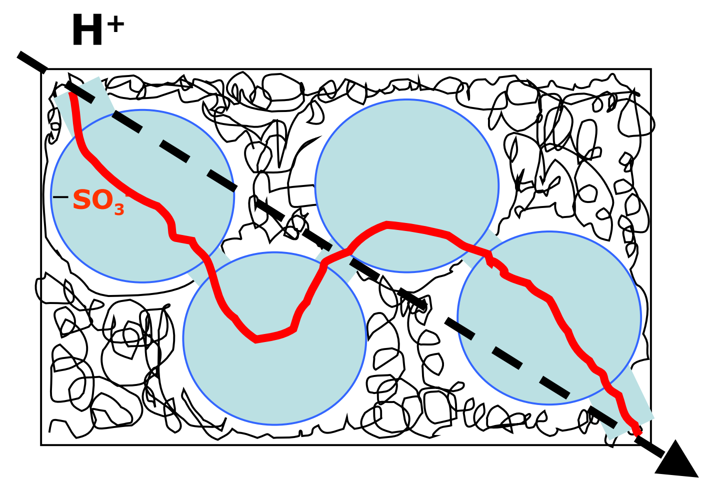
The filler presence leads to the worsening of water (and methanol) transport properties

SPEEK/SnO_2 • n H_2O

Modeling analysis of experimental proton conductivity (EIS)



Sample	t
S06	3.4
S06Sn23	2.8
S06Sn50	2.4



Beneficial and selective filler effect for H^+ trasport

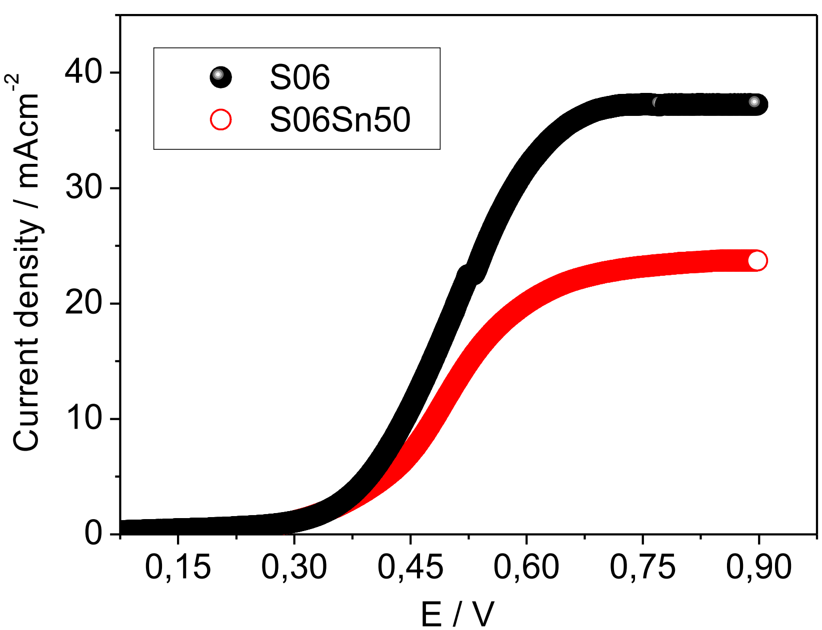
The reduced tortuosity for H^+ trasport leads to enhanced PROTON transport

DMFC: effect of filler on MeOH crossover

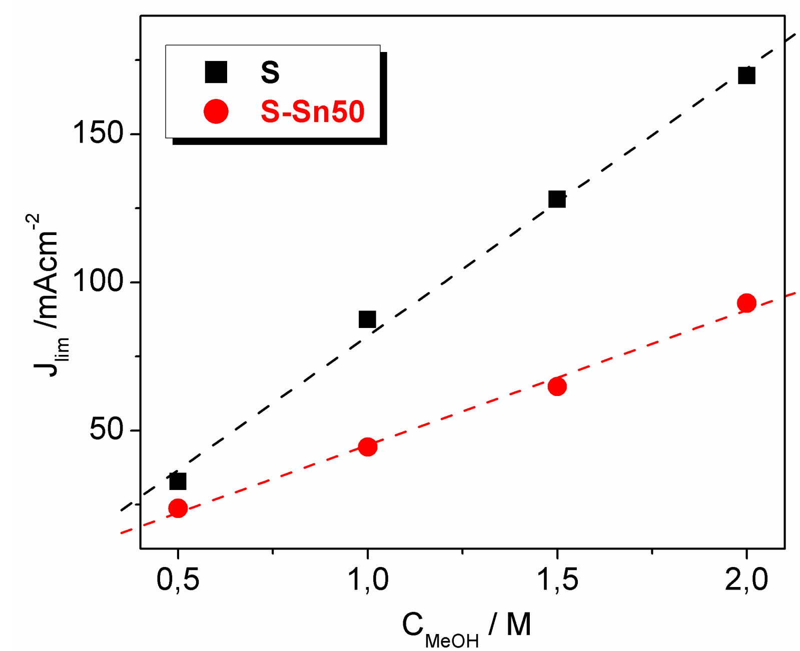
Limiting MeOH permeation current (J_{lim})

voltammetric method under DMFC test conditions supplying methanol and humidified N_2 and imposing an external voltage measuring $\mathbf{J_{lim}}$ resulting from the MeOH electro-oxidation process

J_{lim} vs E; T=60°C; [MeOH]=0.5M

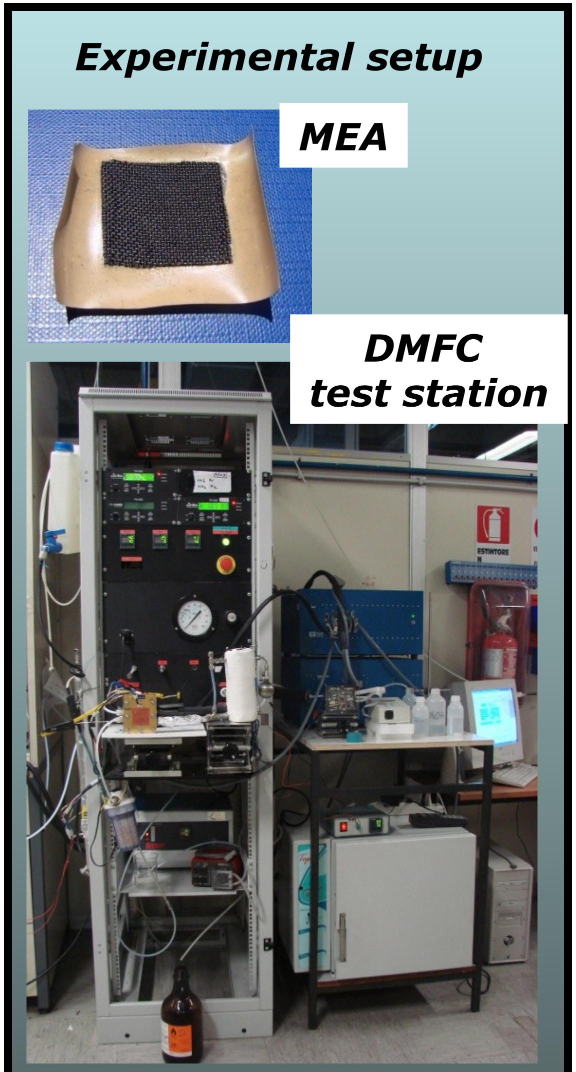


J_{lim} vs [MeOH]; T=60°C



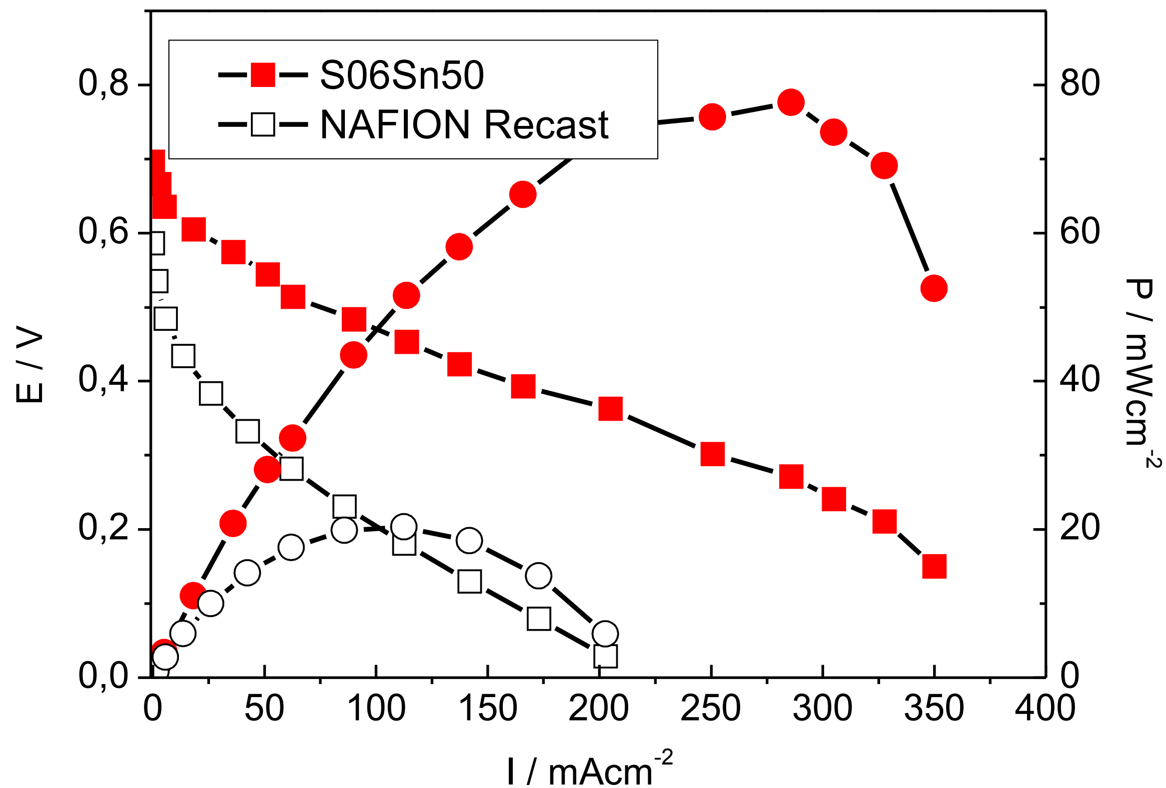
The composite shows lower J_{lim} than that of the unfilled SPEEK, indicating a beneficial effect of the filler in the reduction of the MeOH crossover

DMFC applications



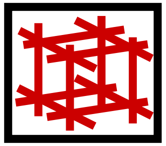
Polarization curves

T=100°C MeOH 2M anode feed O_2 cathode feed



Sample	I ($mAcm^{-2}$)	P ($mWcm^{-2}$)	OCV (mV)
S06Sn50	350	80	700
Nafion recast	200	20	600

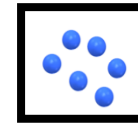
Health: Tissue Engineering



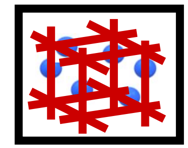
The design of the optimal scaffold as template for the tissue replacement

+

The best cell source for tissue repair



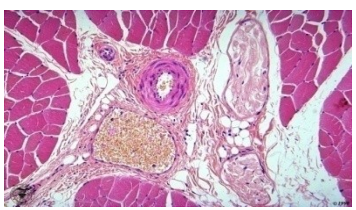
FUNCTIONAL ENGINEERED TISSUE



Polymer Scaffold: high porosity, adequate pore size, biodegradability, biocompatibility, proper mechanical properties

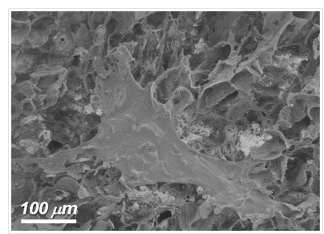
Natural components: hyaluronate, alginate, chitosan, spider silk

Synthetic polymers: poly-L-lactic acid, poly-caprolactone



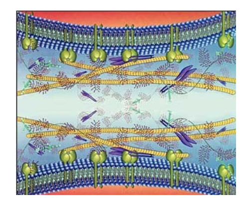
MACRO architecture
mm scale

Vascularization



MICRO architecture
µm scale

Cell size



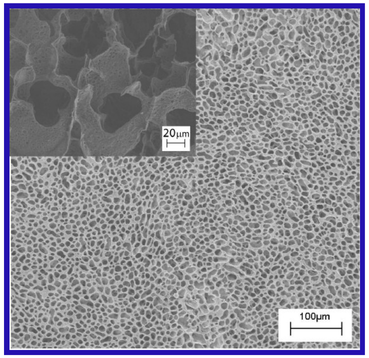
NANO architecture
nm scale

ECM

Cells and scaffolds must be interfaced: different size scales must be merged in a SINGLE STRUCTURE

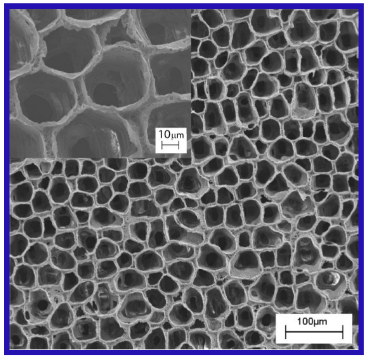
Scaffolds synthesis & processing

PHASE SEPARATION
as a function of T ➡ **DIFFERENT ARCHITECTURE** ⬅ **ELETTROSPINNING**
as a function of experimental setup



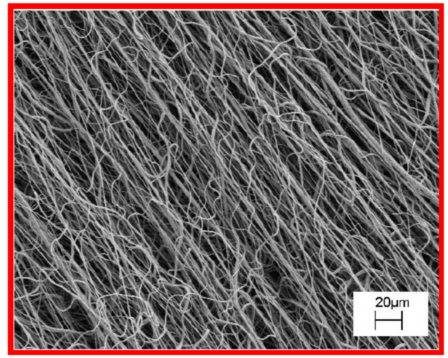
isthermal

porosity partially occluded



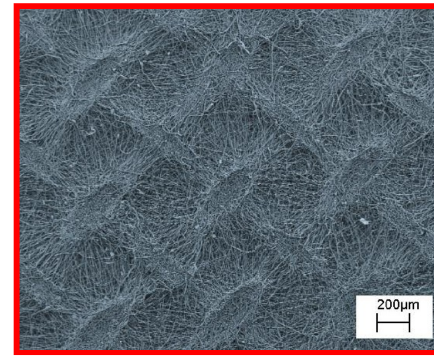
non isothermal

larger, interconneted porosity



parallel Cu bars

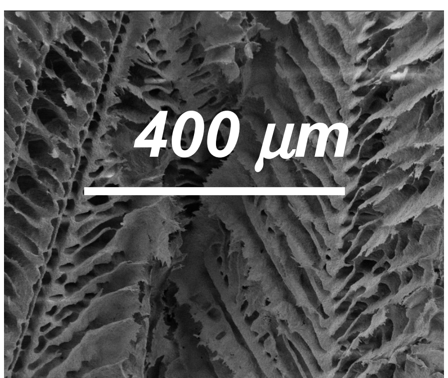
quasi-parallel fibers



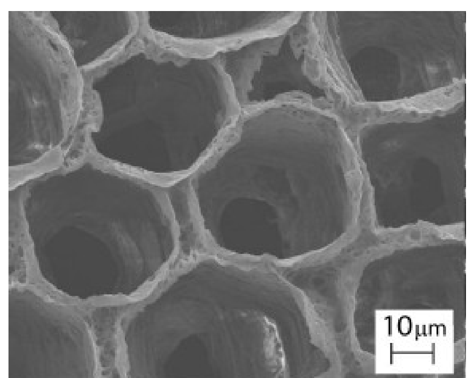
orthogonal Cu bars

macroscopic texture of µ- fibers

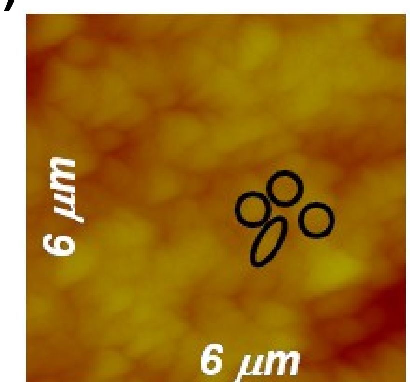
MULTIPLE length scale in a single scaffold (macro – micro - nano scale)



Vascularization



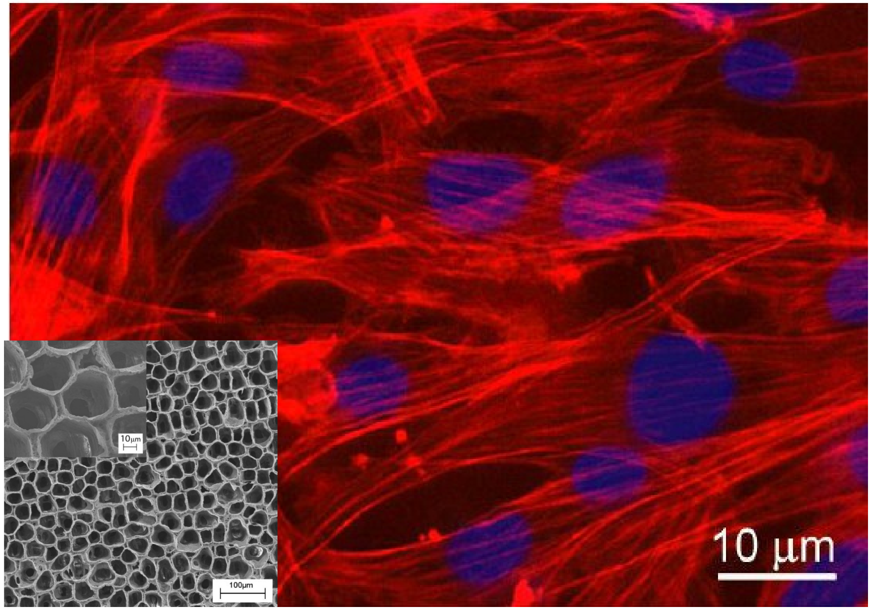
Cell accomodation

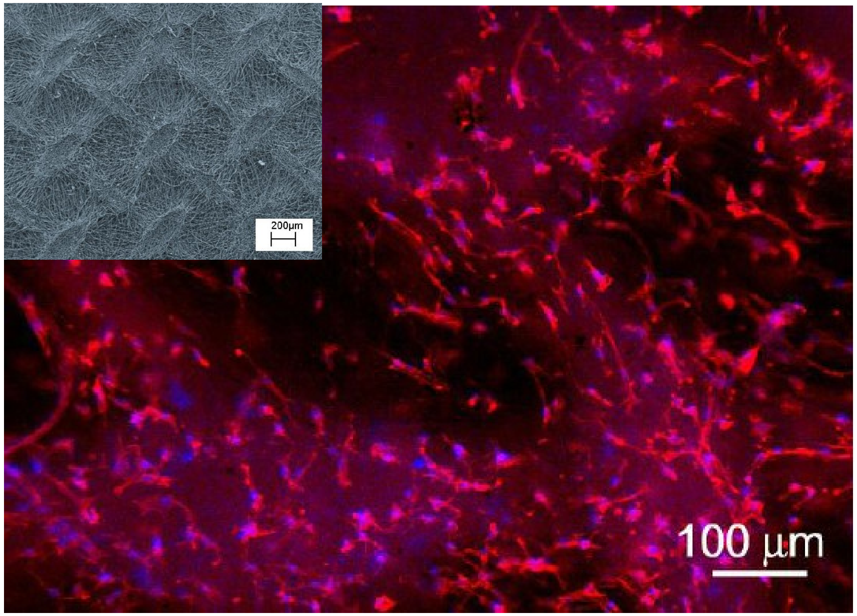


Expression of ECM components

Biological Validation

IMMUNOFLUORESCENCE





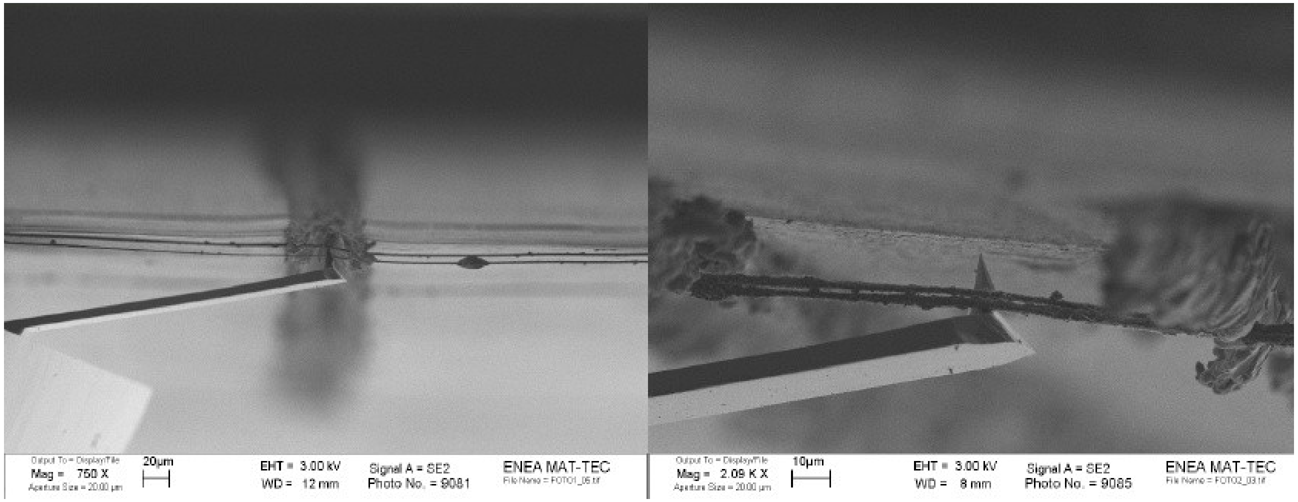
Typical elongated shape and well organized stess fibers

PS: Stem cells were able to colonize the pores and to adhere functionally to the scaffold

ES: Stem cells appeared to concentrate more in regions with higher density of fibers

Spider Silk

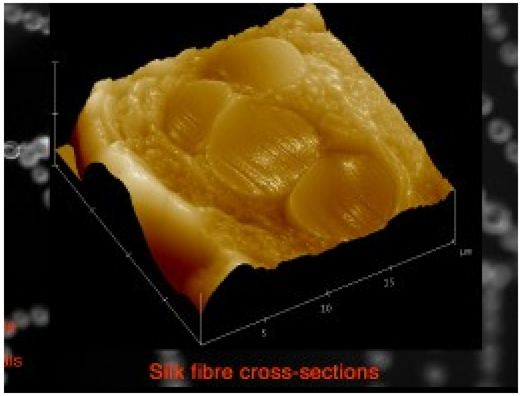
Natural proteic structures for engineered cell growth: tough spider fibers
***Unique mechanical properties:* high tensile strength, elasticity and toughness**



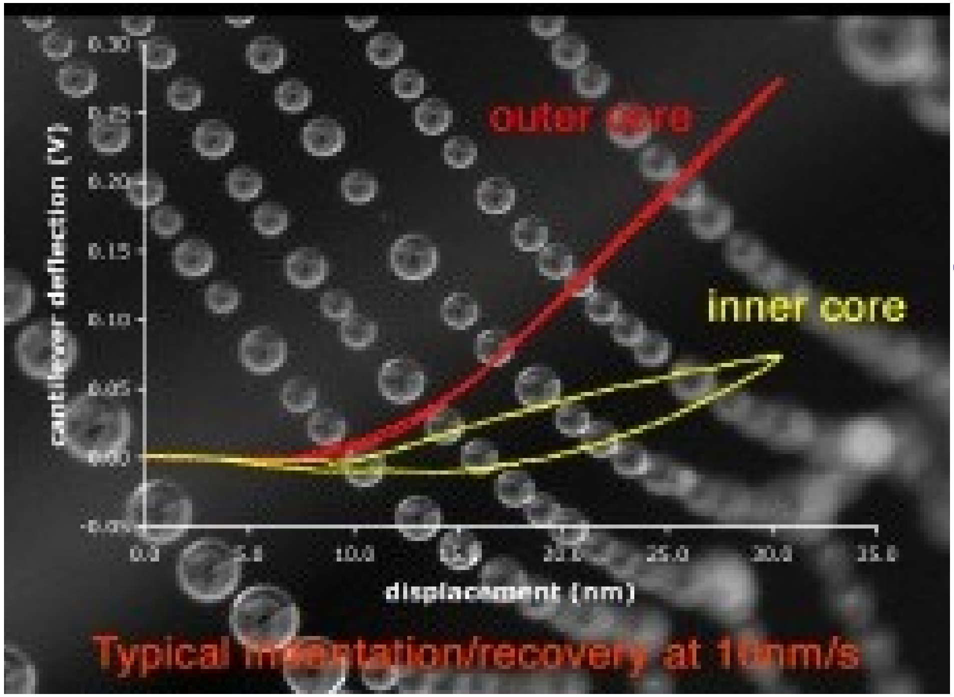
Probing fiber rigidity by AFM under electron microscopy observation

The most significant barrier to the application of silks in vivo is that the mecanichal qualities of synthetic spider silk, which are required for implantation, fall far below that of their natural counterparts.
Before effective synthetic silks can be produced, we need to better understand the mechanisms by which natural spirer silk acts under stress.

Spider Silk



Study of structure-function relationships in spider silk essential to instruct synthetic silk production.
Atomic force microscopy has been used in friction and indentation modes to investigate the fibre microstructure and its influence on viscoelasticity and water-induced softening.



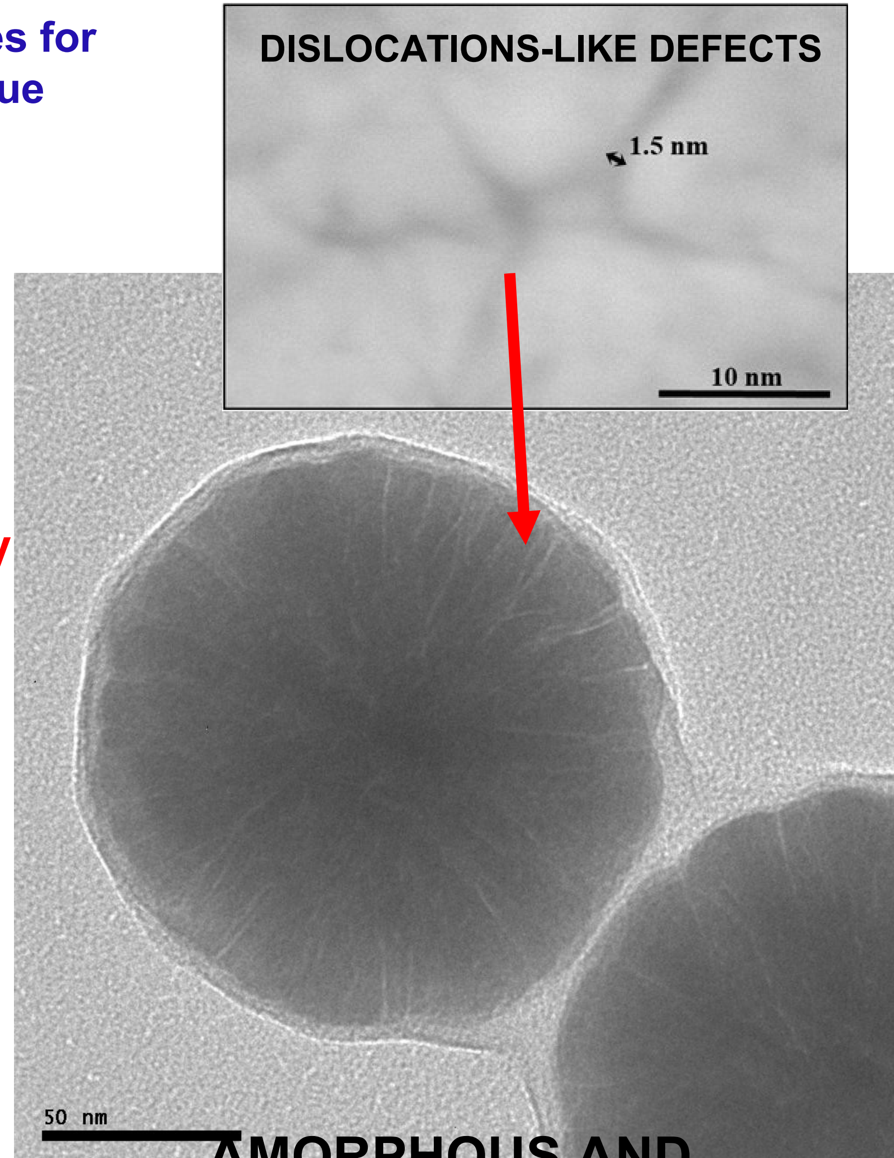
Significant differences in structure and elasticity observed in both inner and outer cores.
Inner core ca.30% softer than outer core.
No strain rate dependence observed in the stifness :this effect in bulk silk may manifest at the micro or interfibrillar scale and not at the nanoscale. The hysteresis in the inner core data, however, show some evidence of viscoelasticity.

Composite nanoparticles (CNP)

Analysis of properties of nanostructures for applications in MEMS/NEMS and tissue engineering

TEM images of Silica coated Co core magnetic nanoparticles (CNP) about 100nm in diameters intended primarily for medical application in Cancer treatments, but also in impact-energy absorbing material due to magneto-mechanical coupling.

After synthesis, a full characterization of individual core-shell nanoparticles (via TEM, SEM, AFM, nanoindentation and numerical modeling) reveals novel properties

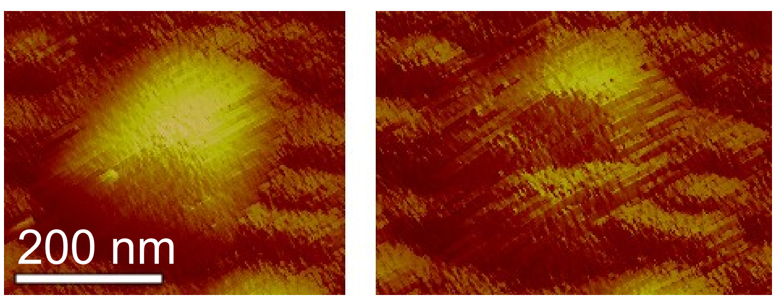


AMORPHOUS AND FULL OF RADIAL DEFECTS

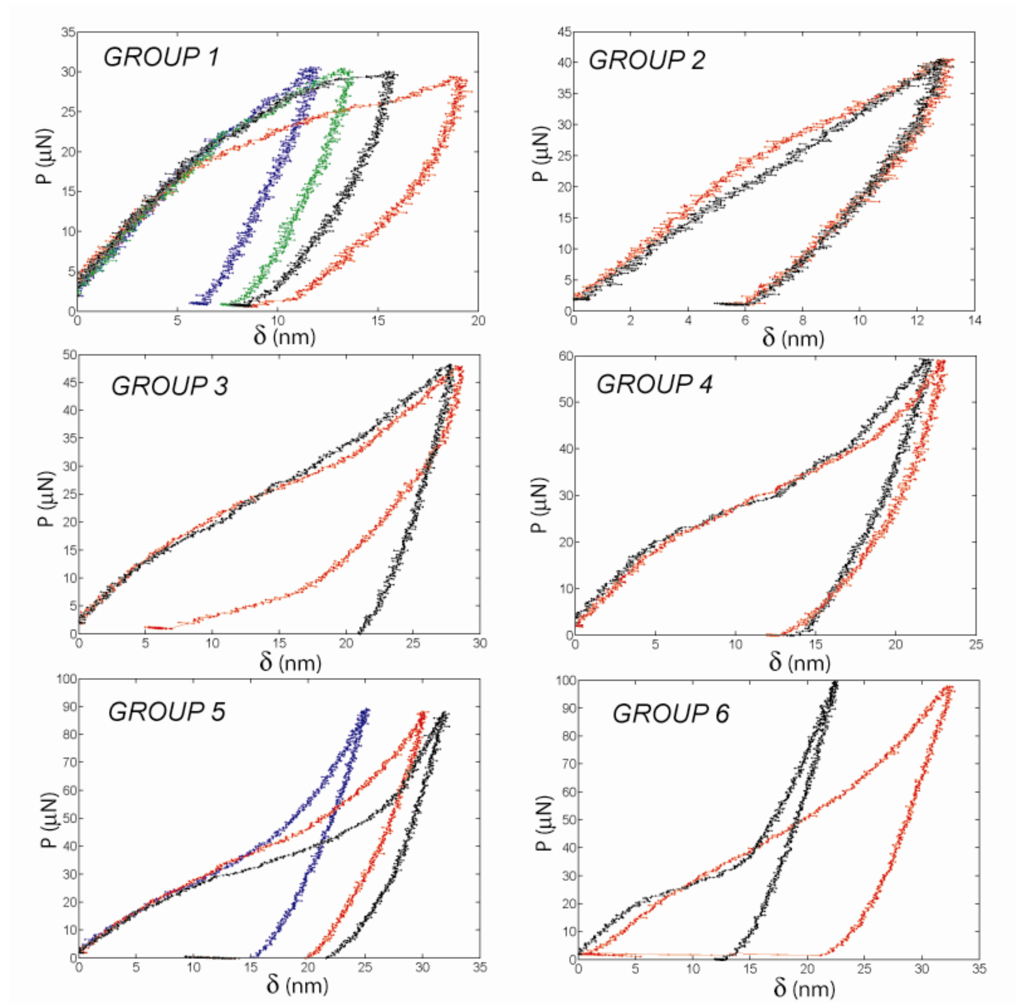
Composite nanoparticles (CNP)

Non conventional in-situ mechanical testing via instrumented nanoindenter were perfomed to measure the CNP compressive response in the 30-300µN load range

AFM image of a particle before and after testing

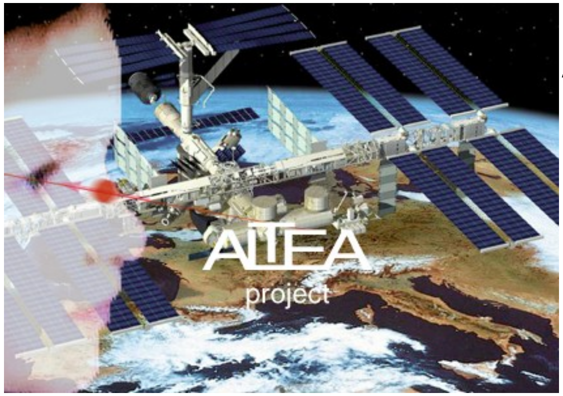


Sample data from compression tests



BIOMEDICAL DEVICES

electroneurological measurements in extreme conditions



Anomalous Long Term Effects in Astronauts

Correlation between passage of cosmic rays particles through the brain and neurological activity during long space missions: physical analysis of cosmic radiation and concurrent EEG acquisition

Main problems of conventional electrophysiological measurements (EEG, VEP etc.) :

Skin cleaning (time consuming)
Liquid electrolytes (not suitable in no gravity conditions)
Electrode materials commonly used are not suitable for use in extreme conditions (space, uncooperative patients, multielectrode registrations, monitoring of epilepsy, emergencies…)

Solutions:
Development of alternative materials for electrolytes

Requirements:
high conductivity (>10^{-3} – 10^{-4} Scm^{-1}), chemical stability, non-toxicity, appropriate mechanical characteristics, low skin/electrolyte interfacial resistance

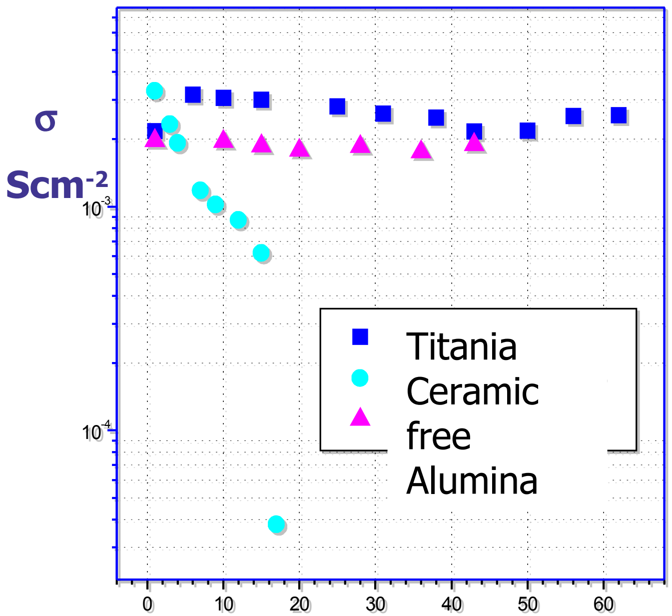
Nanocomposite electrodes

PMMA + DEE + $LiClO_4$ + H_2O + EtOH + x % M_xO_y → IONOCONDUCTING (Li^+) MEMBRANE

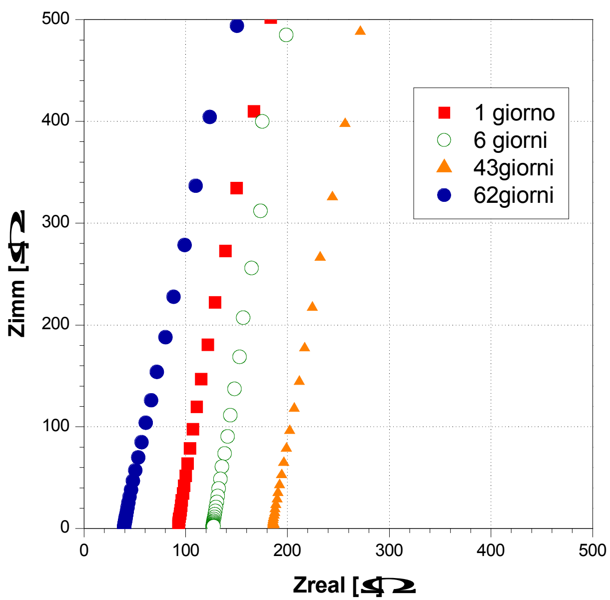
M_xO_y = SiO_2 (7 nm), Al_2O_3 (acidic, basic, neutral) (6 nm), TiO_2 (12 nm)   x = 5-10%

Characterization: EIS, MAS-NMR, ATR-FTIR

$9.88\ 10^{-4} \leq \sigma \leq 3.20\ 10^{-3}$ Scm^{-2}

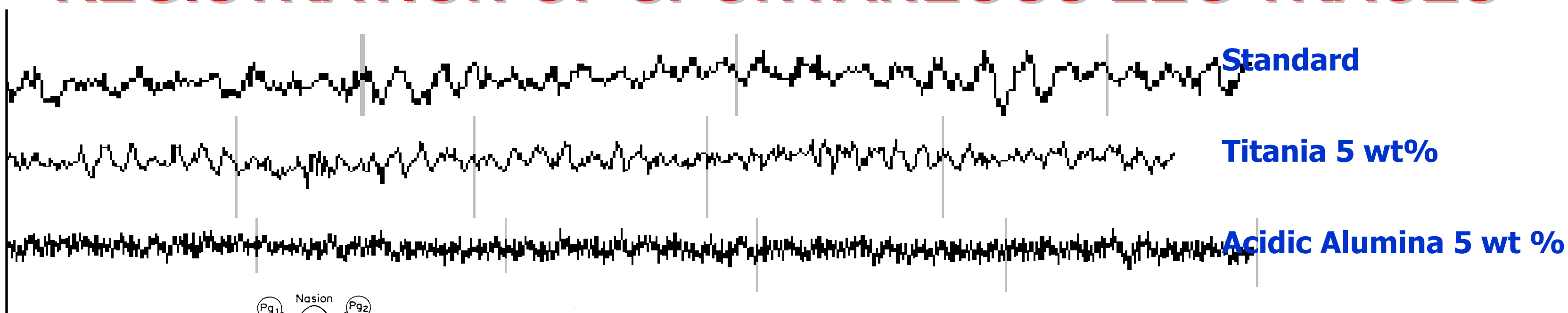


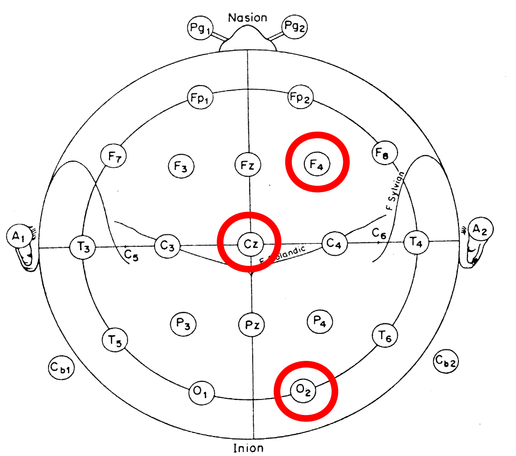
Time evolution of conductivity of nanocomposite membranes containing 5 wt% ceramic powder at RT



Time stability of the nanocomposite membrane:
SS / $LiClO_4$-DEE- PMMA + 5% TiO_2 / SS
(EIS, 1Hz-100 kHz, RT)

NANOCOMPOSITE MEMBRANES ALLOW THE REGISTRATION OF SPONTANEOUS EEG TRACES





Head projection with the standard localization of the electrodes used for neurological registrations.

Skin cleaned for the standard

NO skin preparation or cleaning for the nanocomposite membranes!

SOFCs: conclusions

optimized sol-gel synthesis allowed to obtain pure and homogeneous proton conducting Zr-substituted Y-doped barium carbonate oxides at low processing T

chemical stability under CO_2 atmosphere was evaluated confirming the good chemical stability of Y-doped barium zirconate and the decreasing reactivity of the BCZY oxides with increasing Zr content

hydrogen-air fuel cell tests were carried out using BCZY electrolyte with different Zr-content, finding the best compromise between power output an chemical stability

PLD allowed to prepare a BZY-BCY bilayer electrolyte that seems to be a promising solution to obtain a stable proton conductor electrolyte without compromising much the electrical conductivity.

Further control in the interface microstructure and film thickness might increase the power output performance,

Different electrodes were designed and tested on HTPC based fuel cells

PEMFCs: conclusions

different methods have been explored to modify the physico-chemical properties of conducting polymers to achieve the modulation of properties which is a prerequisite for the selection of proper materials for PEMFCs

combination of different materials and/or chemical modifications of aromatic polymers afford systems where new positive interactions occur between the different components

the presence and proximity of conducting groups on all components contribute to the generation of a cooperative effect

Improvement of thermal, mechanical, solubility and electrochemical properties

Tissue Engineering: conclusions

Nanoscience
Nanotechnology
Innovative Instrumentation

- Combined AFM/SEM observation allow to investigate the mechanical properties of spider silk, setting the base for a deeper understanding of their structure/function properties.
- Phase separation and electrospinning allowed the fabrication 3D multiscale polymeric scaffolds exhibiting features on different length scales, whose properties can be finely tuned by controlling the process parameters.
- Modifying the temperature profile of a phase separation process, is a low-cost and user-friendly operation, enabling scaffold architecture in a broad range of length scales.
- Changing the materials (e.g., polymer, solvent, the composition of the
- solution) and/or the experimental setup (e.g., applied voltage, electrode distance, electrode pattering) can radically transform the appearance of the electrospun fibre network.
- Adult stem cells adhered and proliferated onto the fabricated constructs, demonstrating the cytocompatibility of the materials used.
- The relationship between confined volumes (nanosized structures) and applied stress has been investigated. In core-shell structured silica-coated cobalt boride nanocomposites, a combination of quantitative *in situ* compression tests and contact theory, aided by finite-element analysis for estimating Young's modulus and hardness, led us to show the direct correlation between mechanical data with nanostructural evolution.

Acknowledgements

Those who **really** did the work!

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TODAY TOMORROW TOYOTA

all of you for your attention!

Il mio mestiere vero, quello che ho studiato a scuola e che mi ha dato da vivere fino ad oggi, è il mestiere del chimico. (….)
Noi montiamo e smontiamo e delle costruzioni molto piccole. (….) Siamo come dei ciechi perchè le cose che noi manipoliamo sono troppo piccole per essere viste anche con i microscopi più potenti; e allora abbiamo inventato diversi trucchi intelligenti per riconoscerle e manipolarle senza vederle.

Primo Levi, *La chiave a stella,* 1978