Synchrotron-Based characterization of chemical state and morphology of key components in PEMFC and SOFC

- **Introductory remarks:** FCs and synchrotron-based methods;
- **Model fuel cells for in-situ x-ray microscopy studies;**
- **Selected results:**

<u>PEFC:</u> Electrochemical corrosion of Fe and Ni plates and mass transport of corrosion products;

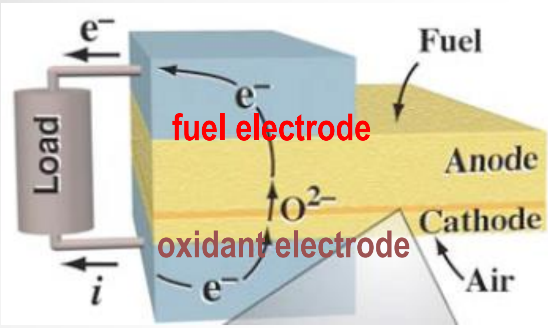
Degradation of Pt/C electrocatalyst

<u>SOFC:</u> Morphology and chemical state of Ni electrodes and Cr interconnects: ambient, temperature and bias effects

- **Conclusion and outlook.**

Fuel Cell:

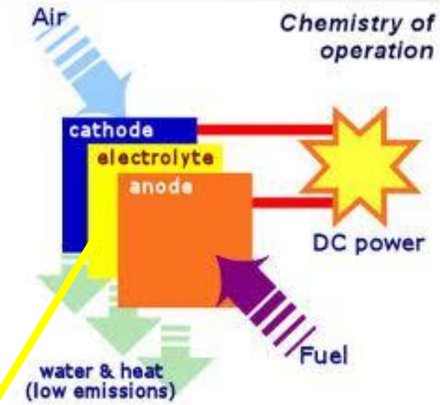
pollution-free conversion of chemical energy to electricity



$$2H_2 + O_2 \rightarrow H_2O$$

$$2H_2 \rightarrow 4H^+ + 4e^-$$

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

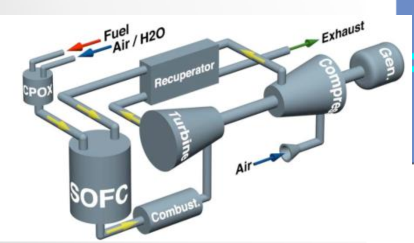


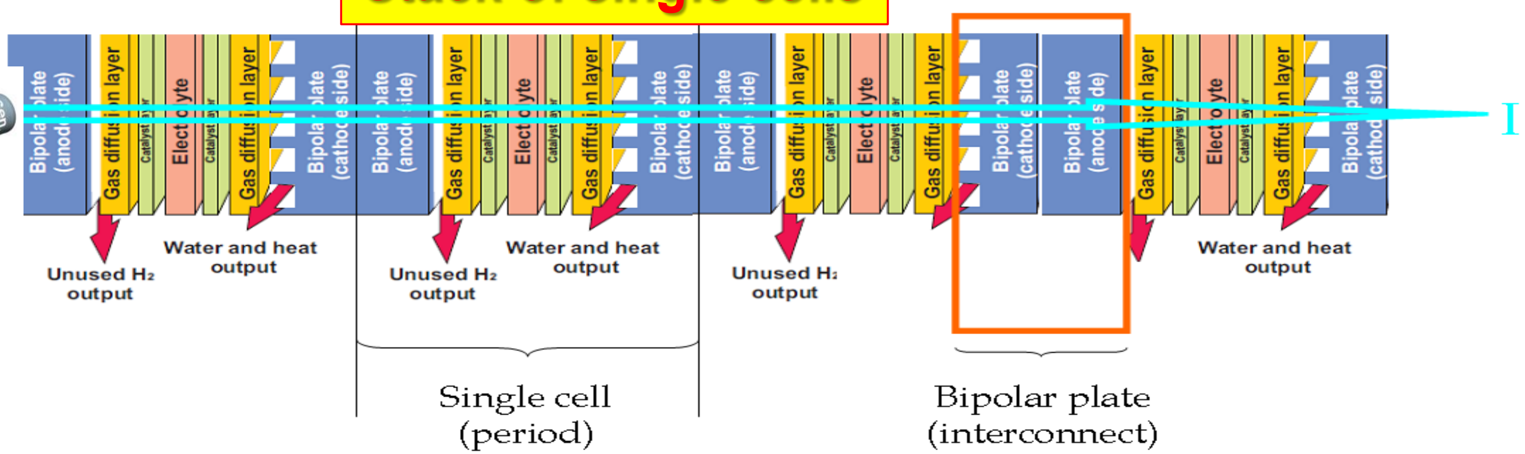
PEFC: (H$^+$ charge carrier) - polymer membrane T< 120°C

SOFC: (O^{2-} charge carrier) – oxide (YSZ, CeO_2..) T~650÷1000°

single cell Ca. 1 V

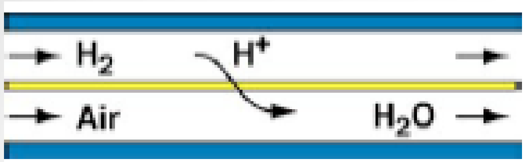
Stack of single cells

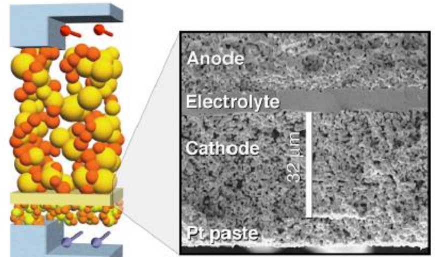




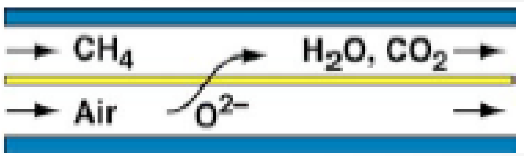
Fuel cells: PEMFC and SOFC

complex dynamic systems using unique material combinations





MEA fabricated by ITN energy Systems



PEMFC

- Electrolyte – proton (H^+)-conductor (Polymers);
- Lower operation temperature (<200°C);
- Requires pure H_2 fuel and oxidant;
- CO is a poison for low T polymers;
- Precious-expensive catalysts (Pt).

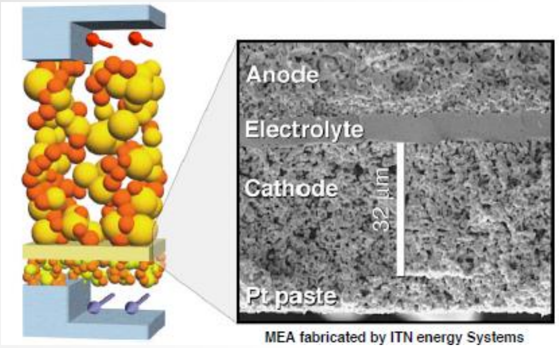
SOFC

- Electrolyte oxygen-ion conductor (YSZ, CeO_2)
- High operation temperature (~700°C)
- Fuel Flexibility;
- CO is not a poison but a fuel;
- Inexpensive catalysts (e.g. Ni, NiCu cerments, $La_xSr_yMn(Co,Fe)O_3$

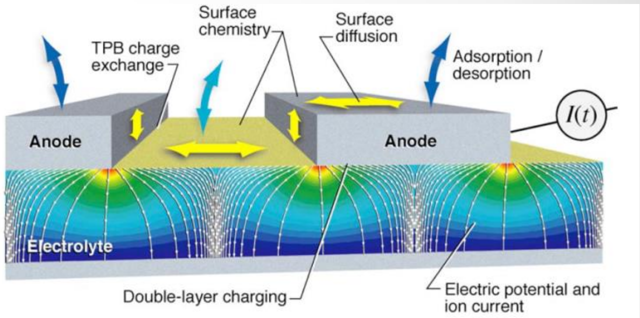
Power efficiency, durability and cost – still not resolved issues !

- **BP corrosion** = R_Ω increase, mass transport of corrosion products can lead to catalyst deactivation, electrolyte degradation, clogging of gas diffusion layer etc
- **Catalyst deactivation** can be due to contaminant deposition (S, C, CO) or sintering;
- **Electrolyte conductivity loss and degradation:** e.g. hydration level of polymer membrane, migration of species to electrolyte, redox processes etc

Operating Fuel Cells:
complex multicomponent dynamic micro-systems



GAP in understanding the relationship between operating conditions – component stability and degradation mechanisms.



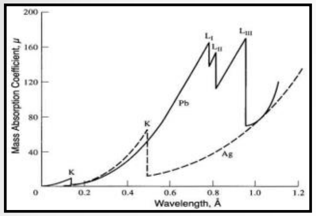
Need monitoring in-situ processes at the key components: interconnects, electrodes and electrolyte:

- ❖ redox cycles: stress-damage
- ❖ side processes: mass transport, interaction between components;
- ❖ morphology and relevant chemical changes..

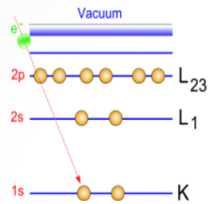
Morphologically complex and nanostructured matter needs methods with sufficient lateral resolution, chemical & surface sensitivity, correlative morphology & structure information.

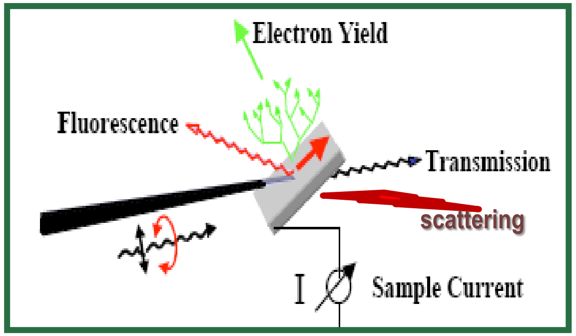
Synchrotrons offer a variety of spectroscopy and microscopy-imaging approaches

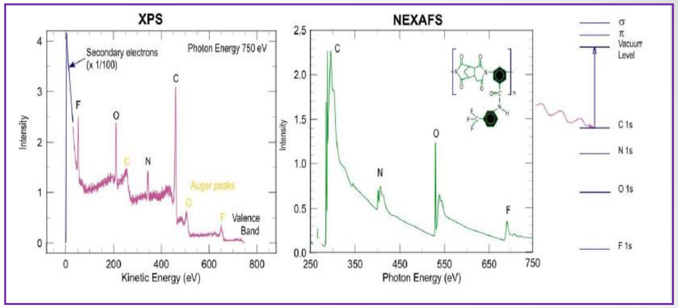
X-ray absorption



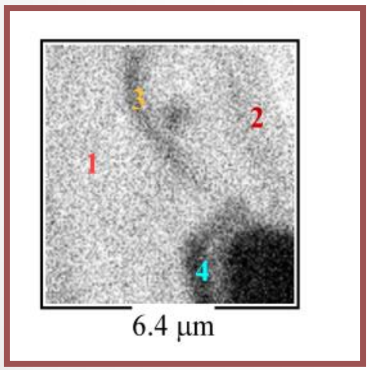
Photon or e⁻ emission

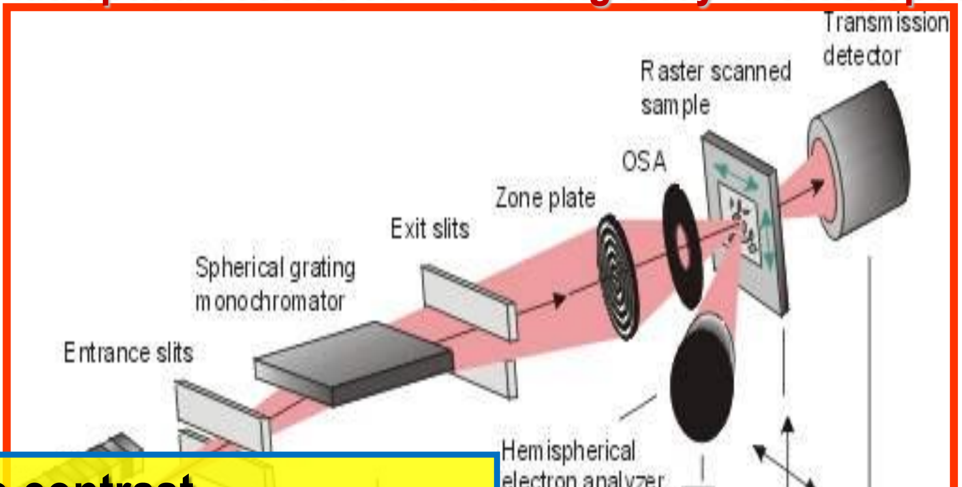






Add spatial resolution - scanning x-ray microscopes





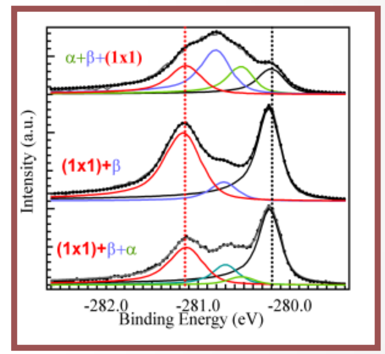


Image contrast

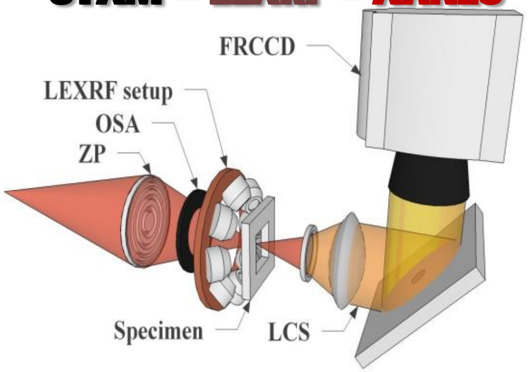
- Morphology: density, thickness..
- Element presence and concentration;
- Chemical state, band-bending, charging;
- Magnetic spin or bond orientation.

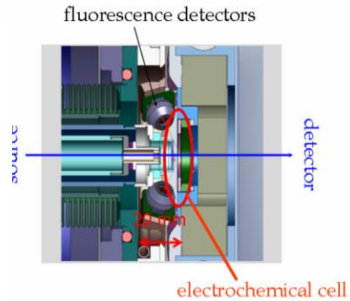
Microspectroscopy:

µ-XPS, µ-XANES or µ-XRF in selected spots – detailed chemical and electronic structure of coexisting micro-phases.

Micro-fabricated Fuel Cells for using in SXMs

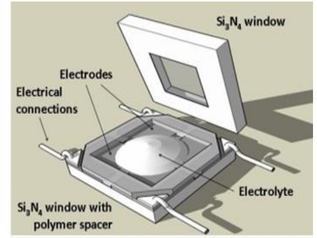
STXM – LEXRF – XANES



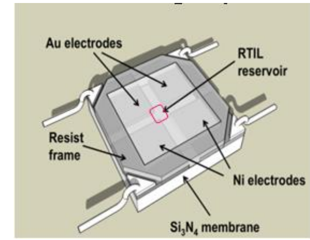


TwinMic

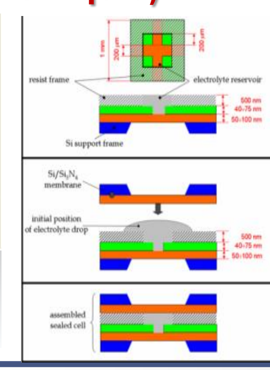
Proton Exchange Membrane (sealed for aqueous Nafion and open with spun RT Ionic Liquid)

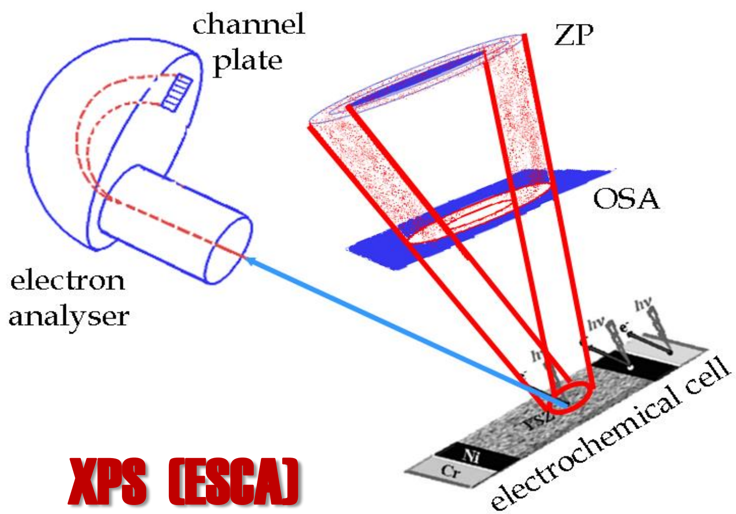


Metallic Plate Corrosion and Uptake of Corrosion Products by Nafion in Polymer Electrolyte Membrane Fuel Cells
B. Bozzini et al, ChemSusChem 3, 1, 2010

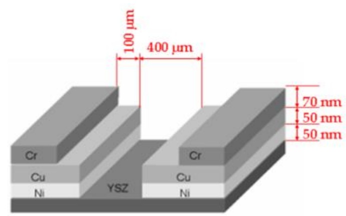


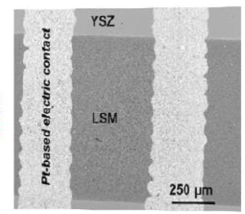
Bozzini et al. PhysChemChemPhys 13 (2011) 7968.

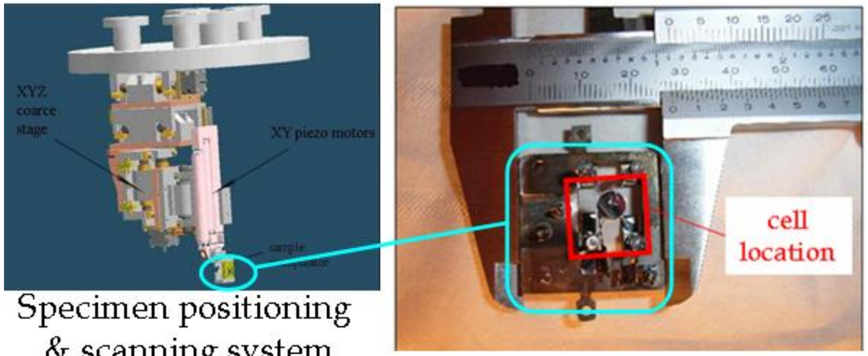




SPEM





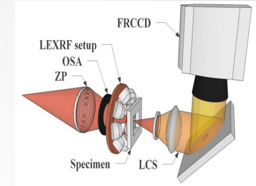


Specimen positioning & scanning system

XPS (ESCA)

PEPFC: metal BP/Nafion interface

Ni, Fe corrosion and Nafion 'poisoning'

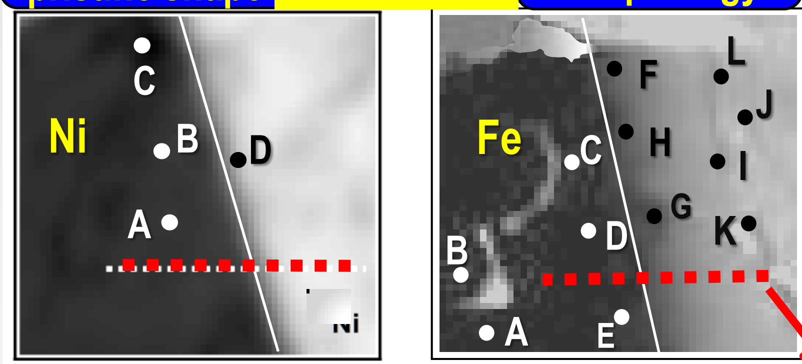


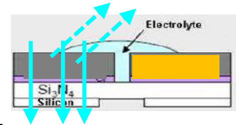
STXM
LEXRF
XANES

Ni- preserves pristine shape

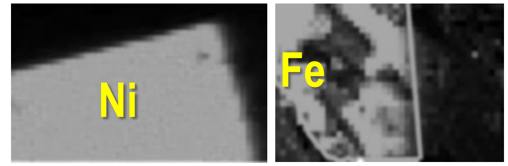
STXM maps

Fe- corrossion morphology

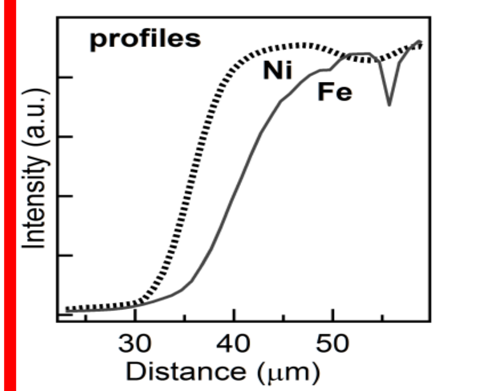


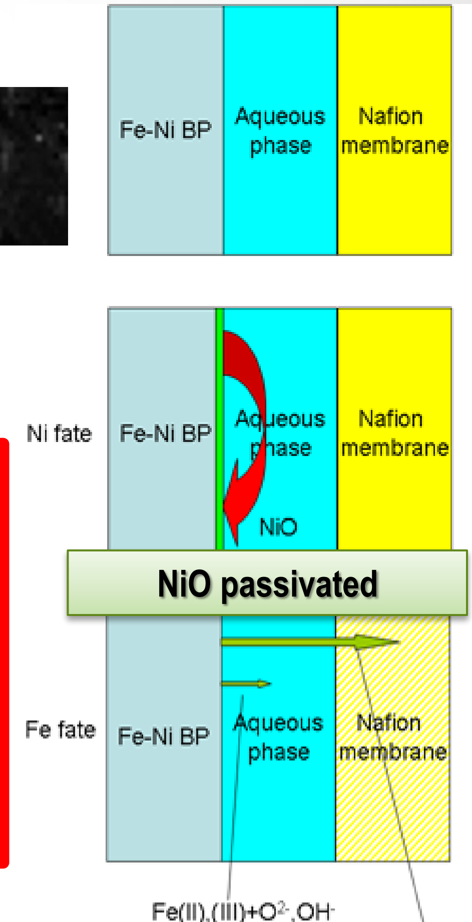


XRF maps

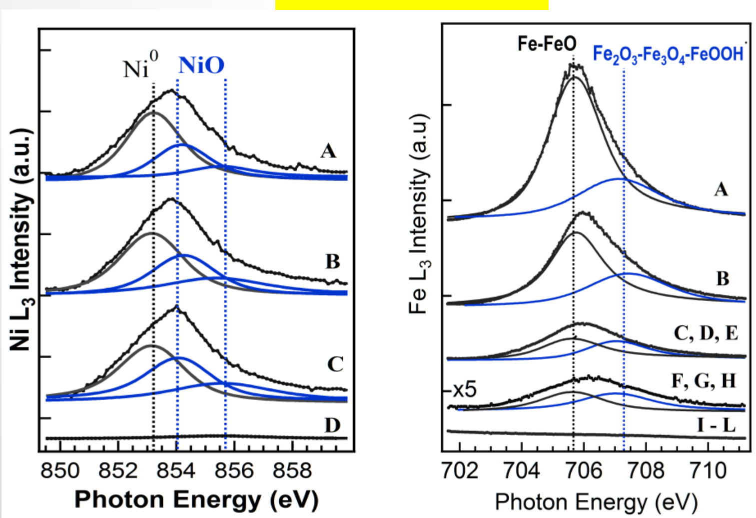


Mass transport across the interface





XAS spectra

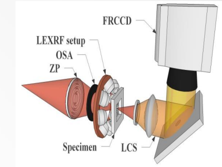


Fe undergoes corrosion: diffusion of corrosion products into Nafion = f(c.d.d.)

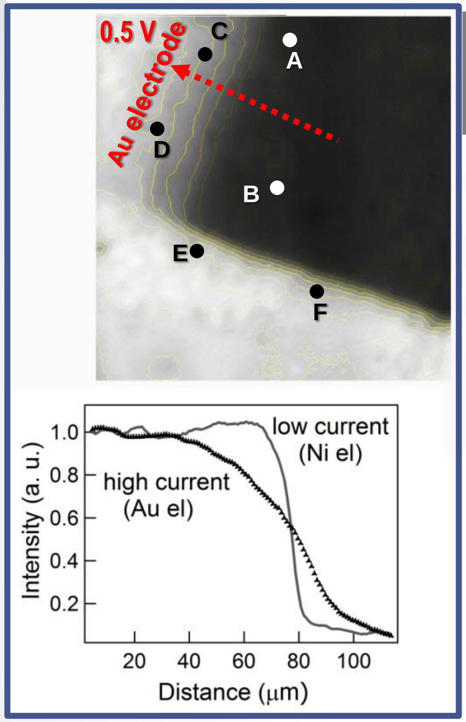
B. Bozzini et al, ChemSusChem 2010, 3, 1, *Microelectr. Eng.* 2011, 88, 2456

PEPFC: metal BP/RTIL[BMP][TFSA] interface

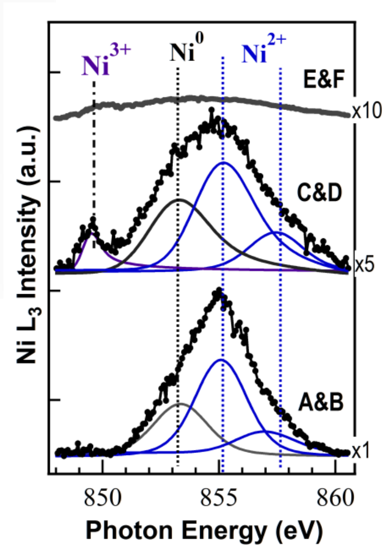
Ni, Fe corrosion and RTIL 'poisoning'



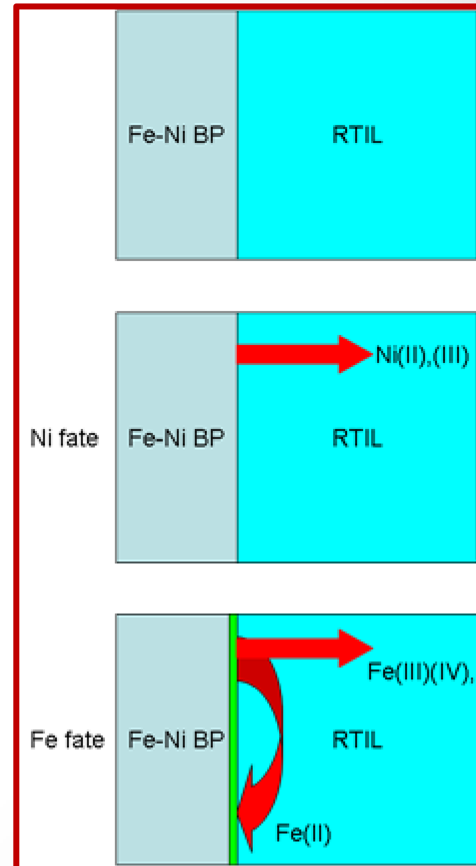
STXM
LEXRF
XANES

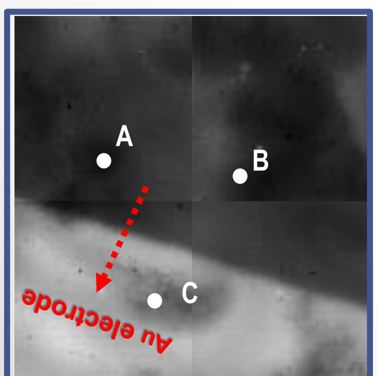


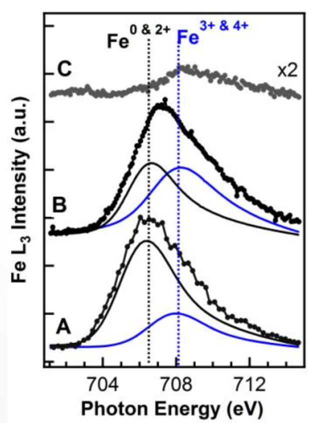
Ni: C.D.D. controlled diffusion in RTIL



Ni corrosion products interact with the RTIL. The localisation of the higher-valence form of oxidised Ni in the high-current density region C, D is coherent with the higher anodic potentials developed there.



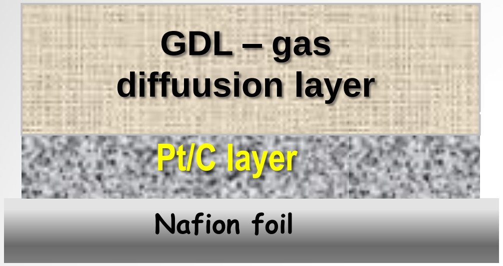


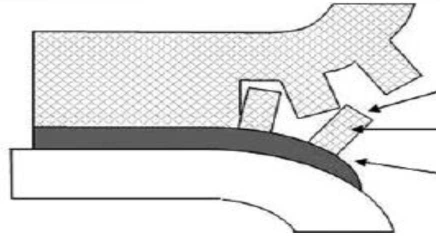


Fe: higher corrosion resistance and less loss of material

B. Bozzini et al, PCCP 13, 2011, 7968 Fuel Cells, 13 (2013) 196

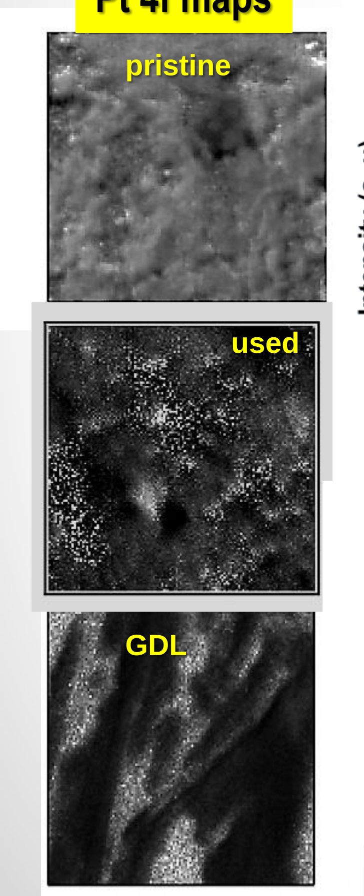
PEPFC: degradation of Pt/C catalyst and GDL



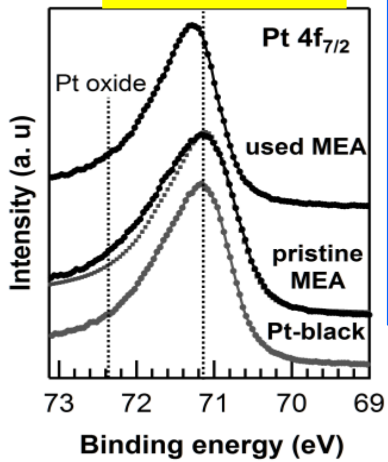


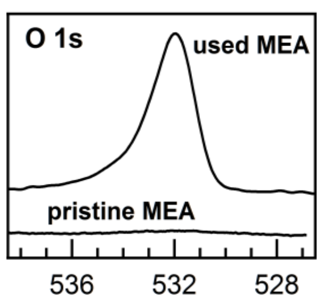
Pt/C cross section and partial removed GDL

Pt 4f maps



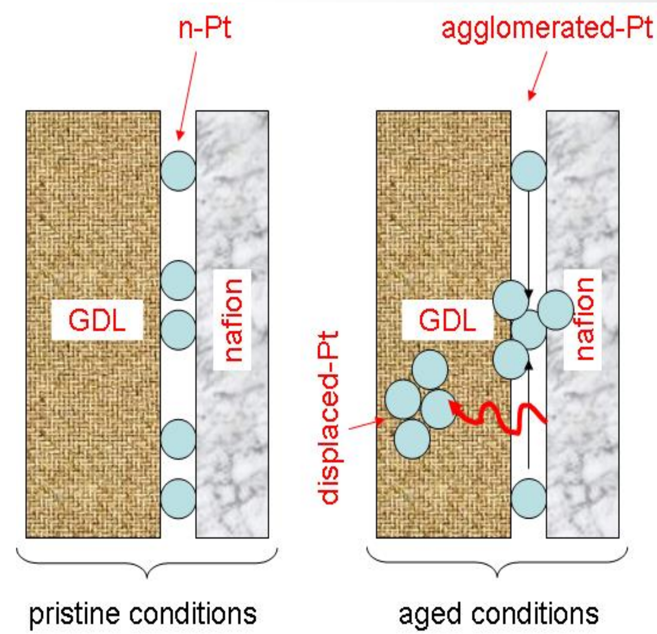
XPS spectra





Pt 4f spectra: preserved metallic state – size effects on the BE and penetration in GDL

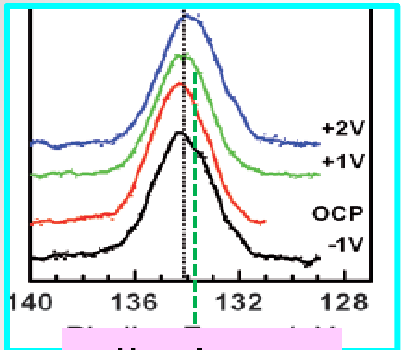
O 1s: BE typical for oxidized C



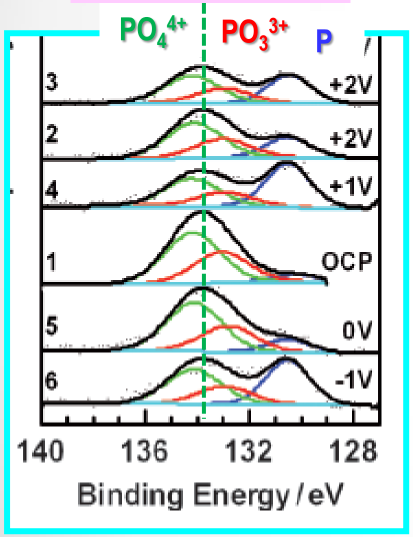
Ageing of the Pt catalyst after 1000 hours of anodic operation: redistribution, aggregation and loss of material due to Pt migration away from the electrode penetrating GDL and C oxidation.

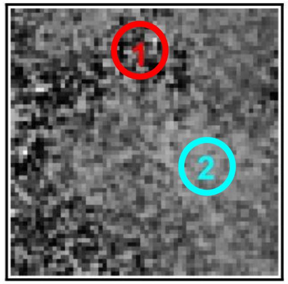
Bozzini et al. J Power Sources 196 (2011) 2513.

HT-PEPFC: Pt/electrolyte interface: morphology and phosphoric acid chemical transformations

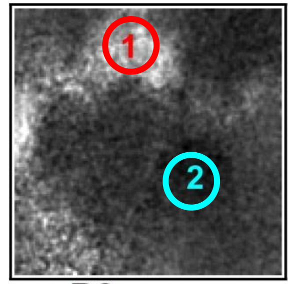


H$_2$ pulses

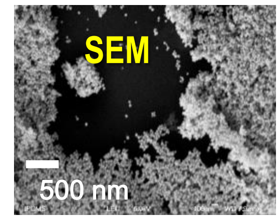


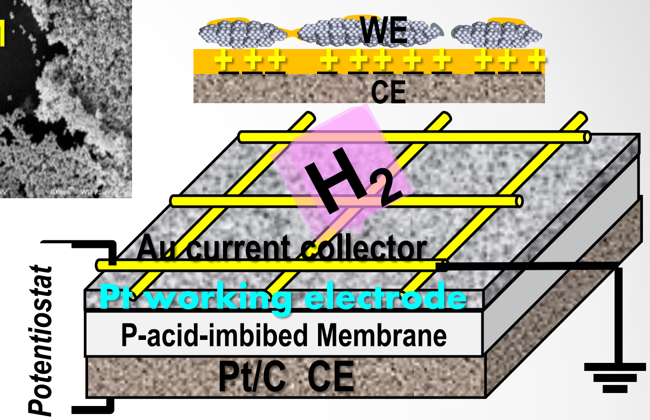


Pt4f map

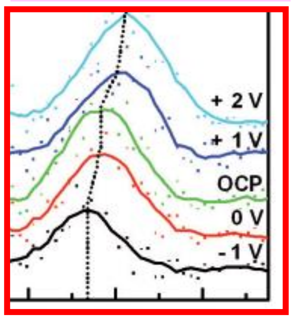


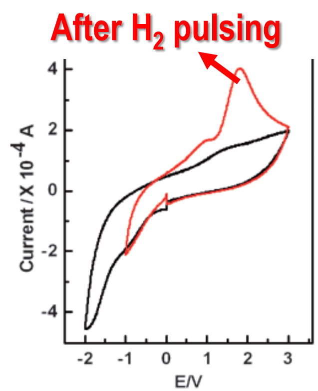
P2p map

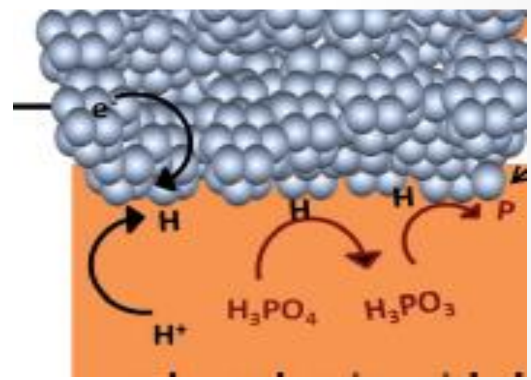




H$_2$ pulses







$$H_3PO_4 + 2H^+ + 2e^- = H_3PO_3 + H_2O$$

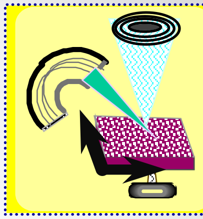
$$H_3PO_4 + 5H^+ + 5e^- = P + 4H_2O$$

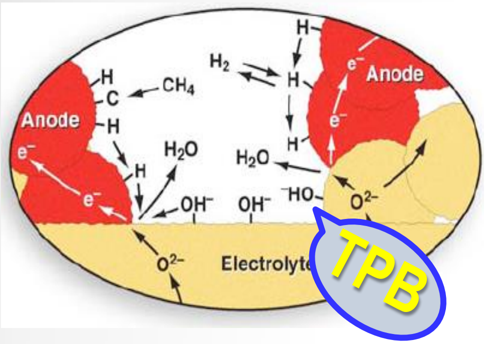
First spectroscopic evidence P-acid reduction occurring at Pt/electrolyte interface independent of polarization – Pt-catalysed chemical process. Electrochemical re-oxidation accounts for peaks in the CV curve after H$_2$ exposure.

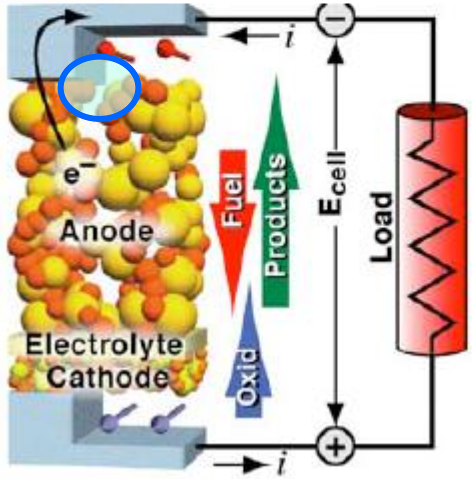
H. Doh et al, ChemElectrChem 2013 DOI: 10.1002/celc.201300134

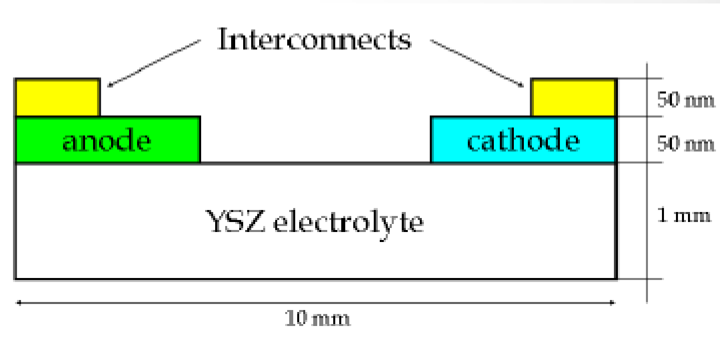
Maya Kiskinova

SOFCs under operating conditions









Correlative information about morphology and composition of all cell components interconnects, electrodes and electrolyte and their interfaces al micro-scale:

In-situ monitoring: (i) single grain electroactivity; (ii) local chemical state dynamics; (iii) overvoltage mapping; (iv) mass transport and structural evolution; (v) deposit of contaminants

SOFC components in pure oxidizing ambient

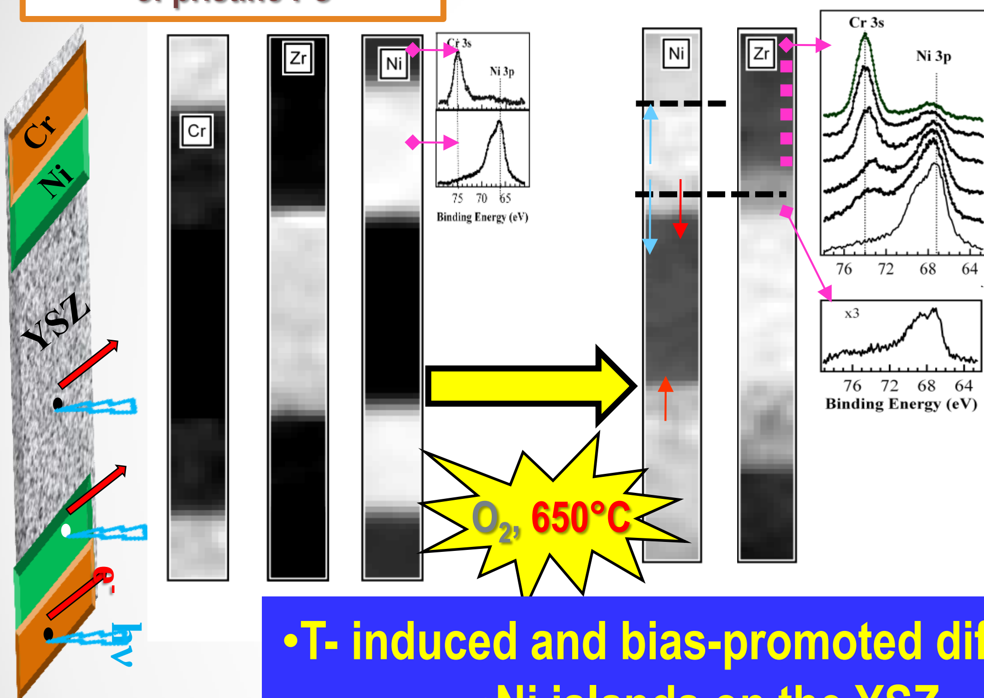
650 C, 10^{-6} mbar O_2 Bias 0.65 - 3.0 V

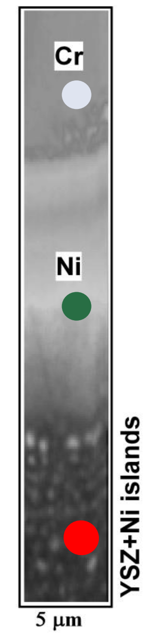
Cr3p, Zr3d and Ni3p maps of pristine FC

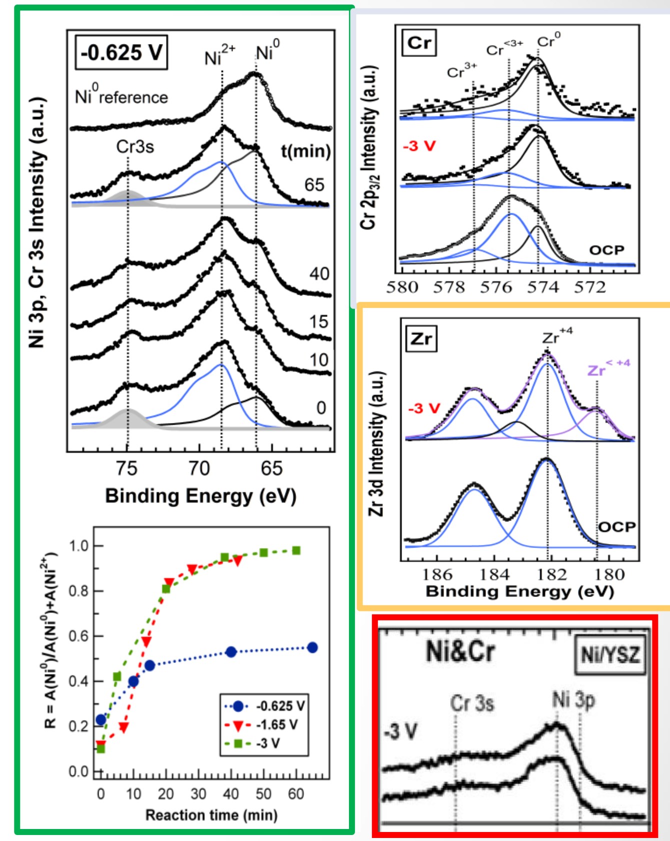
Morphology

Ni map

Electrochemistry

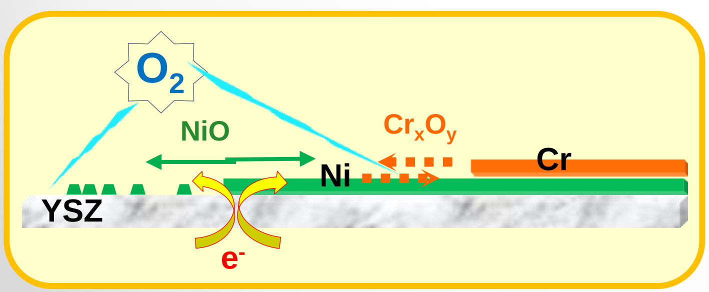






•T- induced and bias-promoted diffusion;

•Ni islands on the YSZ



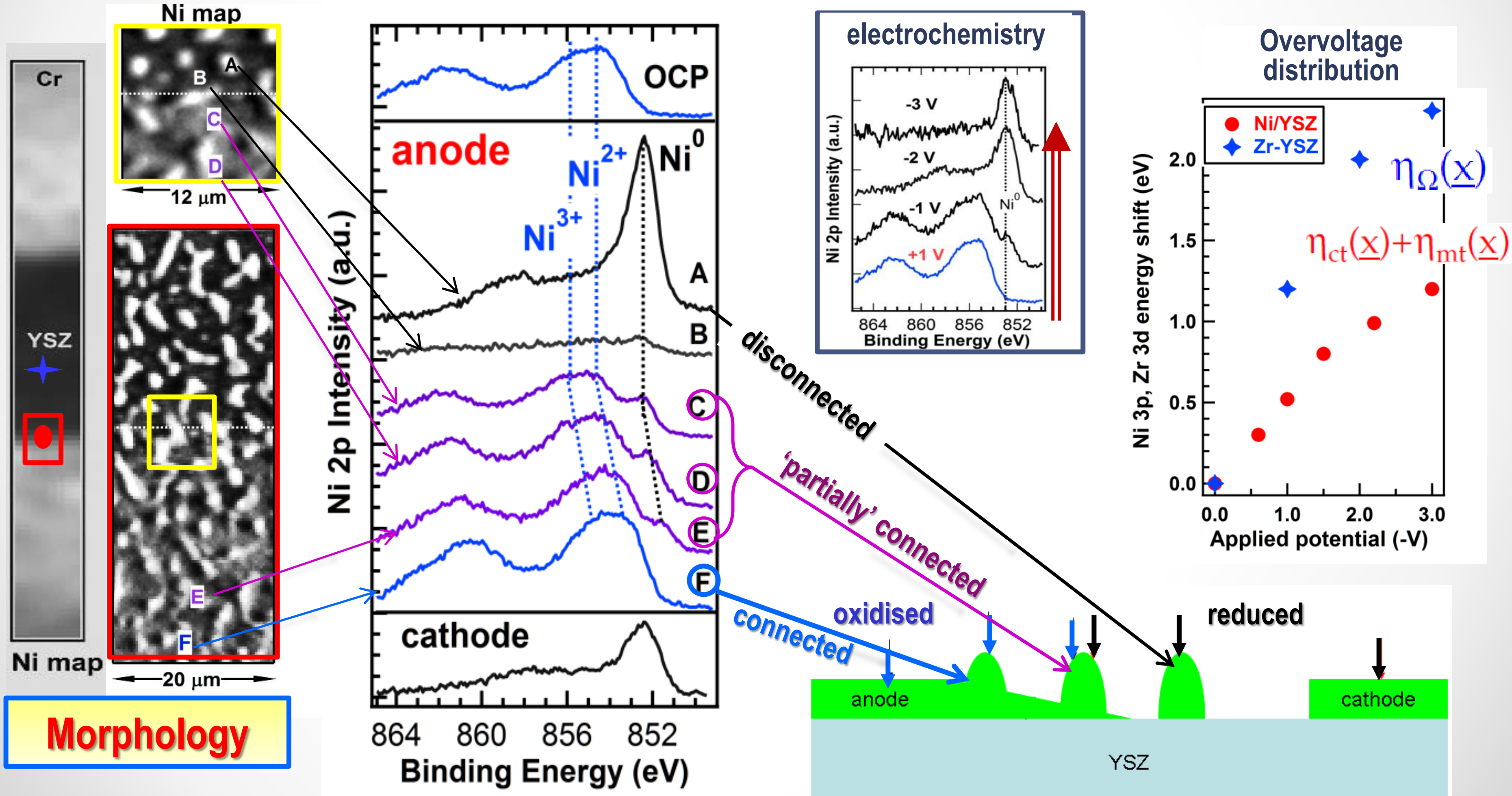
- ❑ Ni reduction already at -0.6 eV; Rate=f(V)
- ❑ Cr and YSZ reduction only at -3 V
- ❑ Intact NiO islands - lack of electron drain.

Bozzini et al. ChemSusChem 3 (2011) 2513.

SOFC: morphology and distribution of electrochemical activity

$C_2H_4+H_2O$:
650°C 10^{-5} mbar

Lateral variations in the degree of Ni oxidation in concert with the over-potential distribution .

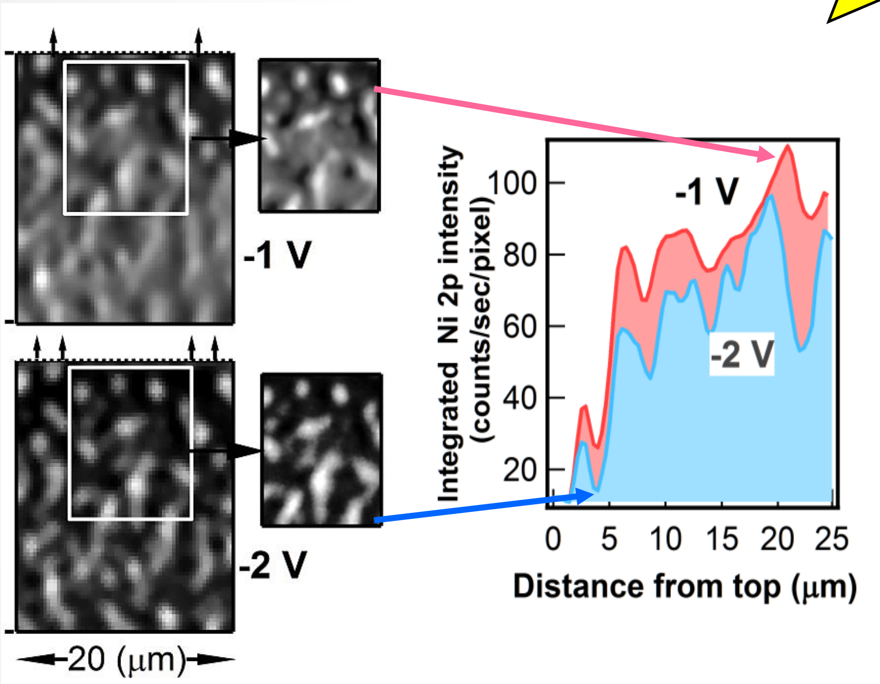


Bozzini et al. *J.Phys, Chem C* 116 (2012) 23188

SOFC: directional electromigration and C deposition

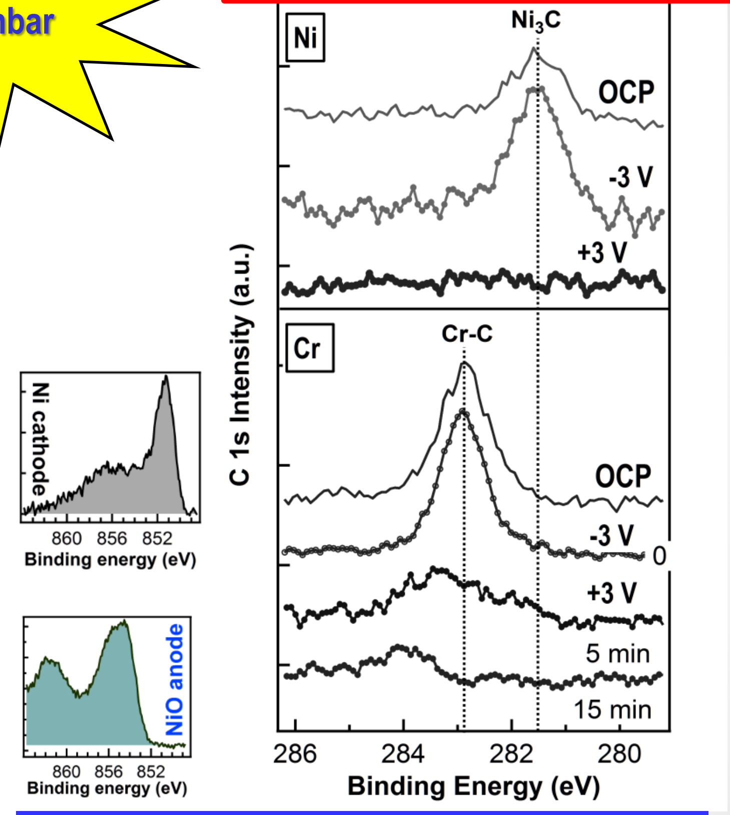
$C_2H_4+H_2O$:
650°C 10^{-5} mbar
Bias

Morphology via Ni maps



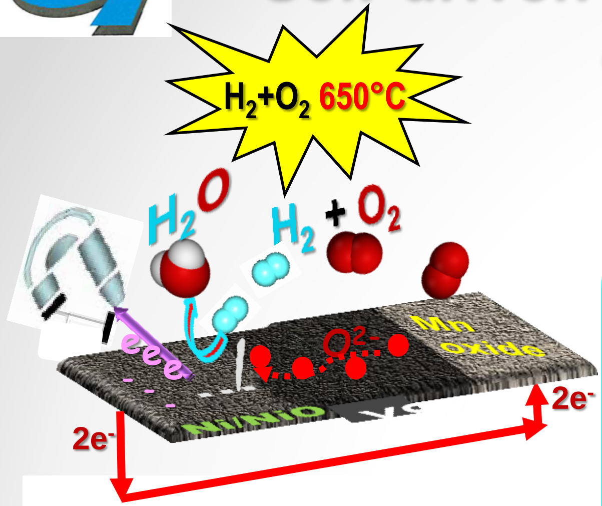
Polarization promoted directional Ni electro migration towards the electrolyte: reliability issues with decreasing Fuel Cell dimensions

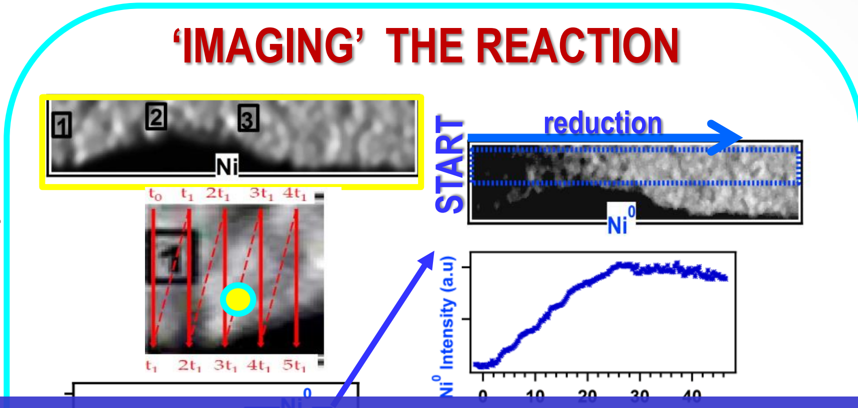
C contaminants: chemistry and electrochemistry

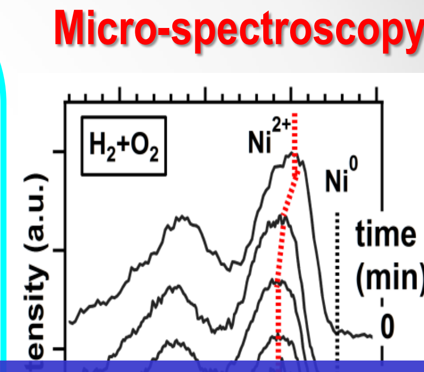


C deposition occurs only at OCP and is promoted by cathodic polarization. Can be removed applying anodic polarization.

Self-driven single Mn/Ni cell: temporal evolution of chemical state and potential







The spectral transients recorded under operating conditions, resulting in generation of electric current, encode both the time-dependent electrochemical kinetics through spectral energy shifts and the electrodes oxidation states resulting from the electrochemical or/and chemical processes:

very good agreement between the numbers predicted for the potential generated from the electrochemical reaction and the measured from the spectral shifts.

B. Bozzini et al, Scientific Reports, DOI: 10.1038/srep02848

Conclusions and Outlook

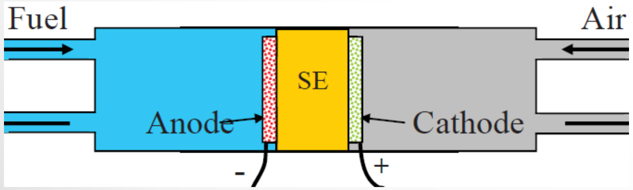
SXM and SPEM can provide unique information about morphological and chemical effects in operating energy-conversion devices, relevant to degradation mechanisms.

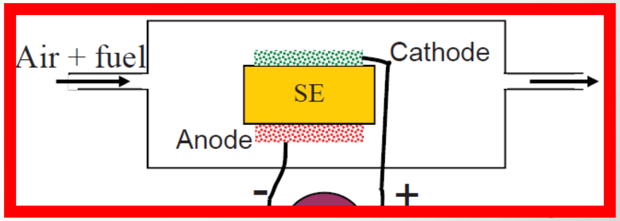
At present model FCs with full control on temperature and potential have allowed assessment of processes at local scales: electrochemical and morphology changes and mass transport.

Next steps:

Set up operational FC systems with full potential, P &T control + in-situ synchronized voltammetry.

Challenges: separating fuel and oxidant and crossing the pressure gap..





THANK YOU!

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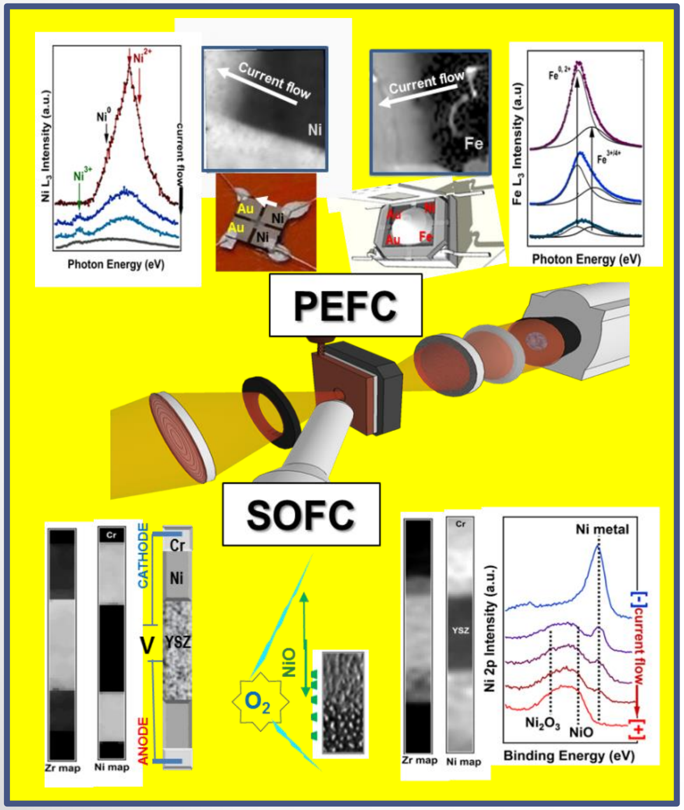
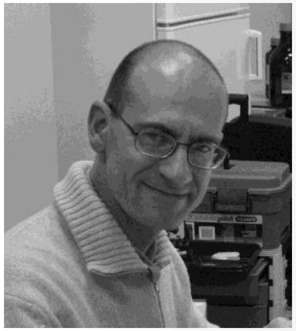
Matteo Amati

Majid Kazemian*
DIAMOND

Burkhard Kaulich *
DIAMOND





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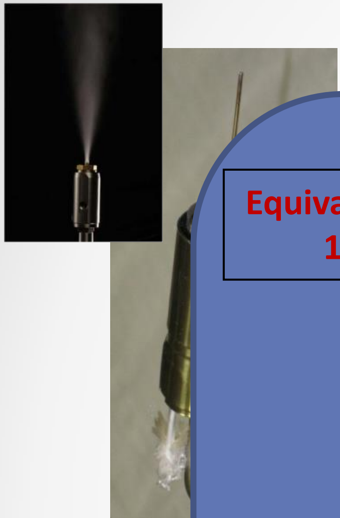
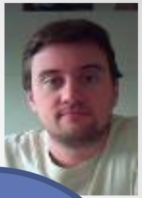
ESCA microscopy: Dynamic 'HP' SPEM Module



➢High frequescy pulsed dosing valve + nozzle

➢UHV compatible.

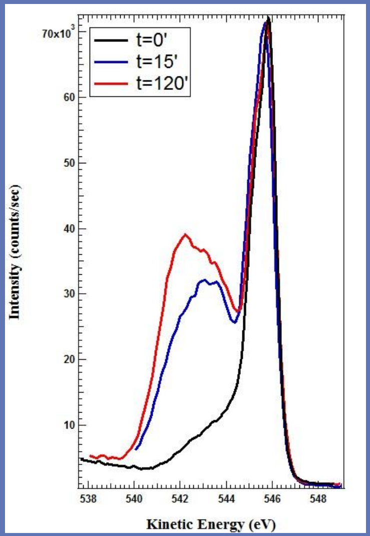


Si oxidation (530°C)

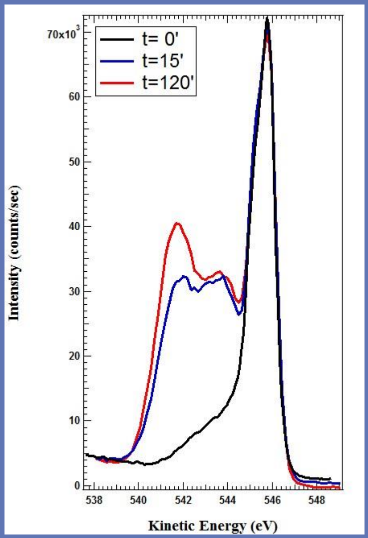
Equivalent Static Pressure
10^{-3} - 10^{-2} mbar

SPEM chamber
Max = 1*10-5 mbar

Static Pressure
1 x 10^{-3} mbar



HP
t_{AP} = 2.73ms
f_{AP} = 300 mHz
P_{valve} = 3.5 bar



Static Pressure
1 x 10^{-2} mbar