UNIVERSITÀ DEGLI STUDI DI PADOVA

Hydrogen and Fuel Cells Related Activities at the University of Padova

Chemistry of Materials for the Metamorphosis and the Storage of Energy (CheMaMSE)

http://www.chimica.unipd.it/lab_DiNoto/index.html

Team Leader – *Prof. Vito Di Noto*

E. Negro

Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, I-35131 Padova (Pd), Italy

5th IPHE H2igher Educational Rounds Rome, 1 December 2014

Members of “CheMaMSE” research group

Team Leader

Prof. Vito Di Noto

Research Associates

Dr. Giuseppe Pace *Dr. Sandra Lavina* *Dr. Enrico Negro*

Postdocs

Dr. Federico Bertasi *Dr. Keti Vezzù*

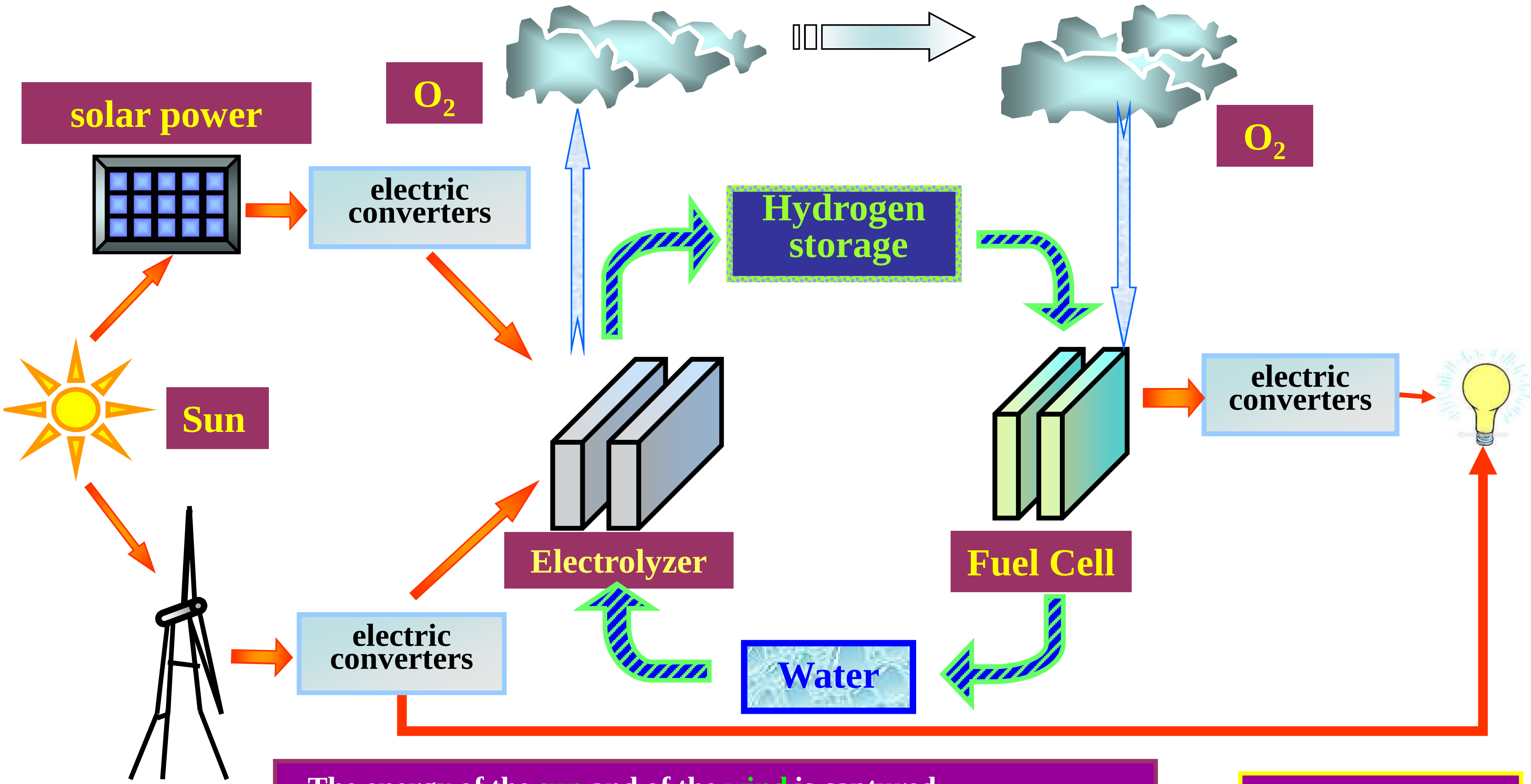
Dr. Ricardo Gonçalves Carvalho *Dr. Graeme Nawn* *Dr. Susana Solano Arana*

Ph.D. Students

Dr. Nicola Boaretto *Dr. Gioele Pagot*

http://www.chimica.unipd.it/lab_DiNoto/index.html

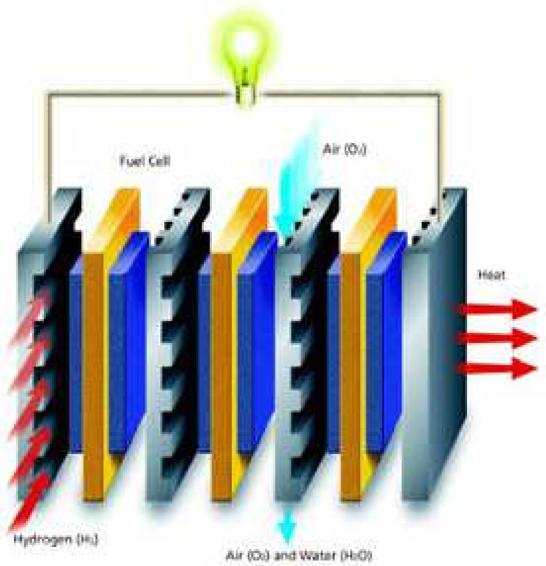
The Hydrogen Economy



- The energy of the sun and of the wind is captured.
- Hydrogen is used as a vector, to store the energy when the sources are not available.
- Fuel cells are used to extract the energy from the hydrogen.

- No CO_2 emissions.
- Delocalized production.

Energy technologies - Introduction



- ***Fuel Cells (FCs)***

Energy conversion devices able to convert the chemical energy stored in the reactants (i.e., H_2, alcohols) **directly into electrical energy, with a high efficiency (over 60%)** and no emissions of pollutants

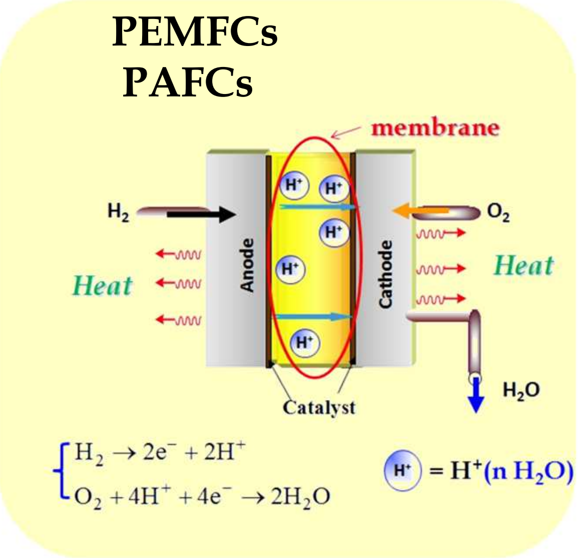
[1]

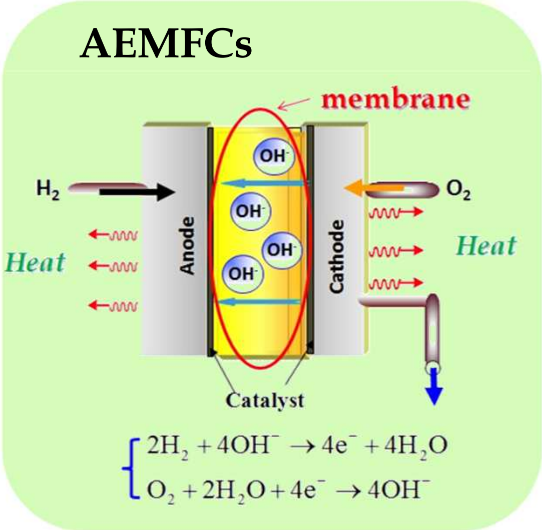
- ***Electrolysers (ELs)***

Use electrical energy to split water into its fundamental components (H_2 and O_2). **High-purity products** (more than 99.9995%) are obtained.

[1] Electrolyzers produced by Strumenti Scientifici Cinel on the basis of the patent WO 2011/080789 A1 developed in collaboration with UNIPD.

Overview of fuel cell families



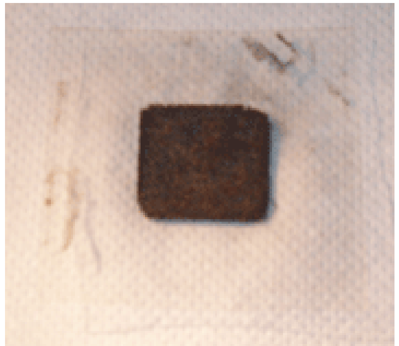


Fuel Cell Type	Temperature	Electrolyte/Charge Carrier	Applications
Phosphoric Acid and Polymer / Phosphoric Acid	150 – 200°C	H_3PO_4, Polymer/ H_3PO_4/ H^+	Distributed power Transportation
Polymer Electrolyte Membrane (PEMFC)	50 – 100°C	Perfluorosulfonic acid / H^+	Distributed power Portable power Transportation
Direct Methanol (DMFC)	50 – 100°C	Perfluorosulfonic acid / H^+	Portable power
Alkaline (AFC)	25 – 75°C 100 – 250°C	Alkaline polymer, KOH / OH^-	Portable power Backup power
Molten Carbonate (MCFC)	600 – 700°C	$(Li, K, Na)_2CO_3$ / CO_3^{2-}	Distributed power
Solid Oxide (SOFC)	500 – 1000°C	Yttria-stabilized Zirconia ($Zr_{0.92}Y_{0.08}O_2$) / O^{2-}	Electric utility Distributed power

The Memebrane-Electrode Assembly

The core functional component of FCs and ELs ***is constituted by an electrolyte separator sandwiched between two bi-dimensional electrodes***

Such an arrangement is a "Membrane-Electrode Assembly" (MEA)



Functions carried out by

ion-exchange membrane

1. Separation between the contents of the anodic and cathodic compartments of the device;
2. Selective ion migration between the two electrodes;
3. Electronic insulation between the two electrodes;

electrode configurations

4. Promotion of the kinetics of the electrochemical processes at both electrodes;
5. Support for the electrochemical processes at the basis of the device operation;
6. Supply of reactants and removal of the reaction products;
7. Electronic contact of electrocatalytic sites with the external circuit.

Overview of the Research Activities

Development of new functional materials

Ion-exchange membranes

- Facile and selective ion migration;
- Negligible electron conductivity;
- Low permeability to the reactants;
- Good mechanical properties.

→ ***Improved power density***

Electrode configurations

- High turnover frequency at low overpotentials;
- Low loading of noble metals.

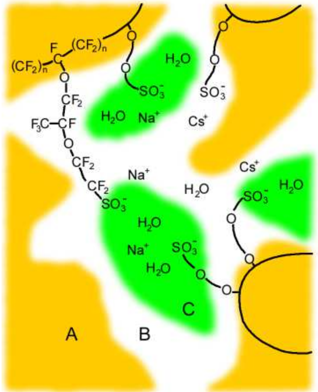
→ ***Improved energy conversion efficiency***

Development of MEAs and tests in single-cell configuration

- Efficient transfer of the performance of the functional materials

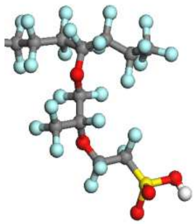
Ion-Exchange Membranes

Proton Exchange Membranes (PEMs)

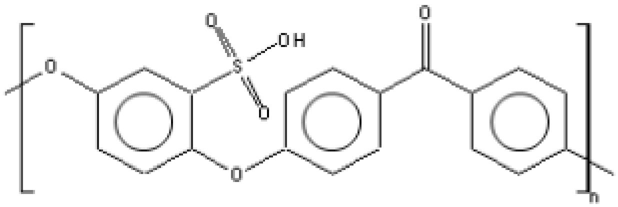


Adapted from: H.L. Yeager, A. Steack, J. Electrochem. Soc., 128, 1880, 1981

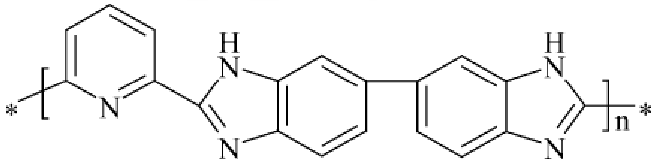
- ✓ {Nafion/[$(ZrO_2)(Ta_2O_5)_{0.119}]_x$} membranes
- ✓ SPEEK with different degrees of sulfonation
- ✓ PBI5N and PBI5N(SiO_2-Im)



Nafion



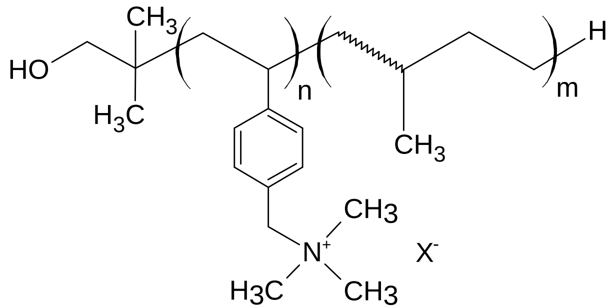
SPEEK



PBI5N

Anion Exchange Membranes (AEMs)

- [PVBTMA][Br]-b-PMB, labeled Br (IEC = 2.2);
- Three [PVBTMA][OH]-b-PMB AEMs, labeled A, B and C, with IEC = 1.14, 1.64 and 2.03, respectively (degree of functionalization, DF, in the range: 41.8 ≤ DF ≤ 80.7%).



[1] V. Di Noto et al., J Power Sources, 198 (2012) 66.
[2] V. Di Noto et al. Int. J. Hydrogen Energy 37 (2012) 6199 .
[3] V. Di Noto et al. Int. J. Hydrogen Energy 37 (2012) 6317 .
[4] V. Di Noto et al. Int. J. Hydrogen Energy 37 (2012) 6169.
[5] V. Di Noto et al., J. Am. Chem. Soc. 134 (2012) 19099-19107.
[6] Di Noto V. et al., RSC Adv. 3 (2013) 18960- 18969

Preparation of nanofiller

ZrO_2 → Hard

DMF

Ta_2O_5 → Soft

Planetary ball Mill

Tungsten carbide grinding jars

10 h
500 rpm

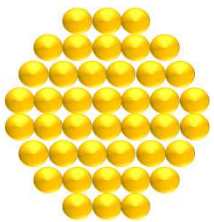
Dispersion A

$[(ZrO_2)(Ta_2O_5)_{0.119}]$

$$0.119 = \frac{mol_{Ta_2O_5}}{mol_{ZrO_2}}$$

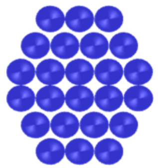
Nanometric "core-shell" clusters of "hard" ZrO_2 oxide homogeneously covered by a layer of "soft" Ta_2O_5 oxide

Mohs' hardness ~8.5



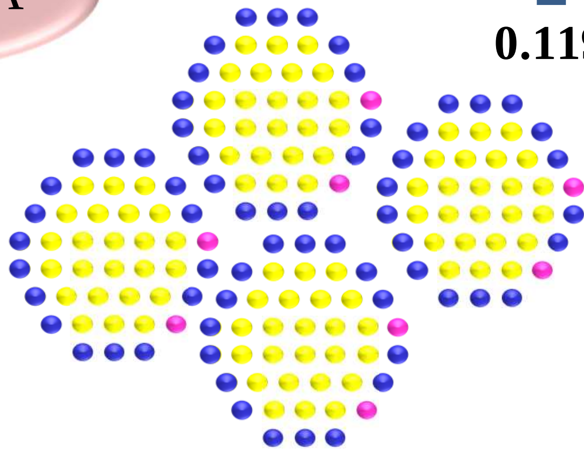
Hard

Mohs' hardness ~7



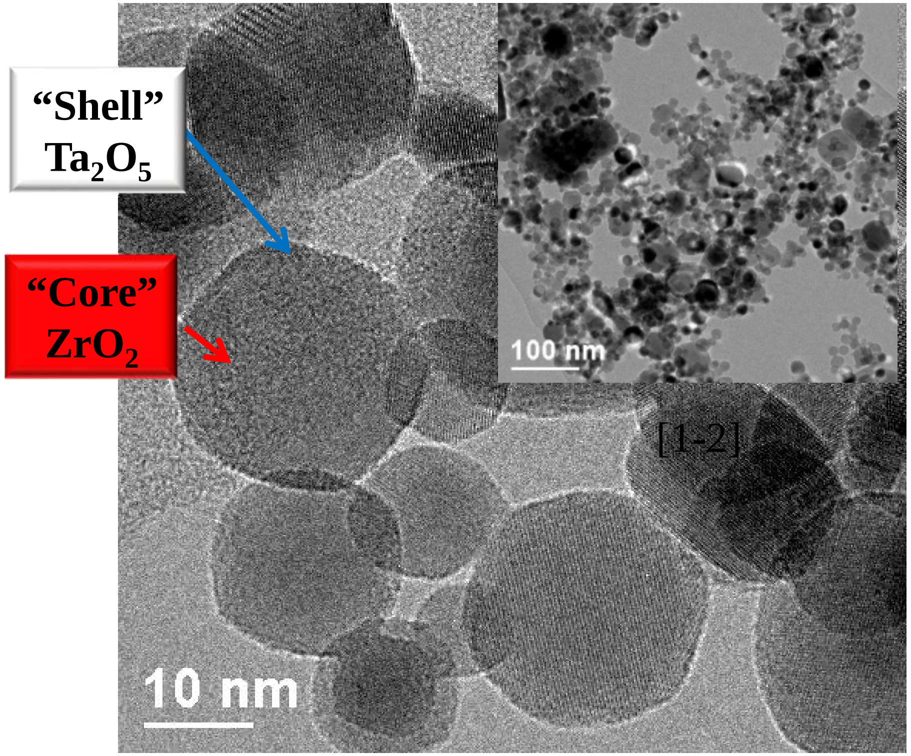
Soft

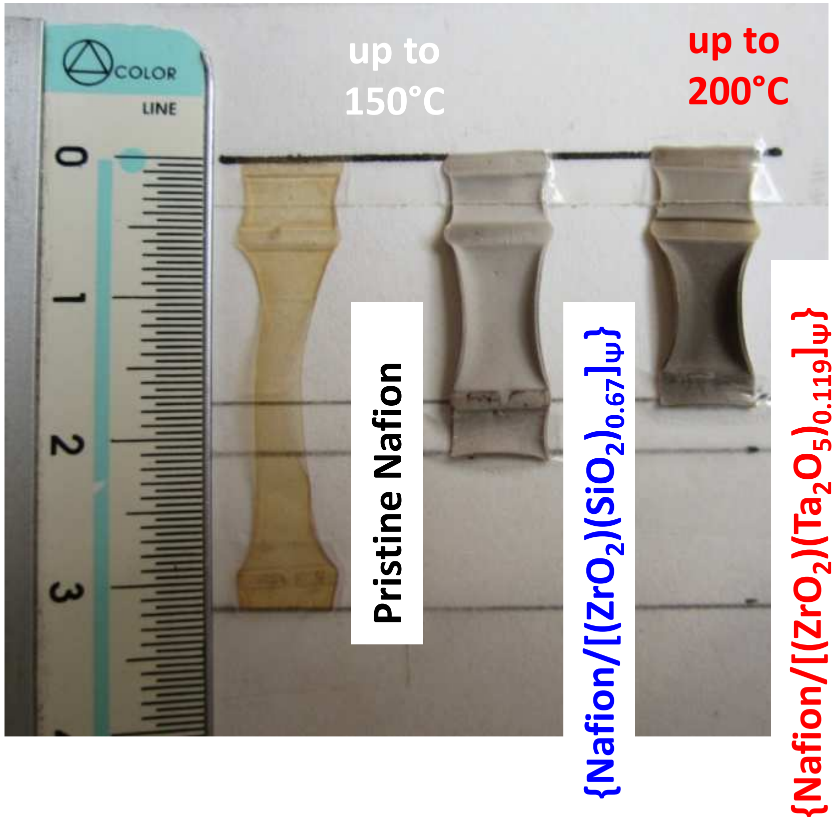
Ball milling



Morphology and mechanical properties

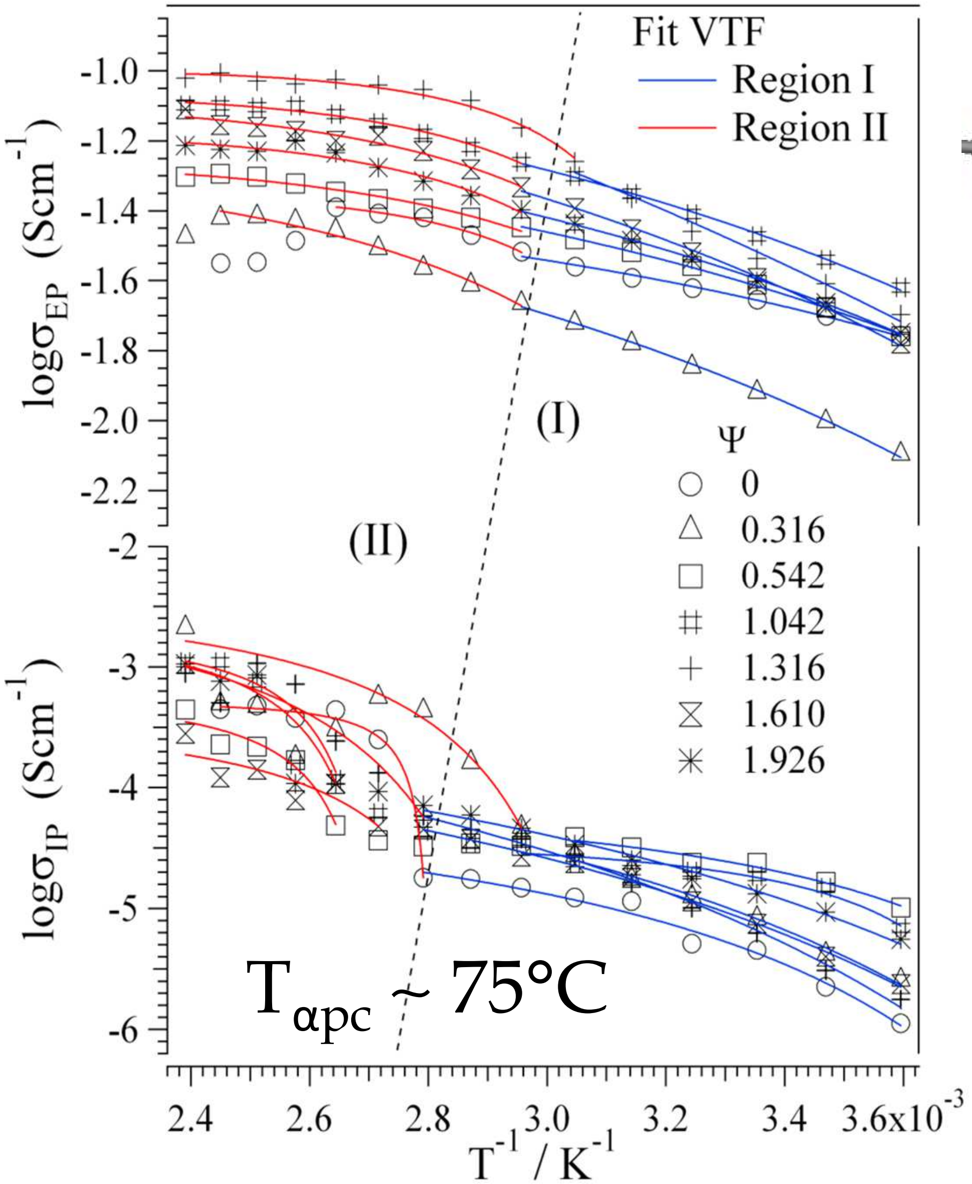
$[(ZrO_2)(Ta_2O_5)_{0.119}]$ Oxo-clusters with a size of ca. 30 nm

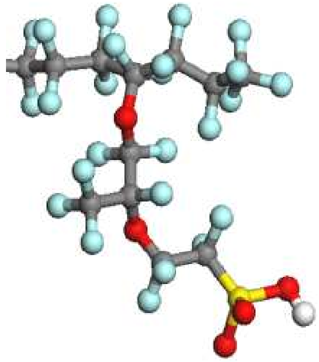




[1] V. Di Noto et al., RSC Adv. 3 (2013) 18960- 18969.
[2] V. Di Noto et al., J. Am. Chem. Soc. 134 (2012) 19099-19107.

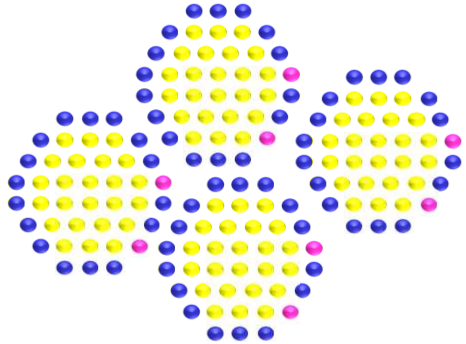
Electrical conductivity – Hybrid systems[1-15]





Nafion

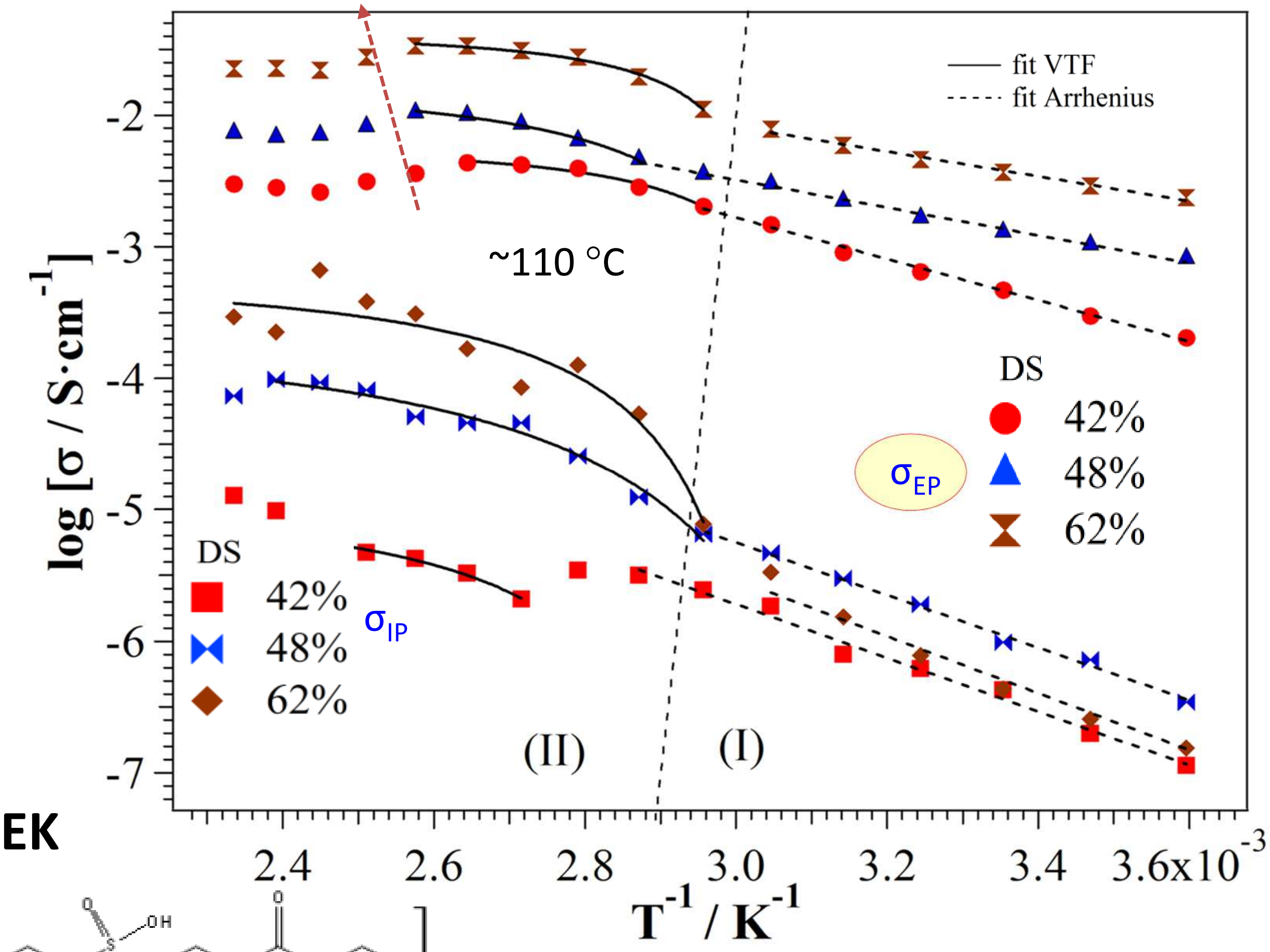
+



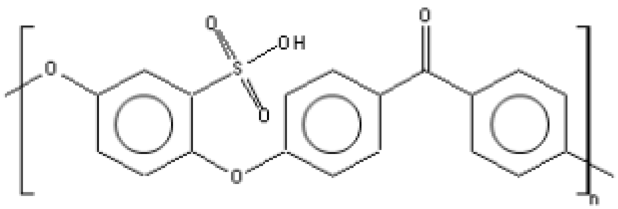
"Core-Shell" nanofiller

[1] V. Di Noto *et al., RSC Adv.* **3**, 18960 (2013).
[2] V. Di Noto *et al., Int. J. Hydrogen Energy* **37**, 6169 (2012).
[3] V. Di Noto *et al., J. Am. Chem. Soc.* **134**, 19099 (2012).
[4] V. Di Noto *et al. Int. J. Hydrogen Energy* **37**, 6199 (2012).
[5] V. Di Noto *et al. Int. J. Hydrogen Energy* **37**, 6317 (2012).
[6] V. Di Noto *et al., Int. J. Hydrog. Energy* **37**, 6169 (2012).
[7] V. Di Noto *et al., J. Power Sources* **195**, 7734 (2010).
[8] V. Di Noto et al., *J. Am. Chem. Soc.* **132**, 2183 (2010).
[9] V. Di Noto et al., *Electrochim. Acta* **55**, 1431 (2010).
[10] V. Di Noto *et al., Electrochim. Acta* **55**, 1355 (2010).
[11] V. Di Noto *et al., J. Power Sources* **187**, 57 (2009).
[12] M. Vittadello et al., *J. Phys. Chem. B* **112**, 16590 (2008).
[13] *V. Di Noto et al., J. Power Sources* **178**, 561 (2008).
[14] V. Di Noto *et al., Electrochim. Acta* **53**, 1618 (2007).
[15] V. Di Noto *et al. J. Phys. Chem. B* **110**, 24972 (2006).

Electrical conductivity – SPEEK[1]

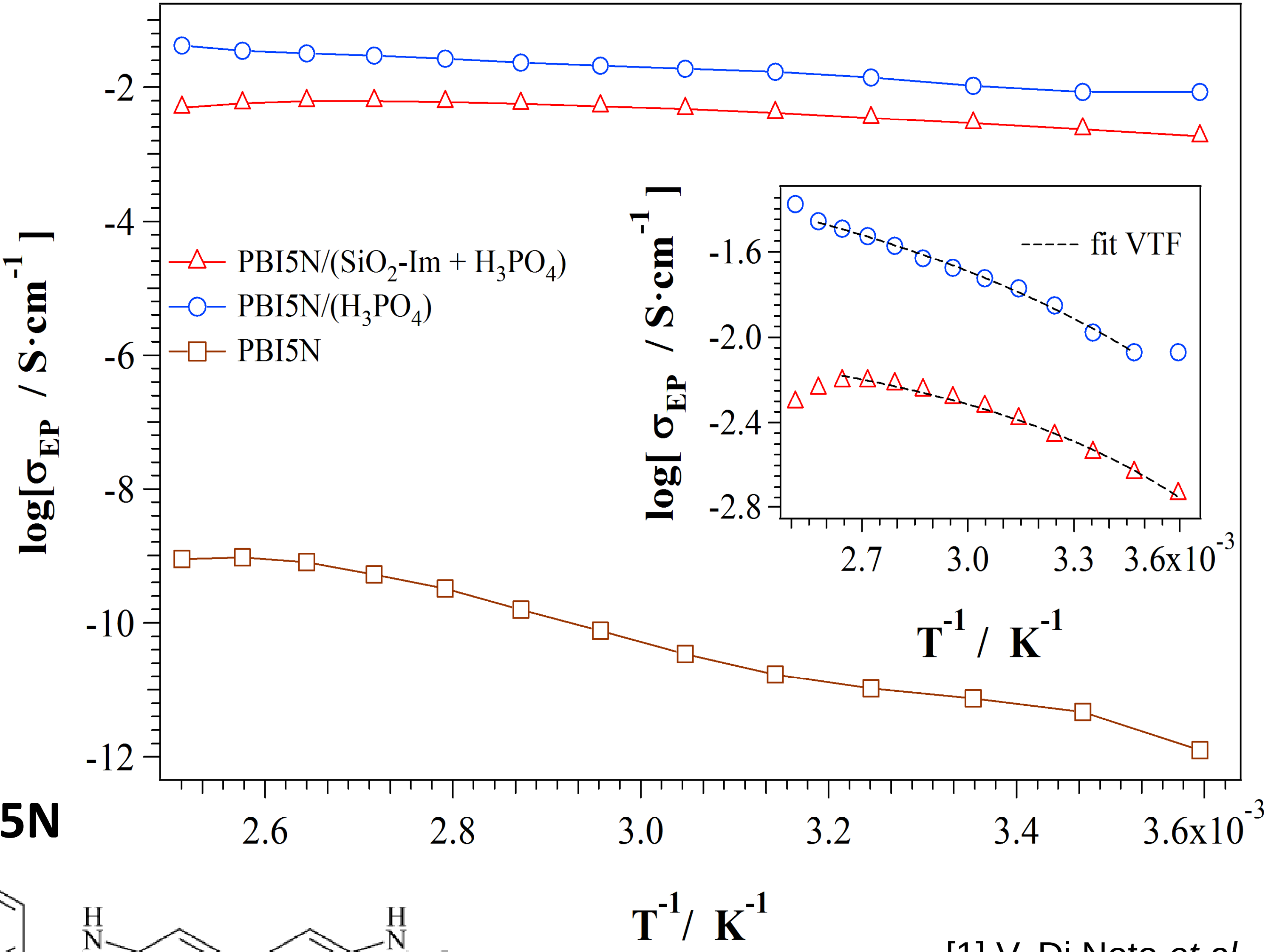


SPEEK

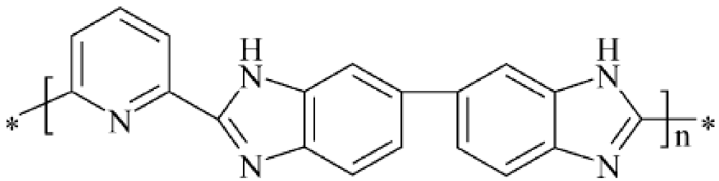


[1] V. Di Noto *et al.*, *J. Membr. Sci.* **390-391**, 58 (2012).

Electrical conductivity – PBI[1]

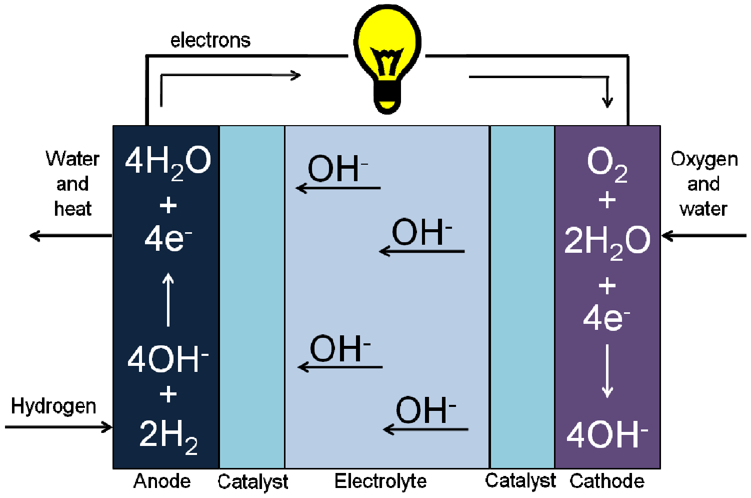


PBI5N



[1] V. Di Noto *et al.*, *Phys. Chem. Chem. Phys.* **13**, 12146 (2011).

Anion Exchange Membrane Fuel Cells



Anode: $3H_2 + 6OH^- \rightarrow 6H_2O + 6e^-$

Cathode: $^3/_2O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$

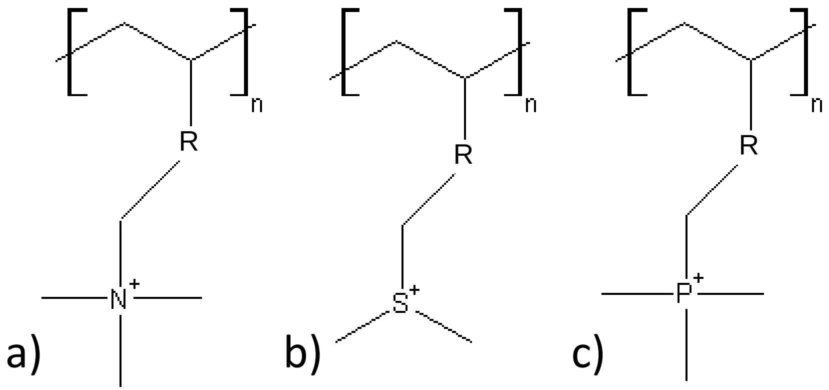
Overall: $3H_2 + {}^3/_2O_2 \rightarrow 3H_2O$

Advantages over PEMFCs

- Facile kinetics at electrodes
- Non-noble metal catalysts (e.g. Ag, Ni, Fe-N/C)
- Reduced fuel crossover

Advantages over traditional AFCs

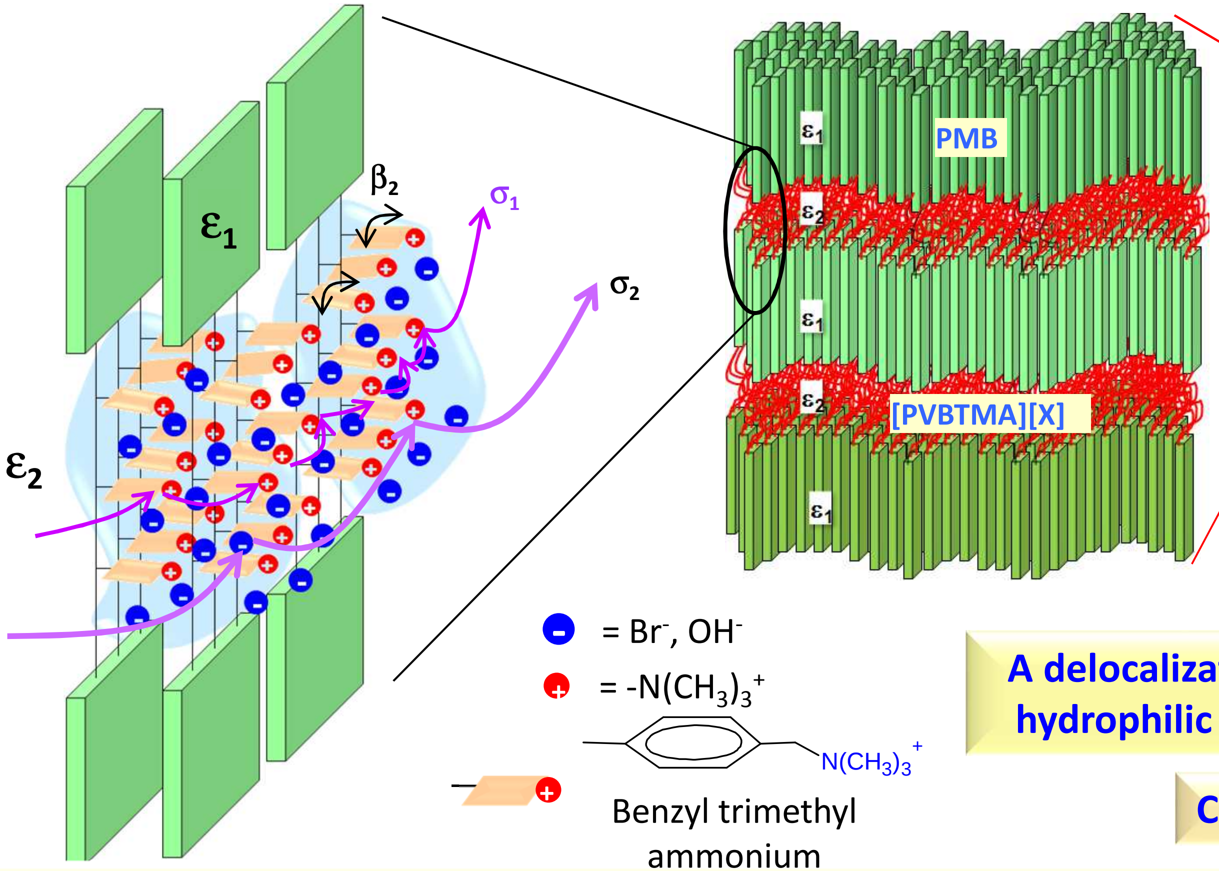
- No corrosive liquid electrolyte (KOH)
- No precipitation of carbonates

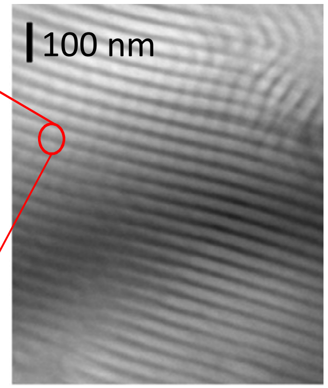


Chemical structures of generalized anion exchange membranes with a) ammonium, b) sulfonium and c) phosphonium anion exchange groups[1]

[1] V. Di Noto et al., Int. J. Hydrogen Energy 37 (2012) 6120-6131.

Conduction mechanism in AEMFCs





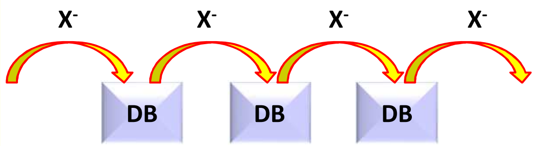
TEM image of [PVBTMA][Br]-*b*-PMB 160-390-81.8 recast from THF

A delocalization body (DB) is the volume of hydrophilic polymer impregnated by H_2O.

Conduction pathways

σ_2: the long-range charge migration process occurs when **X^- are exchanged between different delocalization bodies** (DBs). This phenomenon is modulated by dipole local fluctuation motions of –$BTMA^+$ side groups and of host matrix relaxations.

σ_1: the long-range X^- transfer process occurs by **"hopping" events between –TMA^+ cations**. These phenomena, assisted by β_2 relaxations and H_2O solvation processes, take place along the hydrophobic and hydrophilic interfaces of AEMs.



Comparative conductivity of Ion-Exchange Membranes

Class	Electrolyte group	Best Material	Conductivity@r.t. / $S\cdot cm^{-1}$	Stability T / °C	Ref.
PEMs	Nafion	Nafion wet	$3.0\cdot 10^{-2}$	105	[1]
	Nafion / Nanofiller	$\{Nafion/[(ZrO_2)(Ta_2O_5)_{0.119}]_{13}\}$	$7.1\cdot 10^{-2}$	160	[1]
	SPEEK	SPEEK, DS = 62%	$3.5\cdot 10^{-3}$	110	[2]
	PBI5N	PBI/H_3PO_4	$1.0\cdot 10^{-2}$	250	[3]
AEMs	[PVBTMA][Br]-b-PMB	[PVBTMA][Br]-b-PMB ; wet	$6.68\cdot 10^{-5}$	230	[4]
	[PVBTMA][OH]-b-PMB	[PVBTMA][OH]-b-PMB; DF= 80.7%; wet	$4.44\cdot 10^{-3}$	140	[5]

[1] V. Di Noto, M. Piga, G.A. Giffin, K. Vezzù, T.A. Zawodzinski, J. Am. Chem. Soc. 134 (2012) 19099-19107.

[2] V. Di Noto, M. Piga, G.A. Giffin, G. Pace, J. Membr. Sci. 390-391 (2012) 58-67

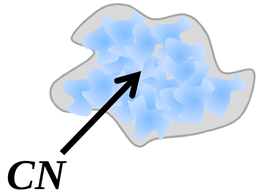
[3] V. Di Noto, M. Piga, G.A. Giffin, E. Quartarone, P. Righetti, P. Mustarelli, A. Magistris, Physical Chemistry Chemical Physics. 13 (2011) 12146-12154.

[4] V. Di Noto et al., submitted

[5] V. Di Noto et al., in preparation

Activities in PEMFC electrocatalysts[1-13]

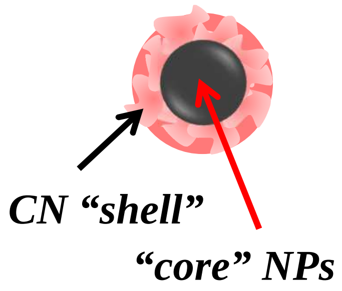
Pristine CN-based electrocatalysts



- Study of the metal composition
- Study of the concentration of N in the matrix
- Investigation of the interplay between the preparation parameters, the morphology and the “ex-situ” and “in-situ” electrochemical performance

$CN = M1M2_a \cdots Mn_z - CN_x\ T_f$

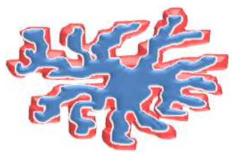
“Core-shell” CN-based ECs



Conductive spherical C-NPs

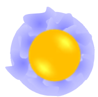
- CN: Pt- and Pd-based systems with Fe, Ni, and Co co-catalysts
- Evaluation of N concentration in the “shell”
- Supports: Carbon NPs (C-NPs).

Nanoporous “cores”



- SX supports with different morphologies
- Study of the interplay between the morphology and both “ex situ” and “in situ” electrochemical performance

Conductive spherical M-NPs

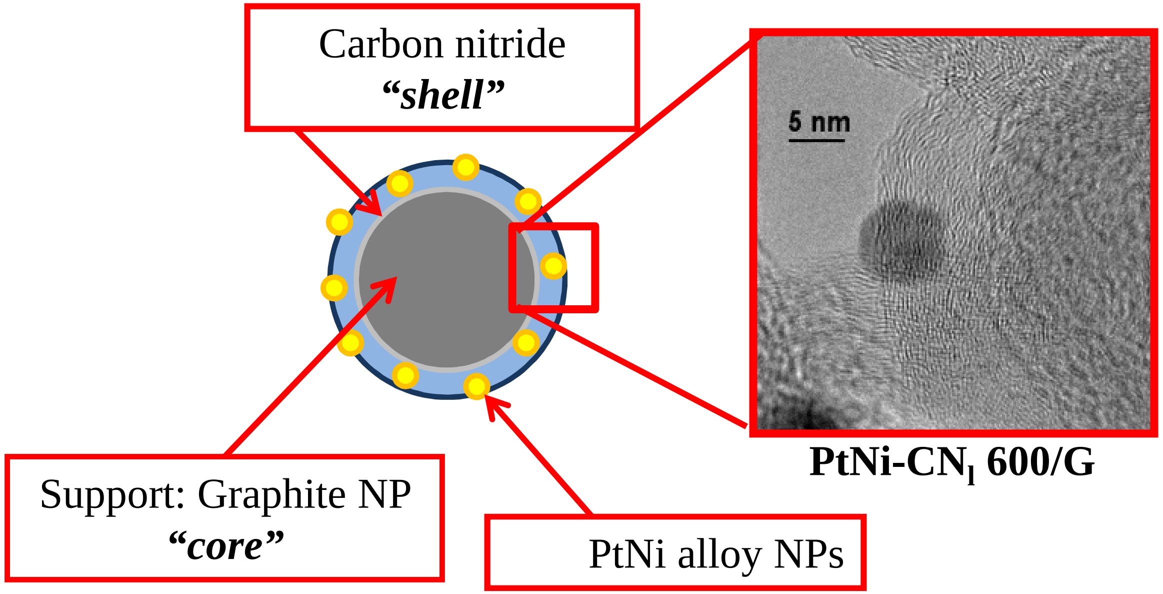


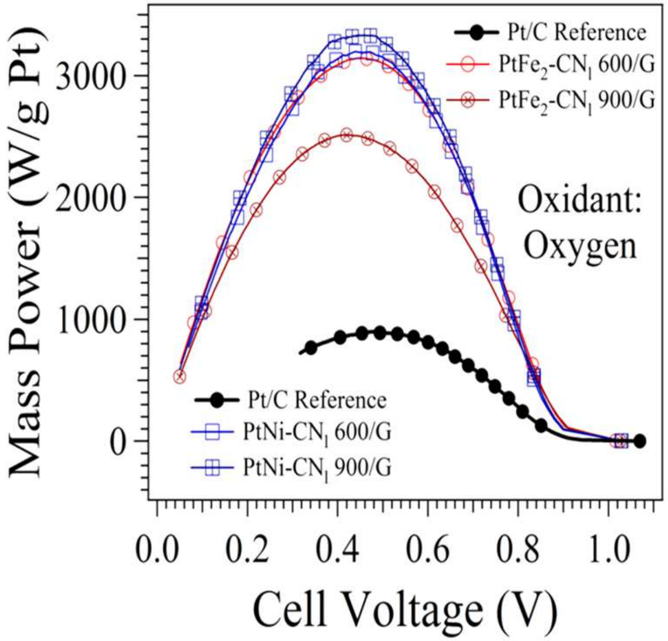
- CN: Pt- and Pd-based systems with Ni, Cu and Co co-catalysts
- Evaluation of N concentration in the “shell”
- Support: Sacrifical Cu or Ni NPs.

[1] V. Di Noto, E. Negro, R. Gliubizzi et. al,, J. Electrochem Soc. 154 (2007) B745.
[2] V. Di Noto, E. Negro, R. Gliubizzi er. al., Adv. Funct. Mater. 17 (2007) 3626.
[3] E. Negro, V. Di Noto, J. Power Sourc. 178 (2008) 561.
[4] V. Di Noto, E. Negro, S. Lavina et al., European Patent PCT/IT2007/000278.
[5] V. Di Noto *et al.*, IJHE, 39 (2014) 2812
[6] E. Negro *et al.*, IJHE, 39 (2014) 2828
[7] V. Di Noto et al., ChemSusChem 5 (2012) 2451.
[8] V. Di Noto, E. Negro, S. Lavina et. al., Electrochim. Acta 53 (2007) 1604
[9] V. Di Noto, E. Negro, M. Piga et. al. ECS Trans. 11 (2007) 249.
[10] V. Di Noto, E. Negro, Italian Patent PD2008A000188.
[11] V. Di Noto, E. Negro, Fuel Cells 10 (2010) 234.
[12] V. Di Noto, ECS Trans. 16 (2008) 123.
[13] Di Noto et al., Electrochim. Acta 55 (2010) 7564

Advances in PEMFC electrocatalysts

"Core-Shell" CN-based electrocatalysts are obtained by supporting a porous CN matrix ("shell") embedding multimetal alloy NPs on conductive "cores"





"Core-Shell" CN-based electrocatalyst [1]

Loading of Pt for:

- ***PtX-CN$_l$ T$_f$/G ~ 0.1 mg/cm^2;***
- ***Reference MEA ~ 1 mg/cm^2.***

The development of "Core-Shell" ECs aims at improving:

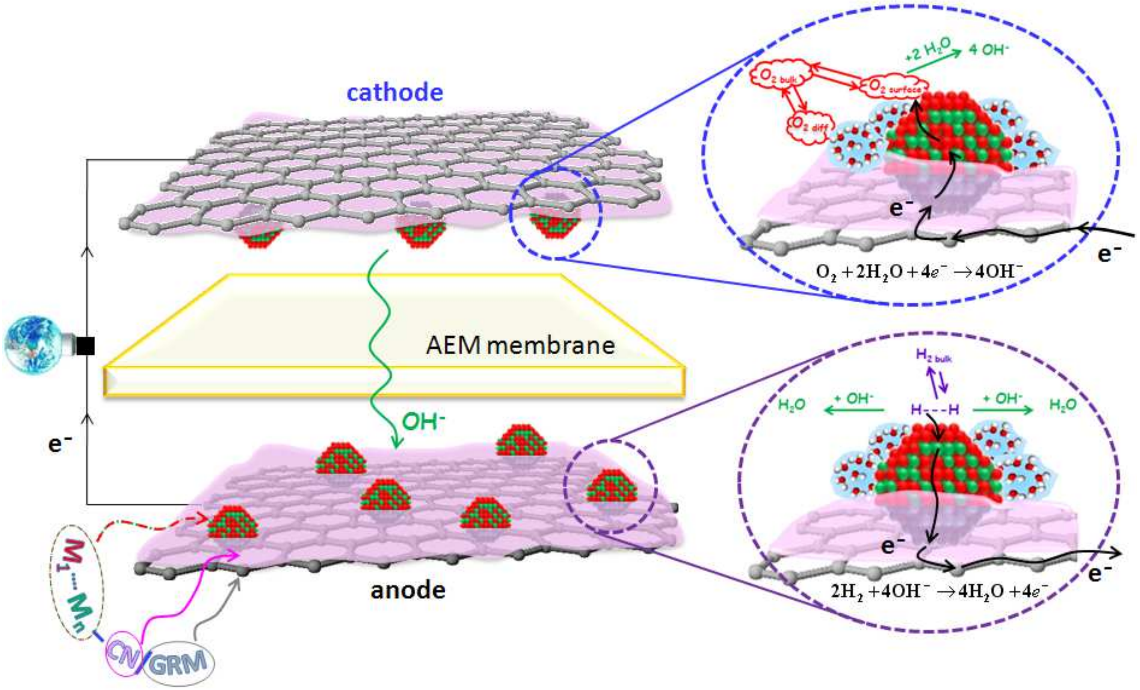
- ***The dispersion of the active sites.*** Facilitate the transport of reactants and products in the electrocatalytic layer (accessibility);
- ***The conductivity of the matrix.***

[1] V. Di Noto, ECS Trans. 16 (2008) 123.
[2] Di Noto et al., Electrochim. Acta 55 (2010) 7564.
[3] V. Di Noto et al., Fuel Cells 10 (2010) 234.
[4] V. Di Noto et al., ChemSusChem 5 (2012) 2451.

AEMFC electrocatalysts supported on graphene and related materials

EU GRAPHENE Flagship ⇨ **GRAFUS – Graphene and related materials as supports for innovative metal carbon nitride electrocatalysts for anion exchange membrane fuel cells**

Anion Exchange Membrane Fuel Cells (AEMFCs) based on $M_1 \cdots M_n$ – CN/GRM



Alloy nanoparticles with sizes lower than 10 nm will be based on Au, Ag, Ni, Fe, Co, Cu, Mn, Mo or on their alloys.

It is reasonably expected that GRAFUS ECs will yield ORR overpotentials as low as ca. 300 mV.

The GRM nano-platelets which constitute the electrocatalyst support will yield:

- ✓ ***a high porosity***,
- ✓ ***a high electron conductivity***.

UNIPD – Collaborations

Prof. Thomas Zawodzinski, Prof. Matthew Mench

THE UNIVERSITY of TENNESSEE UT KNOXVILLE

Development of functional materials to devise single-cell FCs working in operating conditions

Prof. Klaus-Dieter Kreuer

Max-Planck-Institut für Festkörperforschung

Development of models to study the charge transfer and water transport processes in PEMs

Prof. Andrew Herring

CHEMICAL & BIOLOGICAL ENGINEERING COLORADO SCHOOL OF MINES

Preparation and characterization by BES and IR of ion-exchange membranes for application in PEMFCs and AEMFCs

Prof. Steve Greenbaum

CUNY The City University of New York

Characterization of nanofillers and hybrid membranes by NMR and EPR.

Prof. Plamen Atanassov

THE UNIVERSITY of NEW MEXICO

Characterization of anode and cathode electrode configurations by XPS and AFM

Prof. Werner Lehnert

JÜLICH FORSCHUNGSZENTRUM

Determination of performance and durability of HT-PEMFCs

Prof. Michael Popall

Fraunhofer ISC

Development of hybrid inorganic-organic ion-conducting materials for application in PEMFCs

Prof. Jean-Yves Sanchez

LEPMI

Synthesis of ionomer membranes capable to operate at high temperatures (T > 120°C) and under dry conditions

Prof. Sanjeev Mukerjee

Northeastern University College of Science

Development of innovative carbonaceous supports for application in the electrode configurations of PEMFCs and HT-PEMFCs

UNIPD – Collaborations

Prof. John Fontanella / Prof. Mary Wintersgill

UNITED STATES NAVAL ACADEMY
LEADERS TO SERVE THE NATION

Dielectric studies via BES on proton-conducting hybrid membranes at different temperatures and pressures

Prof. Patrik Johansson

Confocal micro-Raman spectroscopy to determine the distribution of water in MEAs

Prof. Noriyoshi Matsumi

JAIST
JAPAN ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY 1990

Development of hybrid inorganic-organic electrolyte membranes

Dr. Radoslav Atanasoski

3M

Preparation of supports characterized by a very large surface area and based on columnar nanofibers of graphite, metals or alloys

Dr. Steve Hamrock
Dr. Greg Haugen

3M

Preparation of perfluorosulfonic ionomers characterized by innovative side chains

Prof. Takeo Furukawa

TOKYO UNIVERSITY OF SCIENCE

Advanced dielectric measurements on ion-conducting materials

Prof. Hiroyuki Ohno

TAT Tokyo University of Agriculture and Technology

Development of electrolyte membranes including ionic liquids and of electrode feeds for RFBs based on ionic liquids

Dr. Robert Mantz

WWW.ARL.ARMY.MIL
UNITED STATES ARMY RESEARCH LABORATORY
ARL

Development of anion exchange hybrid inorganic-organic membranes for applications in AEMFCs

UNIPD – Collaborations

Dr. Detlef Hofmann

Development of models at the molecular and mesoscopic scale of hybrid proton-conducting ionomer membranes

Prof. Gerard Gebel
Dr. Sandrine Lyonnard

Characterization of membranes for PEMFCs and PEMELs by small-angle X-ray scattering and neutron scattering

Prof. Stefano Polizzi

Studies at the nanometric level of the morphology of the FC materials using HR-TEM, electron diffraction, X-ray fluorescence

Dr. Francesco Bonaccorso,
Dr. Vittorio Pellegrini

Development of PGM-free electrocatalysts for AEMFCs based on graphene supports

Selected Research Projects

MIUR: FISR1999; FISR2001; PRIN2006; PRIN2007; PRIN2008

U.S. Army Research Office - Grant W911NF-13-1-0400

Private companies: Strumenti Scientifici CINEL; TEXA S.p.A.; BRETON S.p.A.

Venetian Research Institution - Veneto Nanotech S.C.p.a.

University of Padova: PRAT2011; Strategic Project of the University of Padova "MAESTRA - From Materials for Membrane-Electrode Assemblies to Electric Energy Conversion and Storage Devices"

The European Union – GRAPHENE Flagship : GRAFUS

Thank you for your attention