Microscopic insight on chemical state and morphology of key components in operating proton exchange membrane fuel cells (PEPFCs) and solid oxide fuel cells (SOFCs) using synchrotron based imaging and microspectroscopy

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

PEFC: Electrochemical corrosion of Fe and Ni plates and mass transport of corrosion products;
Degradation of Pt/C electrocatalyst

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

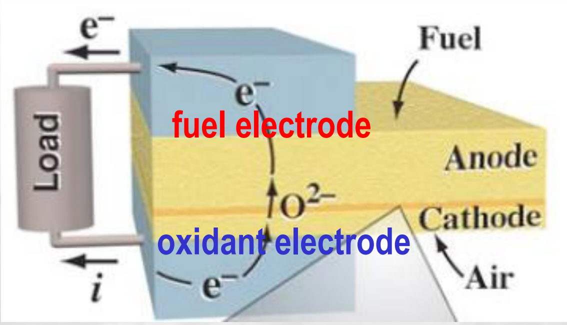
- **Conclusion and outlook.**

ICTP November 30, 2012

Maya Kiskinova

Fuel Cell:

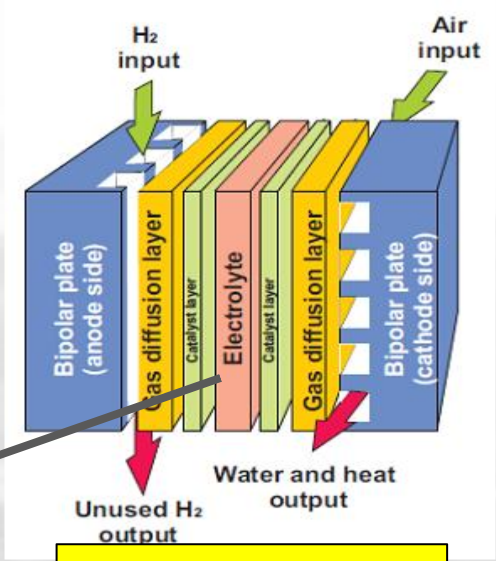
pollution-free conversion of chemical energy to electricity



$$2H_2+O_2 \rightarrow H_2O$$

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

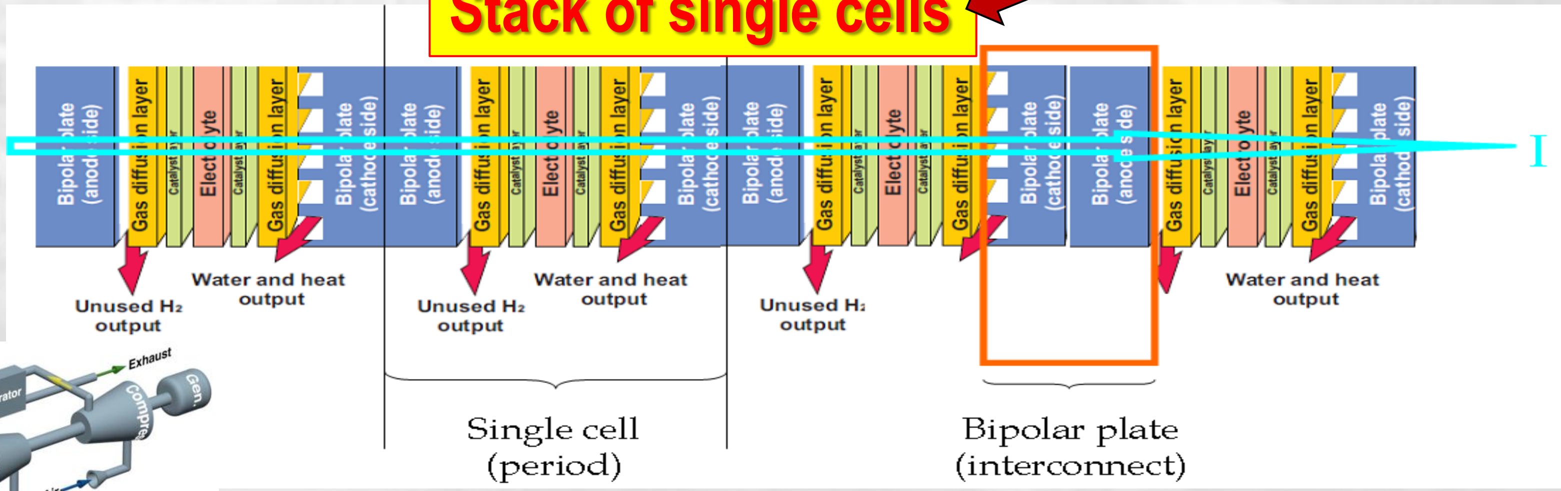
$$O_2 + 4e^- \rightarrow 2O^{2-}$$

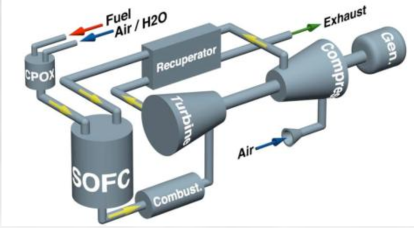


PEFC: (H⁺ charge carrier) - polymer membrane T< 120°C
SOFC: (O^{2-} charge carrier) - oxide (YSZ, CeO_2..) T~650÷1000°

single cell Ca. 1 V

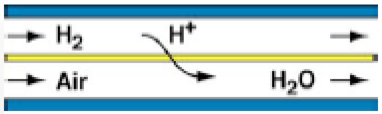
Stack of single cells

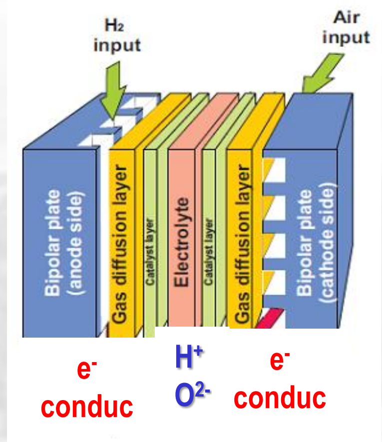


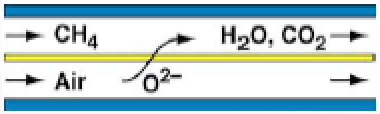


PEMFC and SOFC

complex dynamic systems using unique material combinations







PEMFC

- Electrolyte - proton(H^+) -conducting (polymer, e.g. Nafion);
- Low operation temperature (~100°C);
- Requires pure H_2 fuel and oxidant;
- CO is a poison;
- Precious-expensive catalysts (Pt).

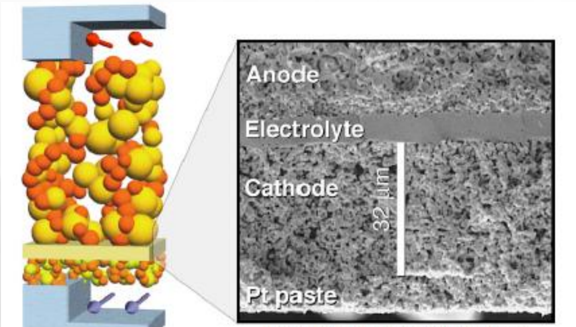
SOFC

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

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

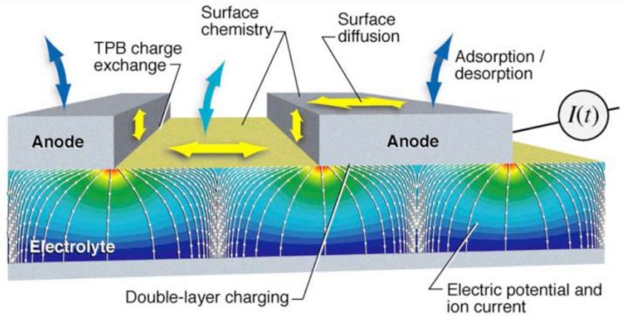
- BP corrosion = R_Ω increase , mass transport of corrosion products can lead to DL clogging, catalyst deactivation, electrolyte degradation
- Catalyst deactivation - poisoning (S, C, CO), sintering;
- Electrolyte ion conductivity loss and degradation: e.g. hydration level of polymer membrane, migration of species from the electrodes , redox processes etc

Operating Fuel Cells:
complex dynamic micro-systems



MEA fabricated by ITN energy Systems

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



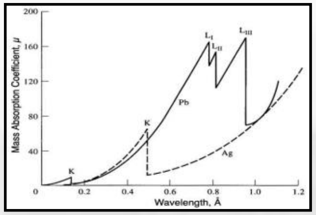
Need monitoring in-situ processes at the key components: interconnects, electrodes and electrolyte:

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

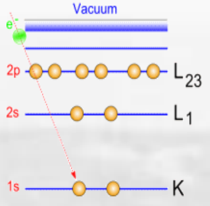
Morphologically complex and nanostructured matter needs methods with sufficient lateral resolution, chemical & surface sensitivity, correlative morphology & structure information.

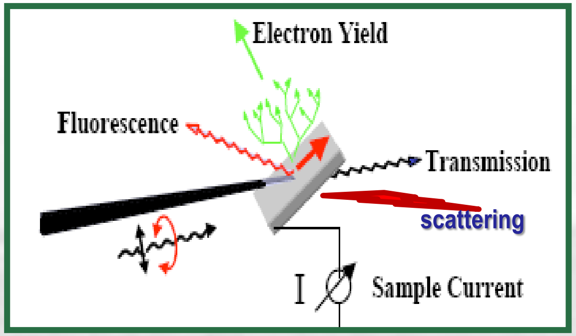
Synchrotrons offer a variety of spectroscopy and microscopy-imaging approaches

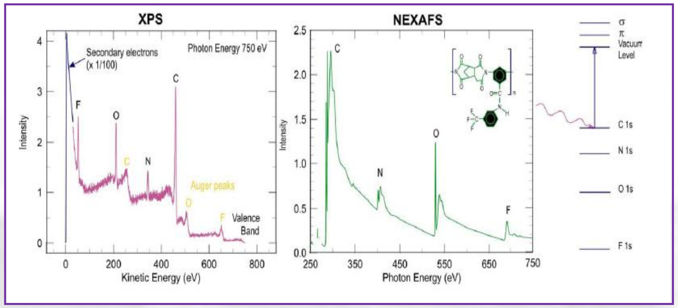
X-ray absorption



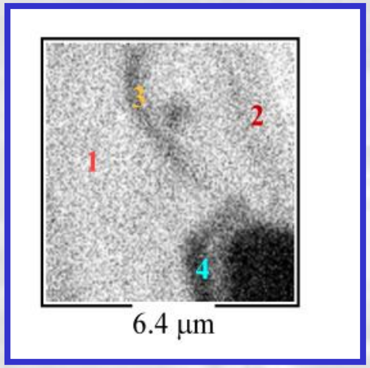
Photon or e⁻ emission

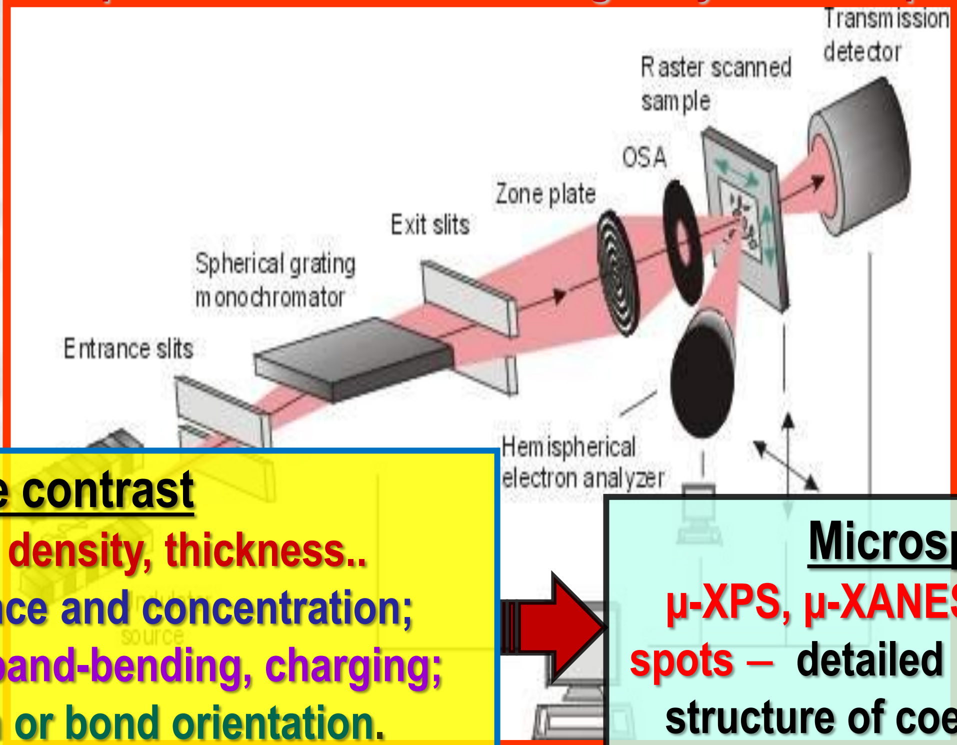






Add spatial resolution - scanning x-ray microscopes





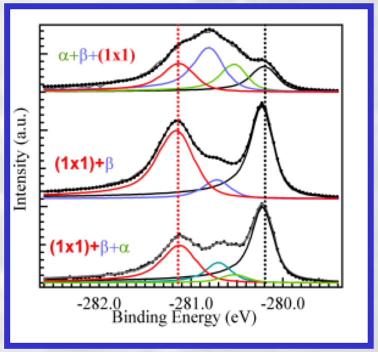


Image contrast

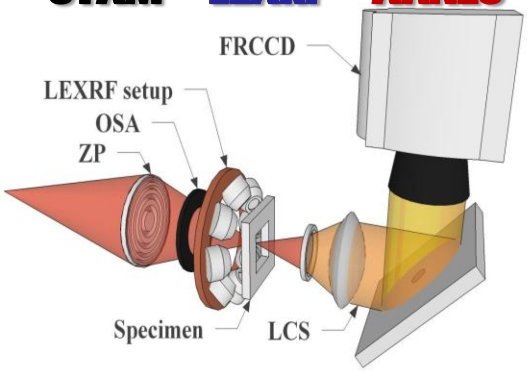
- Morphology: density, thickness..
- Element presence and concentration;
- Chemical state, band-bending, charging;
- Magnetic spin or bond orientation.

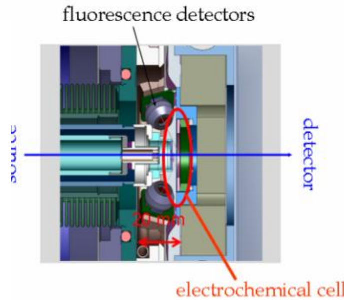
Microspectroscopy:

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

Microfabricated Fuel Cells for SXM and SPEM

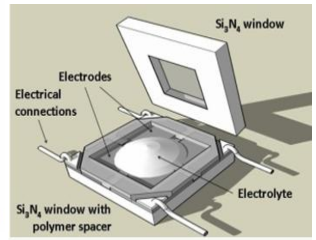
STXM – LEXRF – XANES



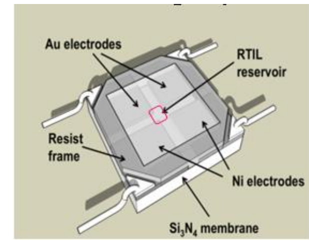


TwinMic

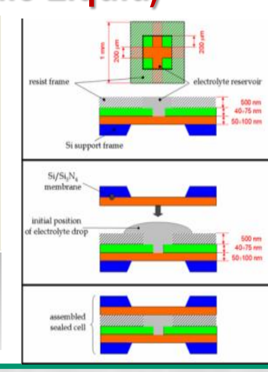
Proton Exchange Membrane (sealed for aqueous Nafion and open with spun RT Ionic Liquid)



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



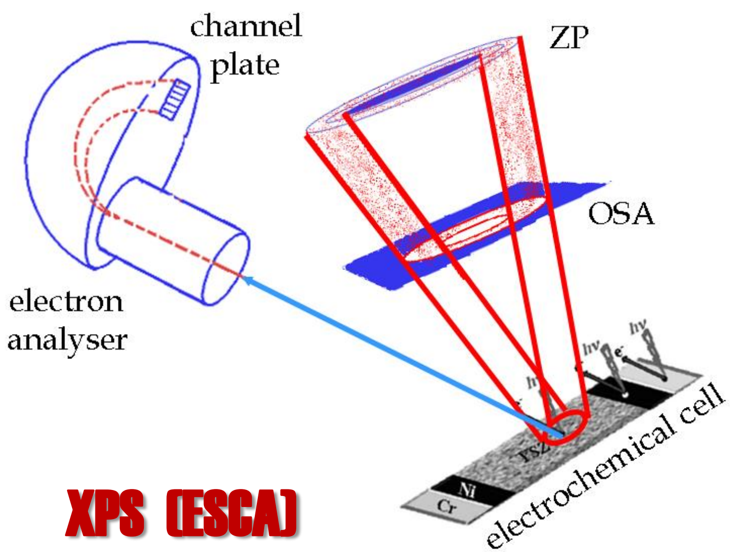
Bozzini et al.
PhysChemChemPhys
13 (2011) 7968.



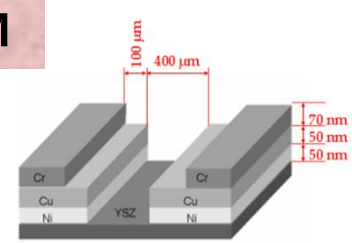
B. Bozzini UNIVERSITÀ DEL SALENTO

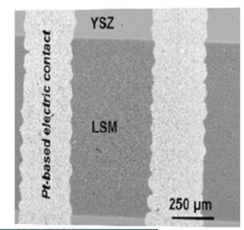
ChemSusChem 3 (2010); 4 (2011),....

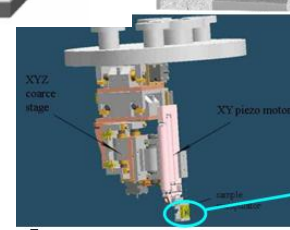
SPEM



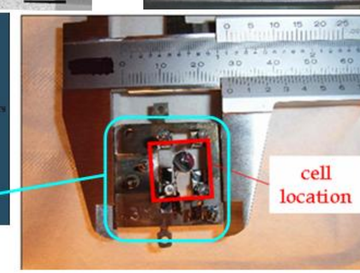
XPS (ESCA)







Specimen positioning & scanning system



B. Luerssen JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN — Angew. Chem. Int. Ed. 45, 2006, 1473....

M. Backhaus CORNING — Solid State Ionincs, 2008....

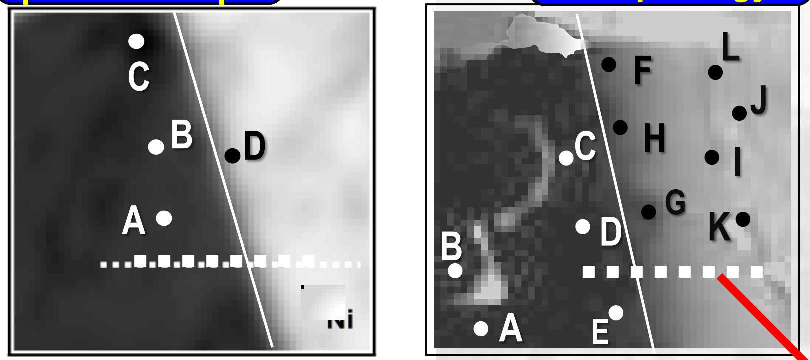
E. Mutoro MIT — PhysChemChemPhys 313, 2011. 3394

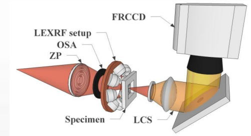
PEPFC: metal BP stability

Ni, Fe corrosion in Nafion and Nafion poisoning

operated at anodic polarization of 0.5 V vs Au electrode

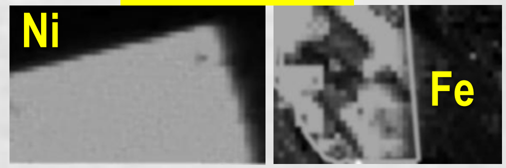
Ni- preserves pristine shape | **STXM maps** | **Fe- corrossion morphology**



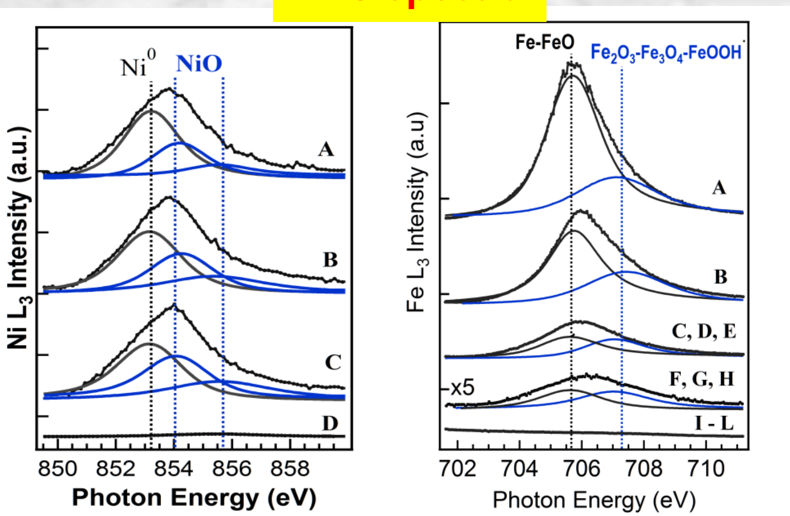


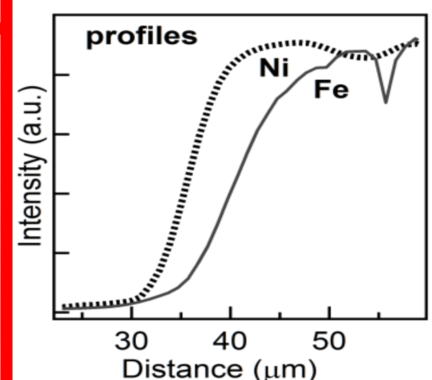
STXM
LEXRF
XANES

XRF maps

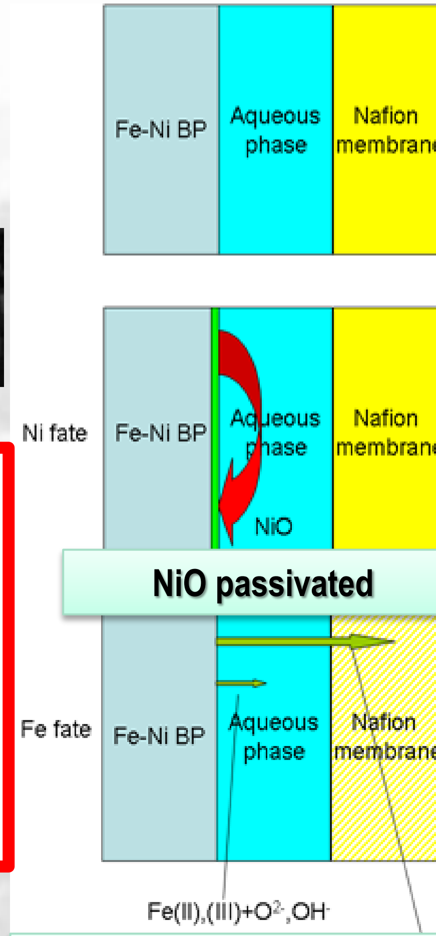


XAS spectra





distribution across interface



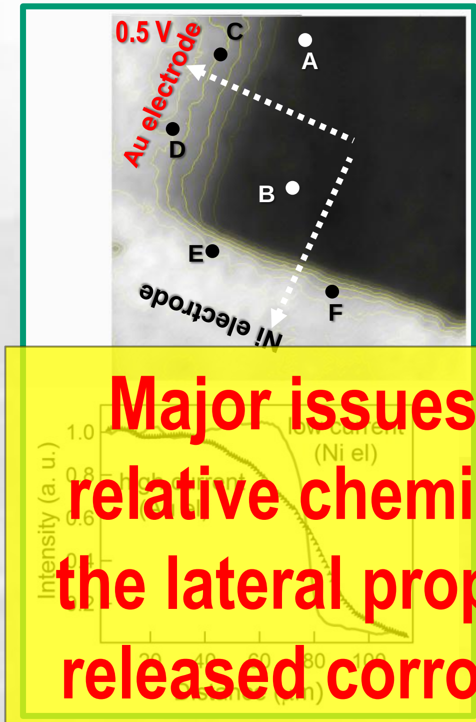
NiO passivated

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

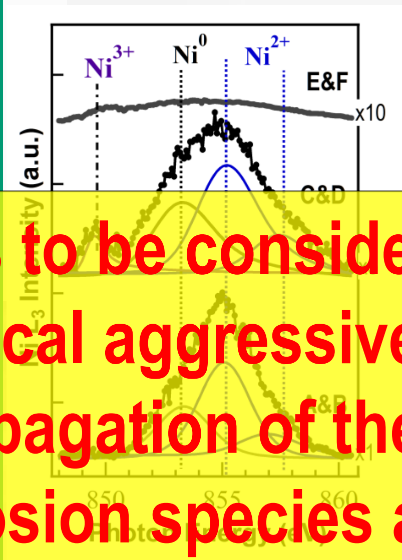
B. Bozzini et al, ChemSusChem 2010, 3, 1, *Microelectr. Eng.* 2011, 88, 2456

PEPFC: metal BP stability

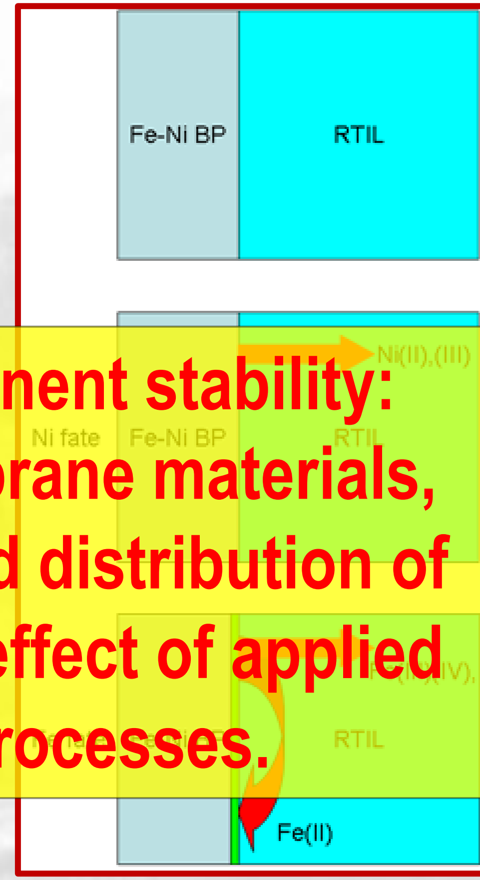
Ni, Fe corrosion in RTIL and RTIL poisoning



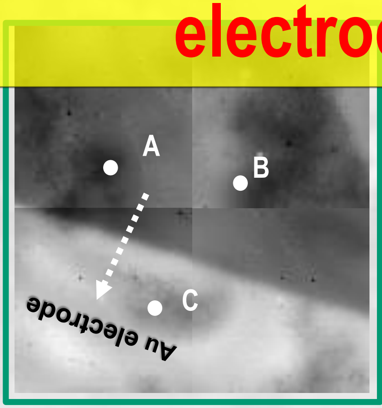
Ni: C.D.D controlled diffusion IN RTIL

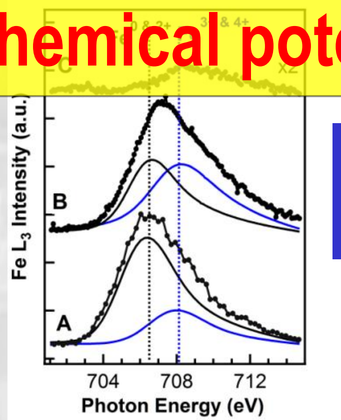


Ni corrosion products interact with the RTIL. The localisation of the higher-valence form of oxidised Ni in the high-current density region is consistent with the higher anodic potentials developed there.



Major issues to be considered for component stability: relative chemical aggressiveness of membrane materials, the lateral propagation of the corrosion and distribution of released corrosion species as well as the effect of applied electrochemical potential on these processes.

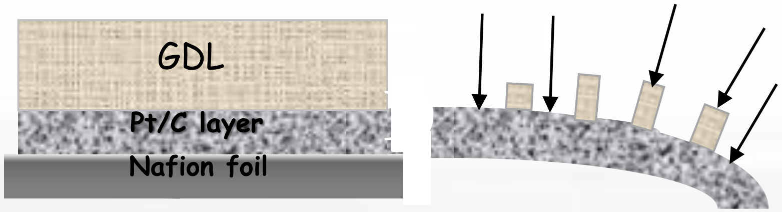




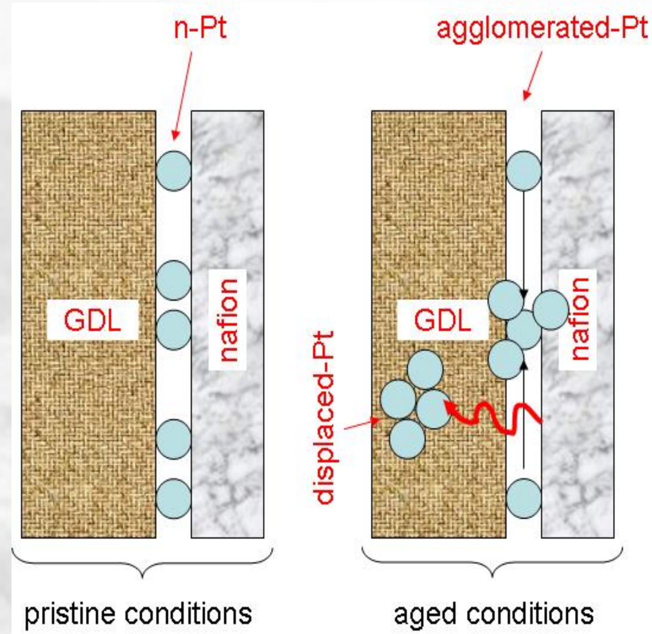
Fe: higher corrosion resistance

B. Bozzini et al, PCCP 13, 2011, 7968
Fuel Cells 2012 in press

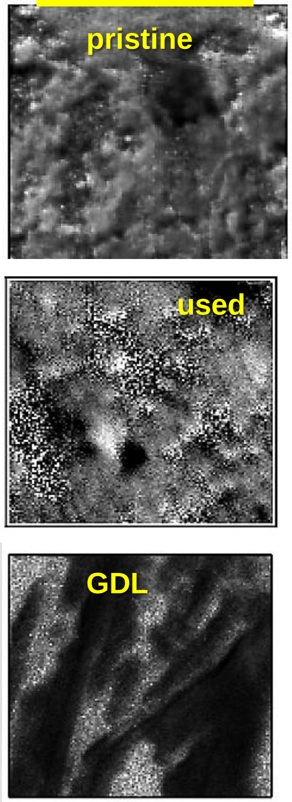
PEPFC: degradation of Pt/C catalyst and GDL



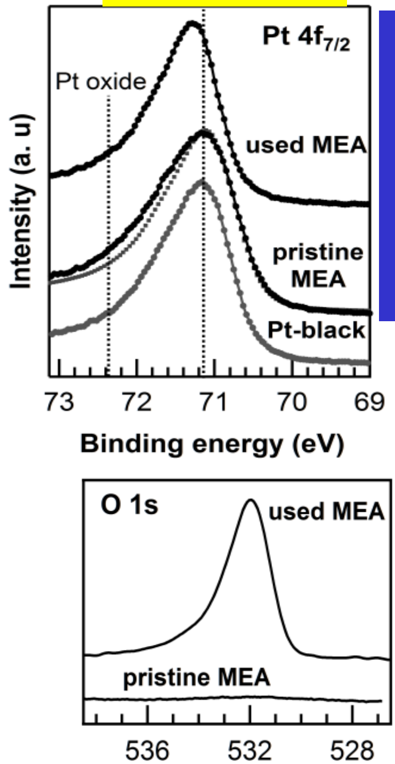
(i) detachment and mass transport into the electrolyte; (ii) aggregation (iii) poisoning by corrosion products?



Pt 4f maps



XPS spectra



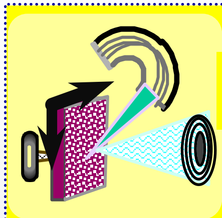
Pt 4f spectra: preserved metallic state – size effects on the BE and penetration in GDL

O 1s: BE typical for oxidised C

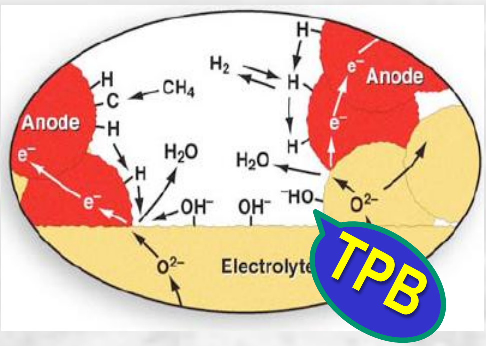
Ageing of the Pt catalyst in anodic membrane-electrode assembly after 1000 hours of operation: redistribution, aggregation and loss of material due to Pt migration away from the electrode and C oxidation.

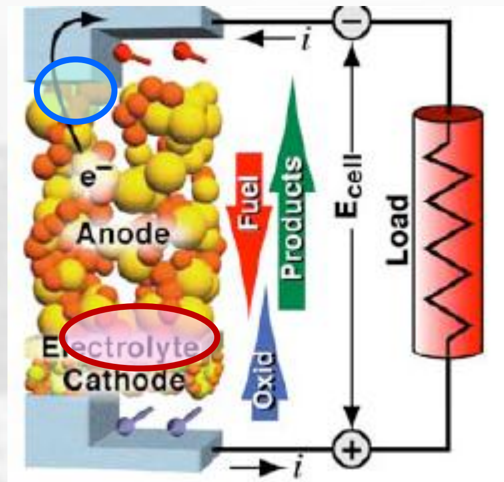
Bozzini et al. J Power Sources 196 (2011) 2513.

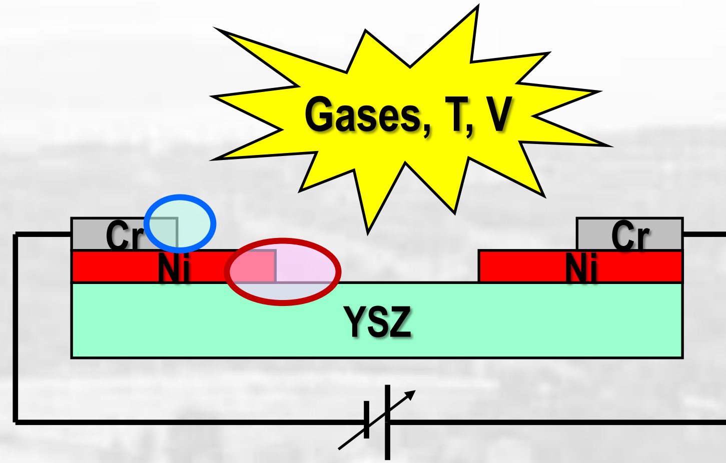
SOFCs under operating conditions



Correlative information about chemical state, overpotentials and morphology







SPEM using model cells allows in-situ monitoring processes obscured from observation in the device at the interfaces between interconnects, electrodes and electrolyte.

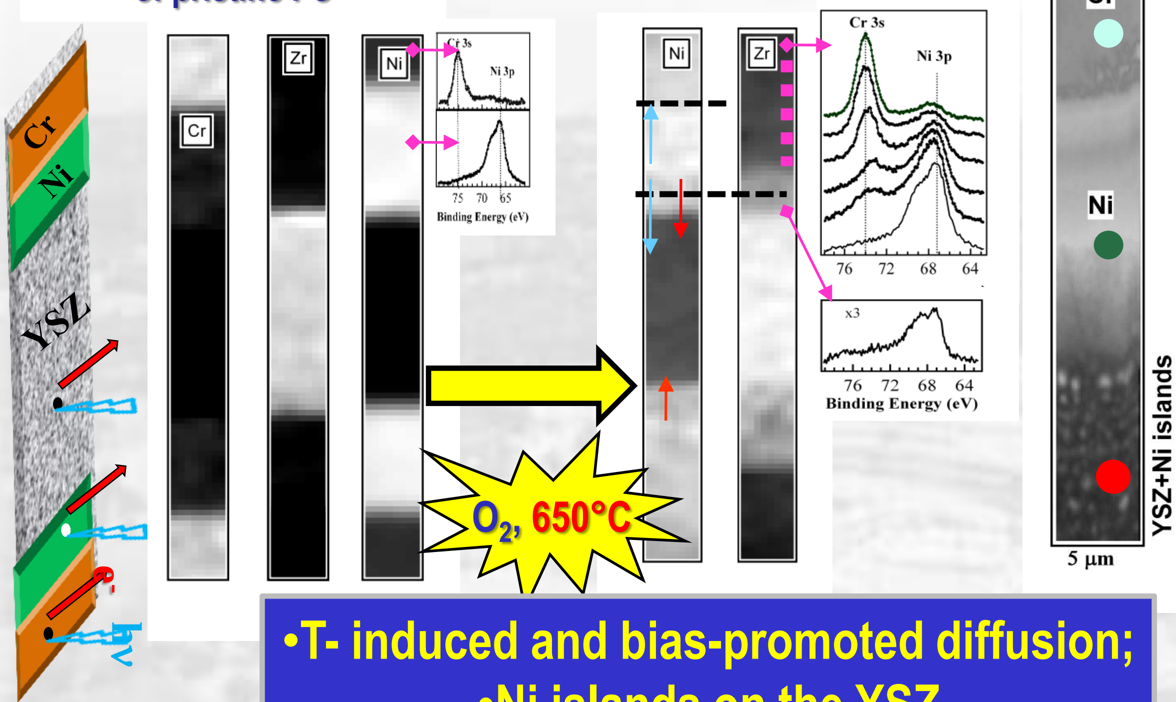
- Redox-cycles (e.g. Ni⇔NiO) morphology-chemistry: gas, T, bias
- Mass transport - High T, Bias.

SOFC in oxidizing ambient

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

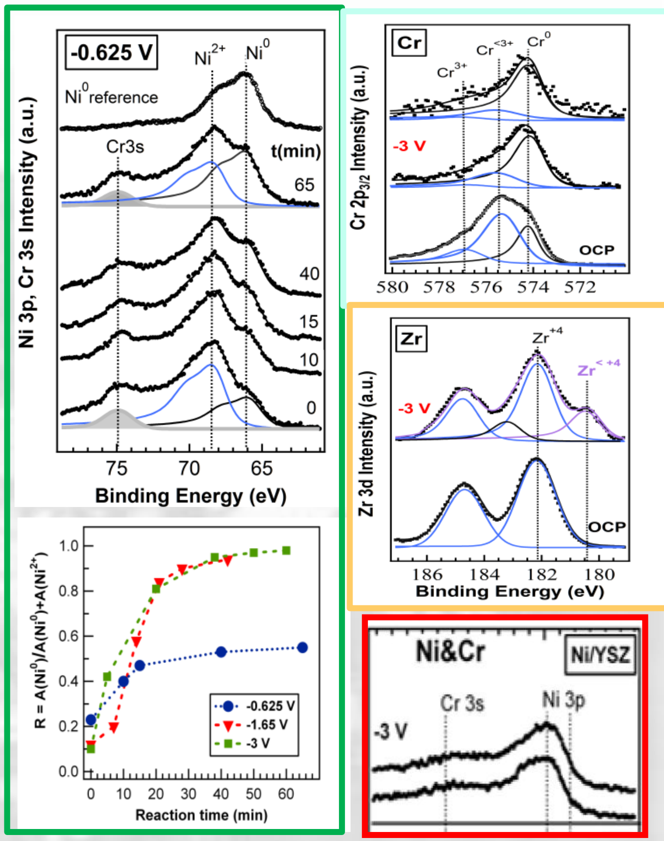
Morphology

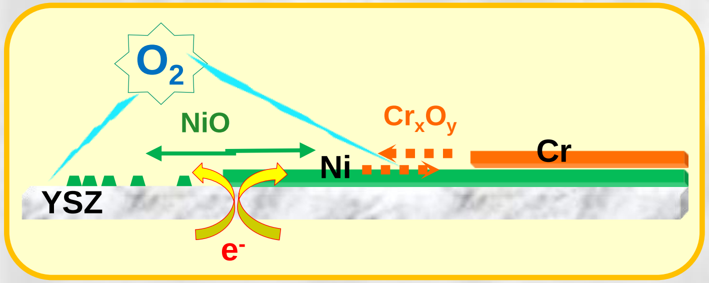
Cr3p, Zr3d and Ni3p maps of pristine FC



•T- induced and bias-promoted diffusion;
•Ni islands on the YSZ

Electrochemistry





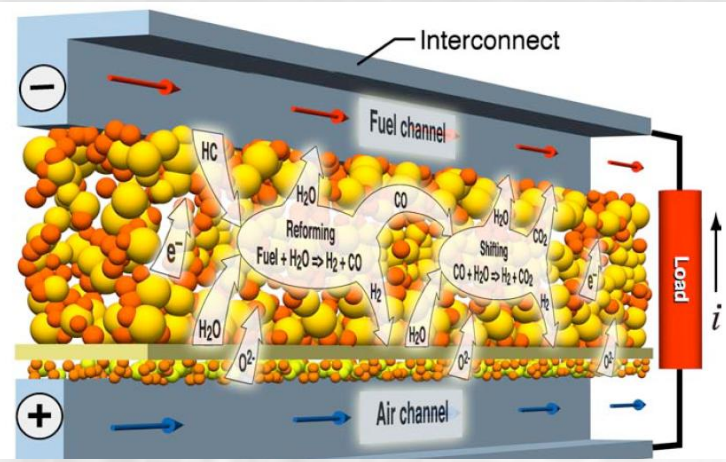
- ❑ Ni reduction already at -0.6 eV; R=f(V)
- ❑ Cr and YSZ reduction only at -3 V
- ❑ Intact NiO islands - lack of electron drain.

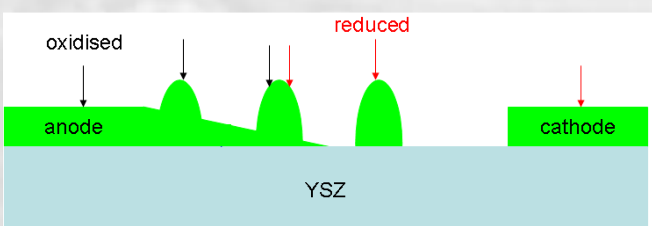
Bozzini et al. ChemSusChem 3 (2011) 2513.

SOFC using hydrocarbon fuel

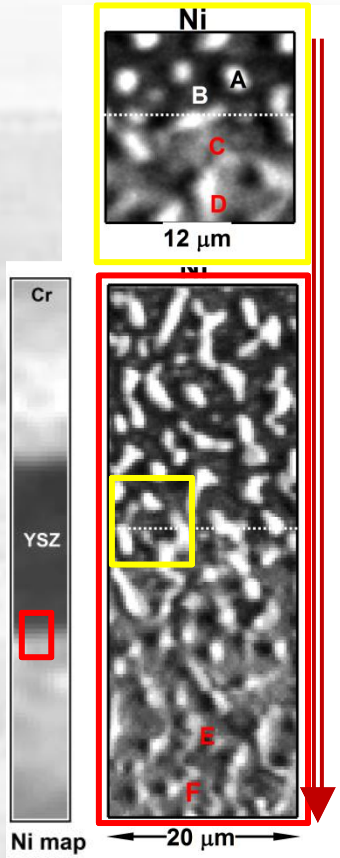
650 C 10^{-5} mbar $C_2H_4 + H_2O$, Bias ± 1 - 3.0 V

C_2H_4+H_2O 650°C



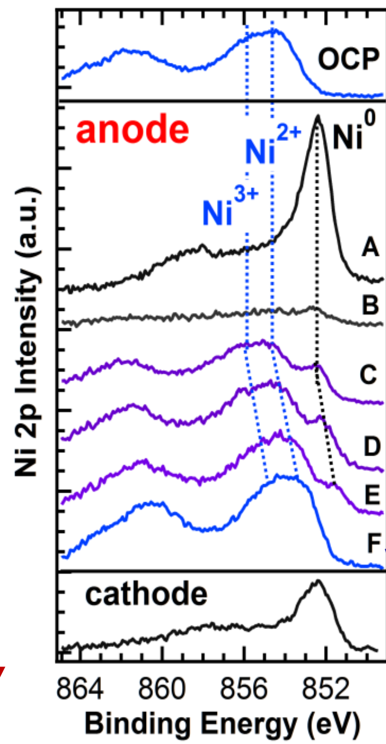


Morphology

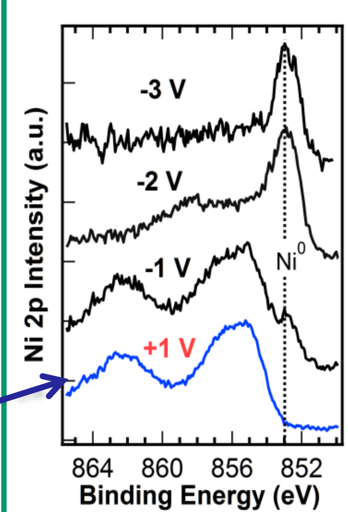


Electrochemistry

Distribution electrochem. activity



Reversible red-ox process



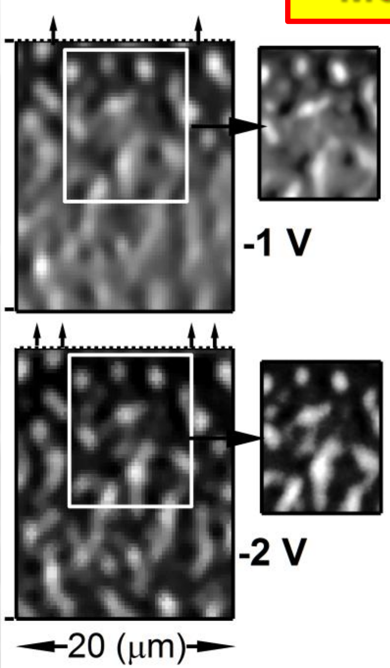
Lateral variations of the degree of Ni oxidation in concert with the local anodic potential.

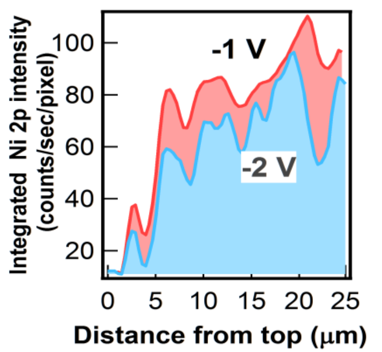
Bozzini et al. J. Phys. Chem. C, 2012 in press

SOFC: directional electromigration and C deposition

650 C, 10^{-5} mbar $C_2H_4 + H_2O$ Bias ± 1 - 3.0 V

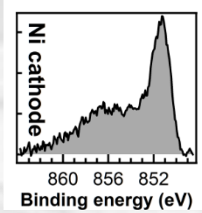
Morphology

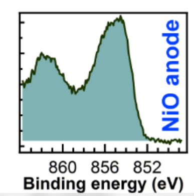


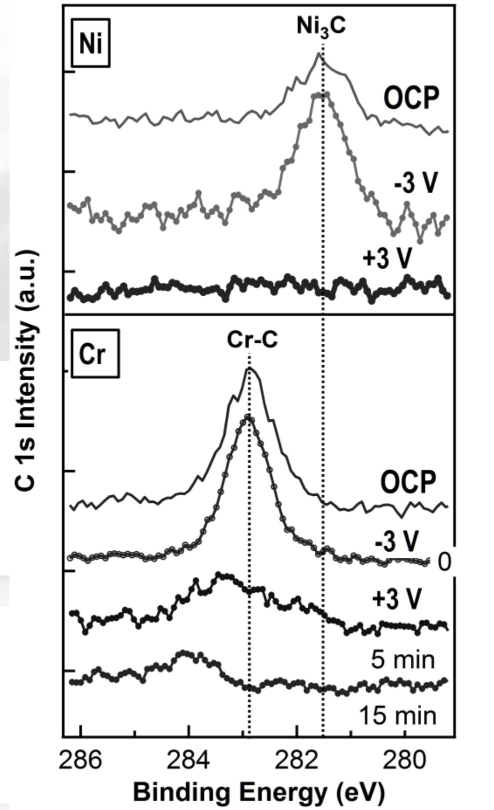


$C_2H_4+H_2O$ 650°C

Electrochemistry



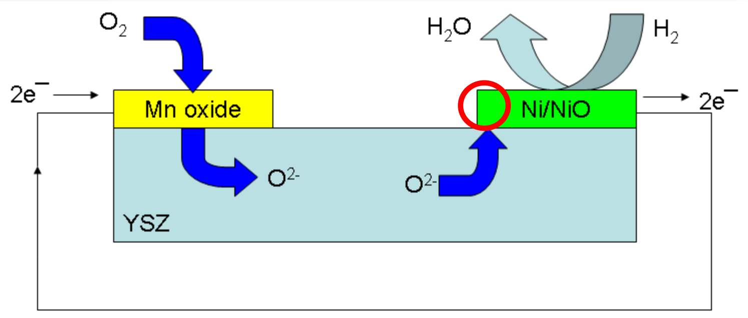




Polarization promoted directional Ni electro migration towards the electrolyte: reliability issues for the interconnects with decreasing FC dimensions

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

Self-driven single Mn/Ni cell: oxygen and hydrogen as catodically and anodically reactive gases: mapping spectral shift with time and space and the current with potentiostat



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

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

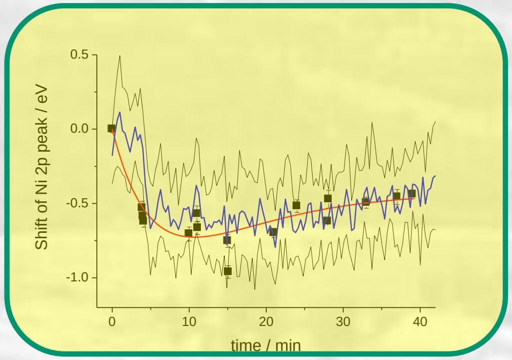
$2H_2 + O_2 \rightarrow 2H_2O$

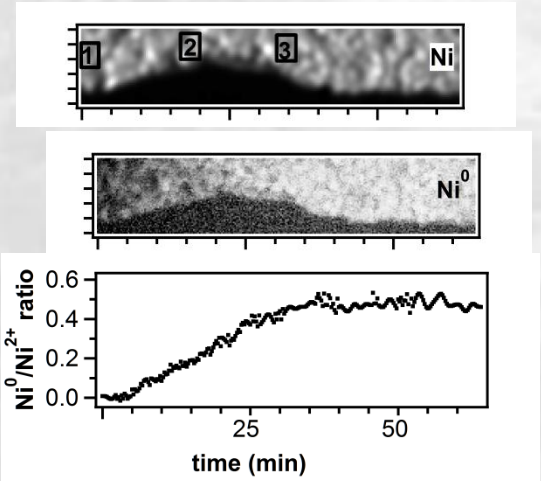
$\Delta G(1\ \text{mbar}) = -367\ \text{kJ/mol} \Rightarrow E = 0.95\ \text{V}$

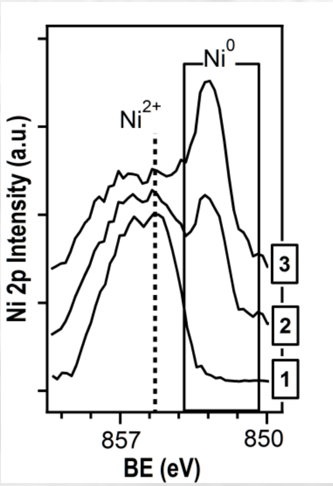
$\Delta G(10^{-5}\ \text{mbar}) = -322\ \text{kJ/mol} \Rightarrow E = 0.83\ \text{V}$

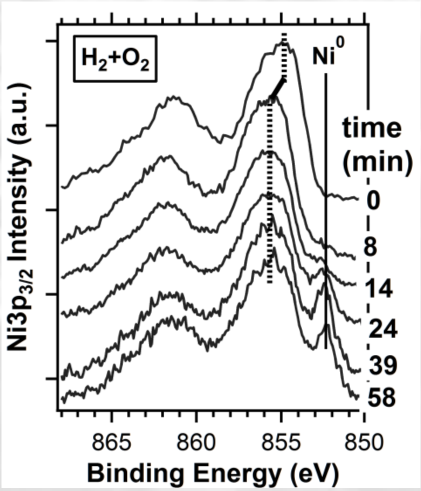
$\Delta G(10^{-6}\ \text{mbar}) = -314\ \text{kJ/mol} \Rightarrow E = 0.81\ \text{V}$

Switch from O_2 to H_2 or $O_2 + H_2$ ambient









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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, pressure and T control

+

in-situ synchronized voltammetry.

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

THANK YOU!

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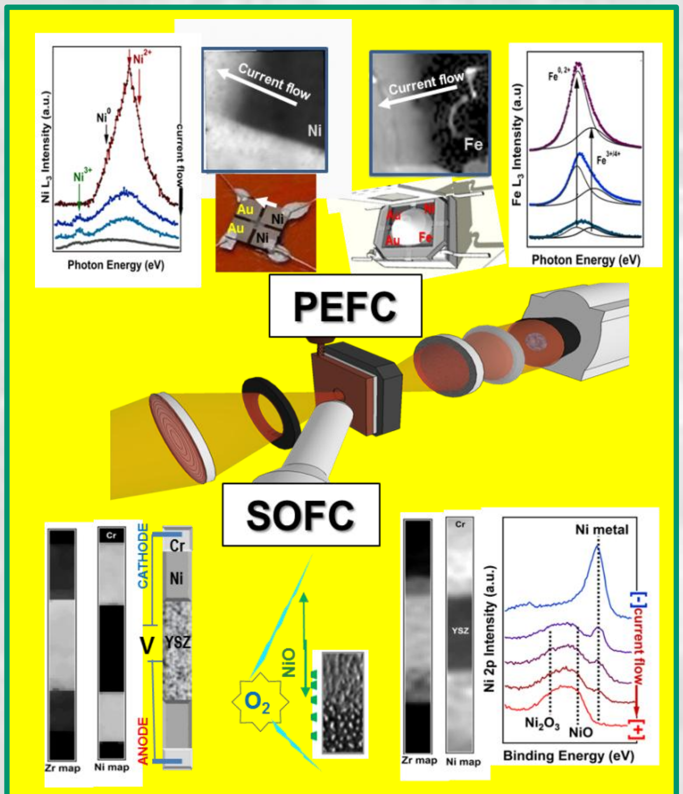
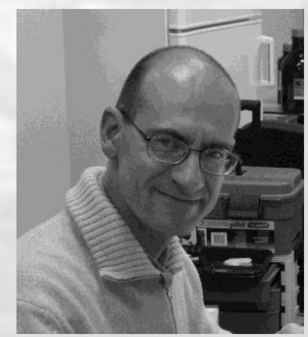
Mauro Prasciolo* DESY





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ICTP November 30, 2012

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