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In situ Electrochemical Studies of Fuel Cells by Soft-X-Ray Spectromicroscopy

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In situ Electrochemical Studies of Fuel Cells by Soft-X-Ray Spectromicroscopy

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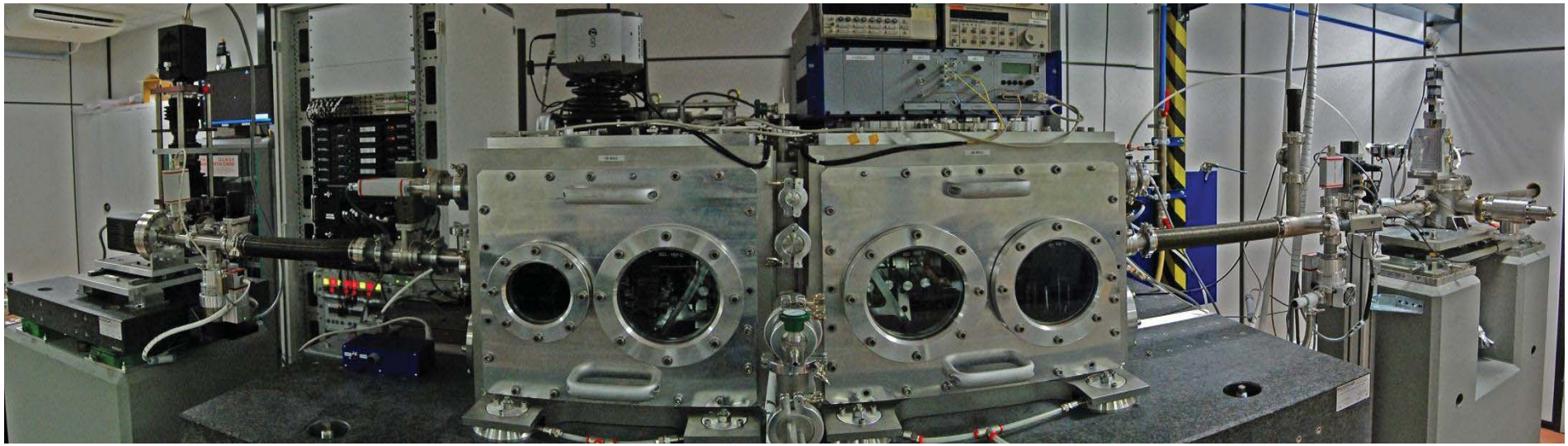
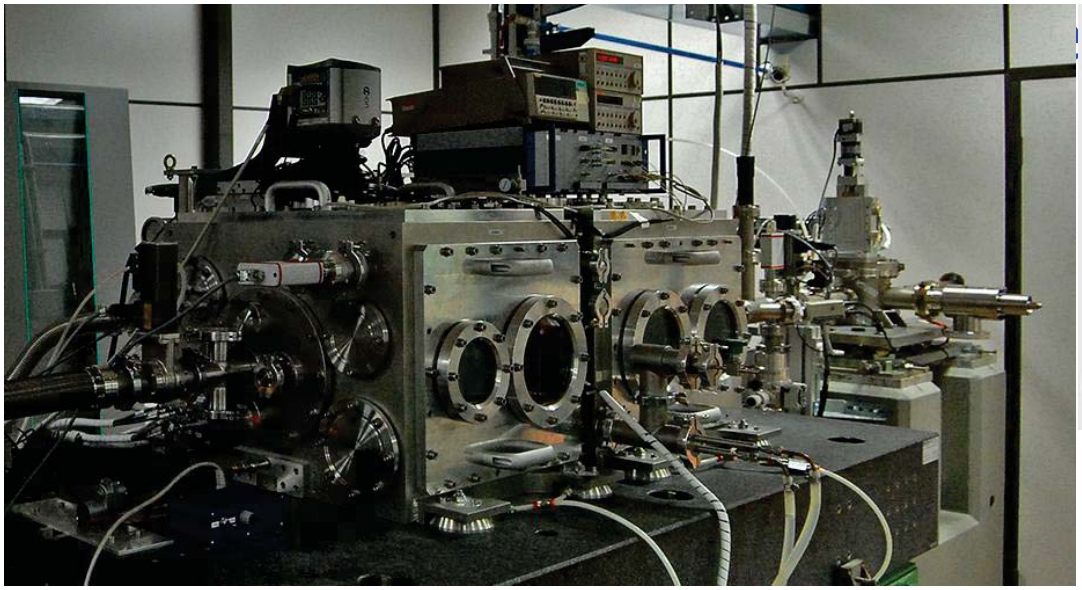
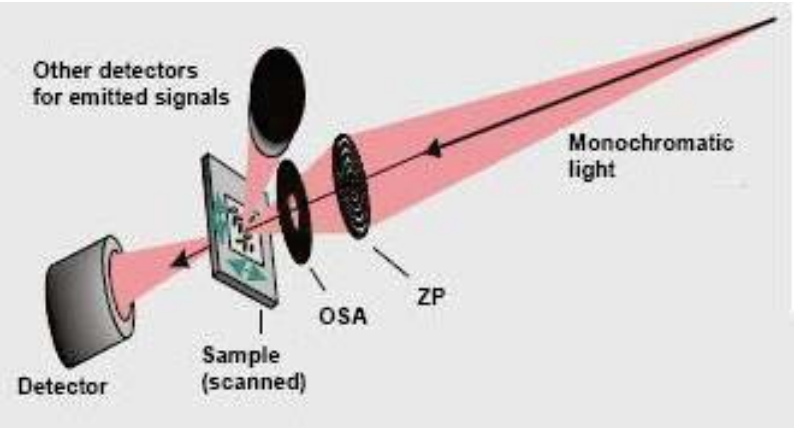


Scanning Transmission X-ray Microscope (STXM) at Elettra





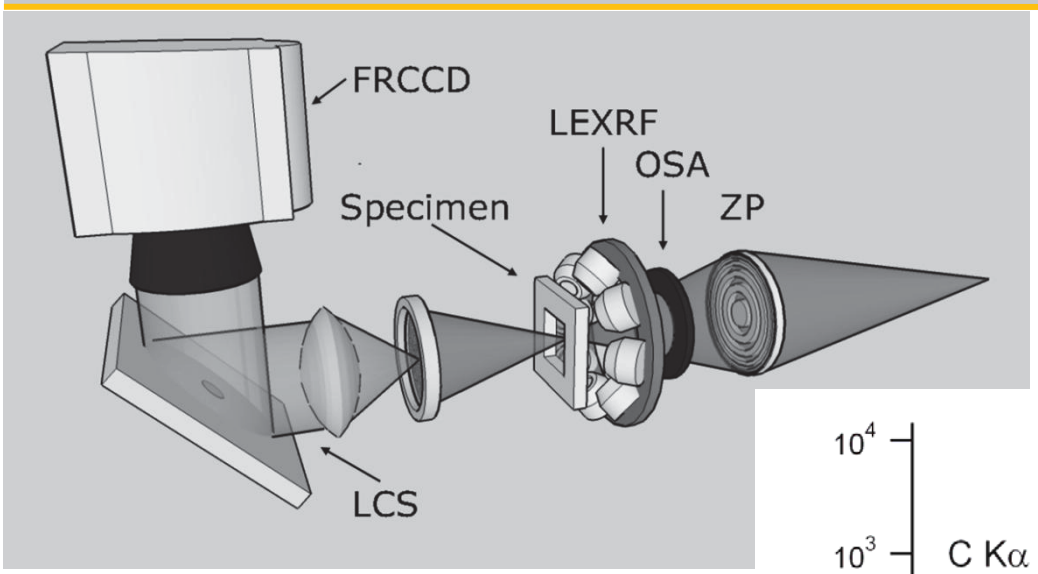
– Lateral resolution down to 50 nm

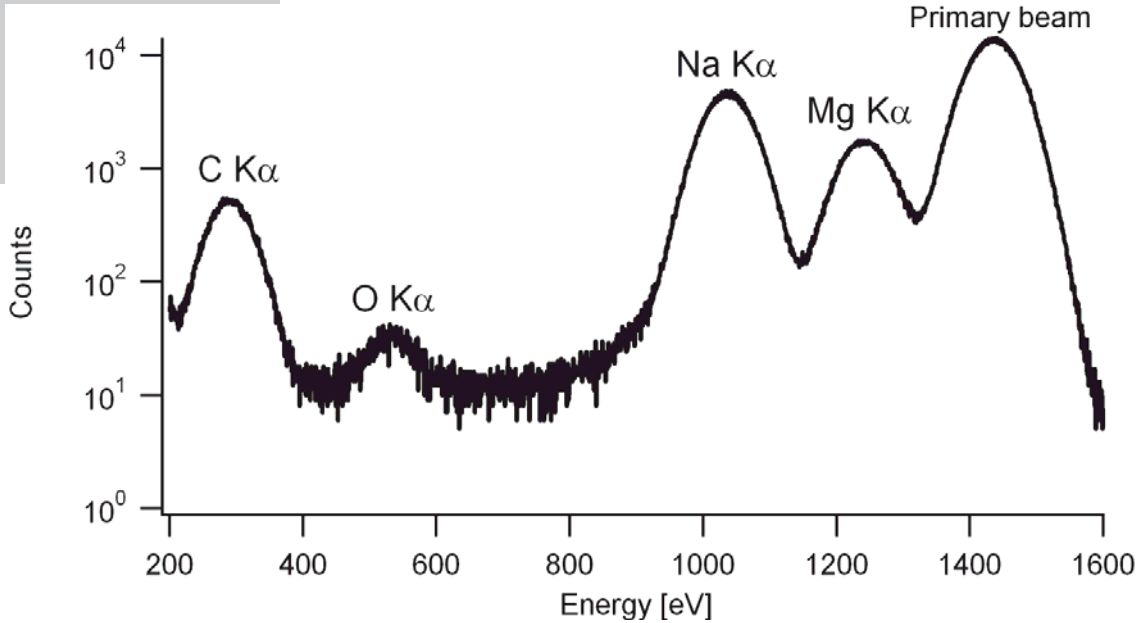
– Absorption and Phase contrast
Imaging, XANES, XRF

– Photon energy range:
400÷2200 eV

B. Kaulich et al, TwinMic: A European Twin X-ray Microscopy Station Commissioned at ELETTRA, in Proc. 8th Int. Conf. X-ray microscopy (eds. S. Aoki, Y. Kagoshima, Y. Suzuki), Conf. Proc. Series IPAP 7, pp. 22-25.
G.R. Morrison et al, A fast-readout CCD system for configured-detector imaging in STXM, in Proc. 8th Int. Conf. X-ray microscopy (eds. S. Aoki, Y. Kagoshima, Y. Suzuki), Conf. Proc. Series IPAP 7, 377-379.
A. Gianoncelli, et al, A fast read-out CCD camera system for scanning X-ray microscopy, Appl. Phys.Lett. 89 (2006), 251117.

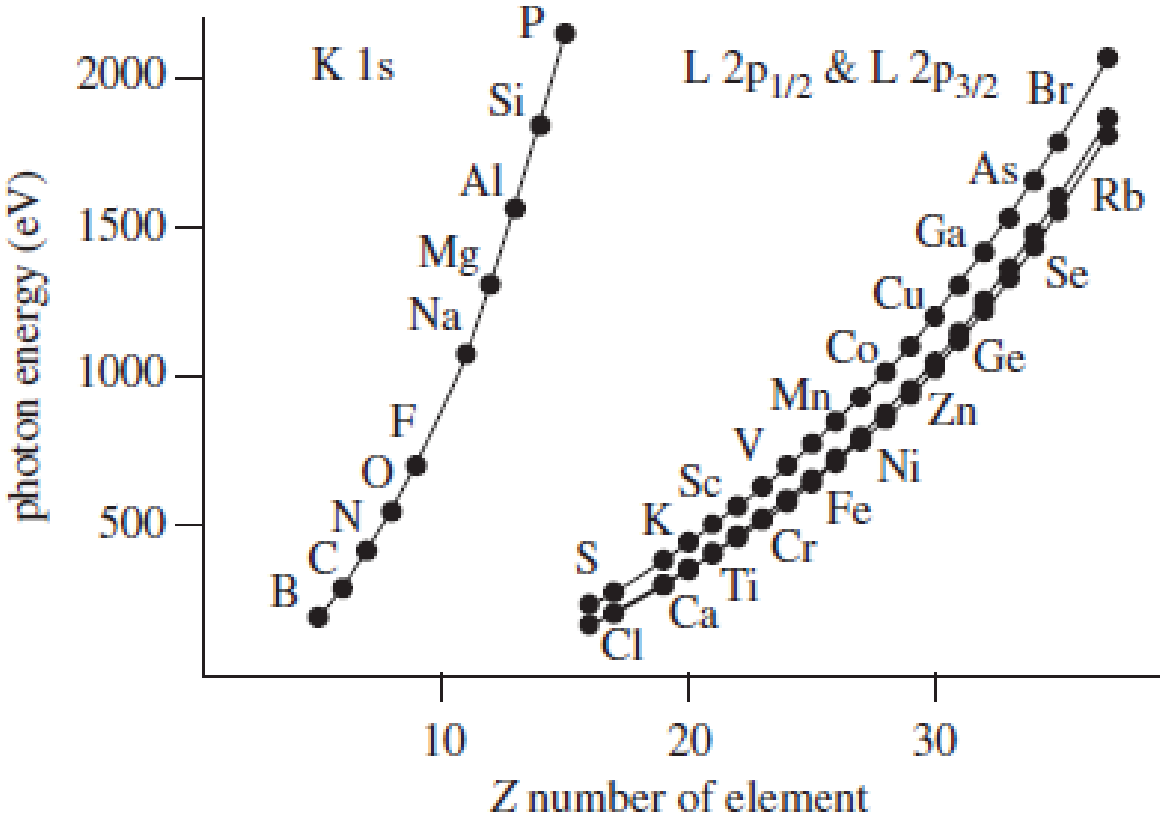
Low Energy X-ray Fluorescence system





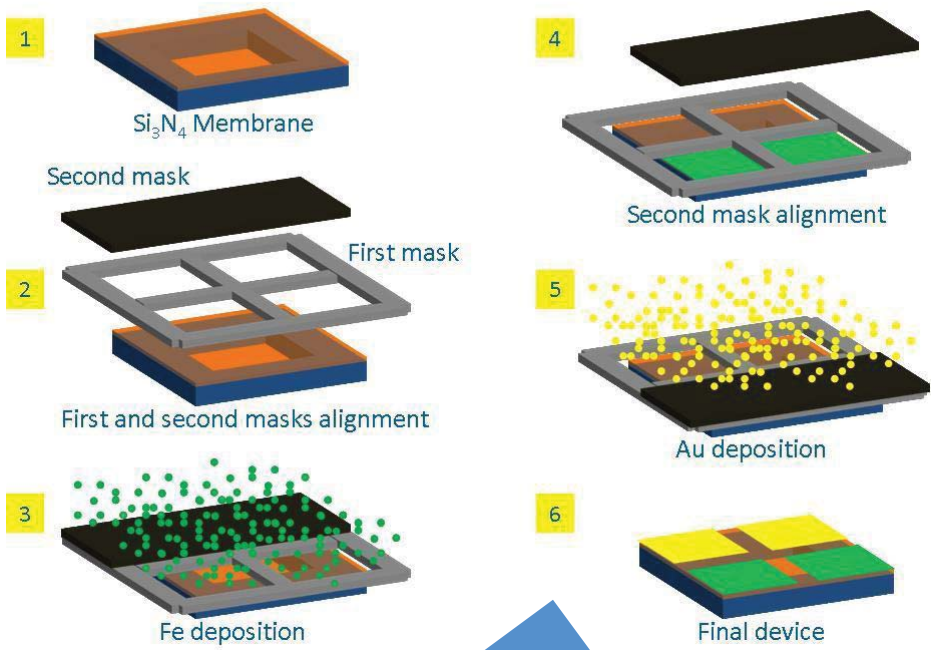
A. Gianoncelli et al, Simultaneous Soft X-ray Transmission and Emission Microscopy, Nucl. Instr. and Meth. A 608 (1), 195-198.
B. Kaulich et al, Low-energy X-ray fluorescence microscopy opening new opportunities for bio-related research, J. R. Soc. Interface 6 (Suppl 5), S641-S647.

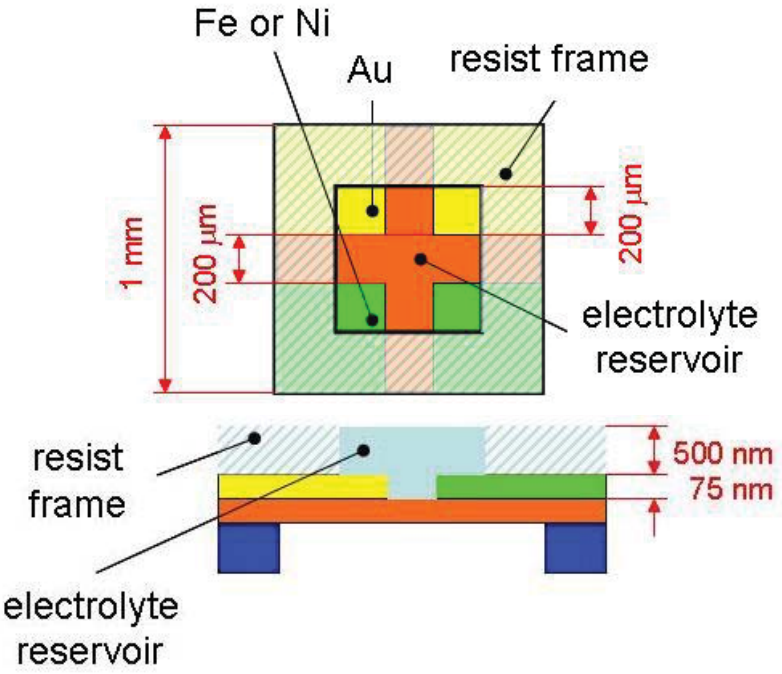
Elements accessible by TwinMic (XANES, XRF, AEI)



B. Kaulich et al, Low-energy X-ray fluorescence microscopy opening new opportunities for bio-related research, J. R. Soc. Interface 6 (Suppl 5), S641-S647.

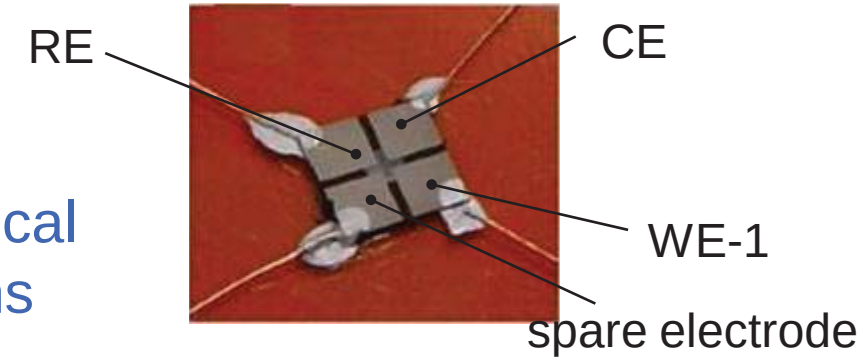
Vacuum-compatible electrochemical cells for SXSM : 1: electrodic system





Electrolyte casting or spinning

Electrochemical connections

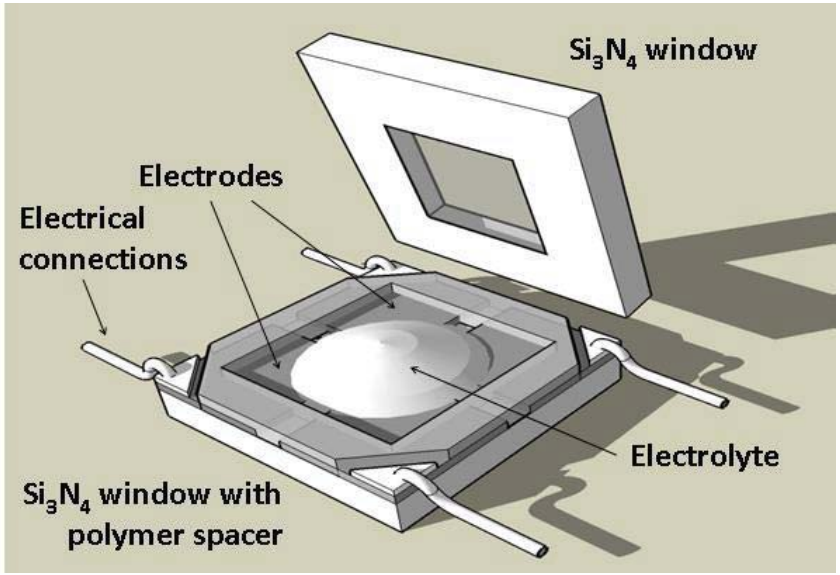


Vacuum-compatible electrochemical cells for SXSM 2: choice of the electrolyte (Why ILs?)

Choice of electrolyte

Non vacuum-compatible (acqueous solutions)

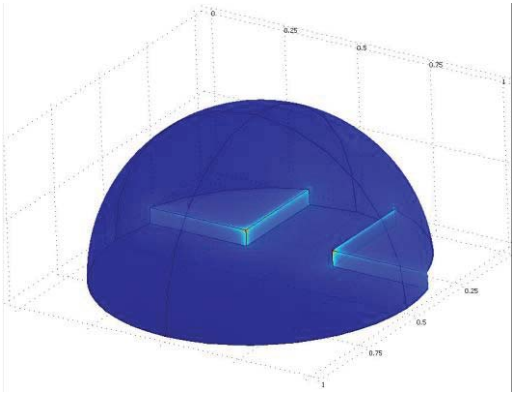
Sealed cell



3D primary cdd

1-butyl-1-methyl-pyrrolidinium bis (trifluoromethylsulfonyl) imide

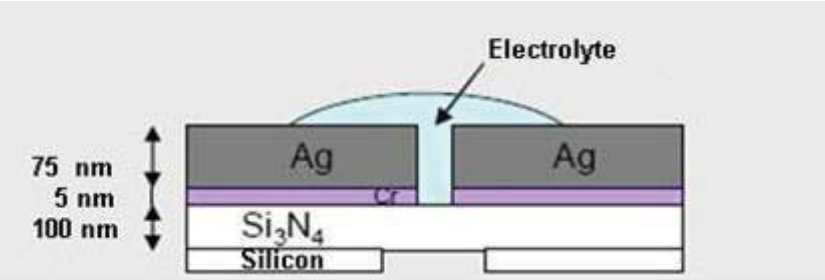
Open cell



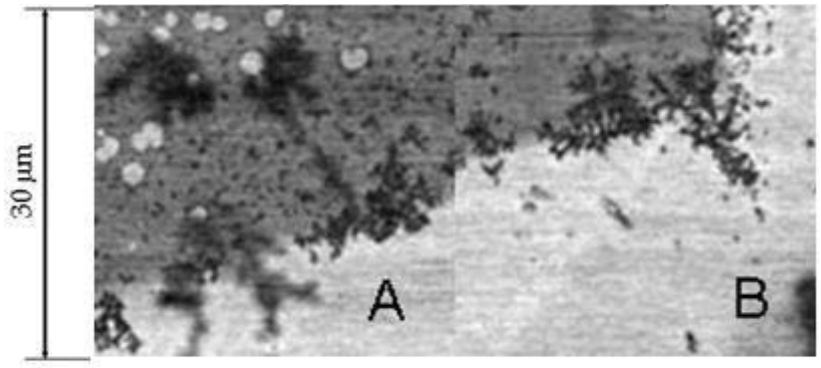
Systems investigated by in situ SXMS: a selection of results

1) Feasibility tests with dynamic Ag redox
   [Bozzini et al. Electrochem. Comm. 10 (2008) 1680]
2) Stability of Fe and Ni BPs in aqueous SO_4^{2-} ± F^-:
   corrosion of BPs as such ($R_\Omega\uparrow$, pinholes, fate of corrosion products: formation of dendrites, shorting paths, mechanical damage)
   [Bozzini et al. J. Phys. Chem. C 113 (2009) 9783]
3) Pickup of Fe and Ni BP corrosion products by Nafion
   generation of corrosion products & their fate wrt PEM poisoning
   [Bozzini et al. ChemSusChem 7 (2010) 864]
4) Stability of Fe and Ni BPs in [BMP][TFSI]
   corrosion of BPs in novel, ideally hydrating electrolyte, fate of corrosion products
5) Anodic (fuel: $NaBH_4$) and cathodic (oxidiser: O_2 10^{-6} mbar) half-cells with of Fe BPs in galvanic contact with Pt catalyst, el-lyte: Nafion/[BMP][TFSI] composite
   result of FC operation on corrosion of anodic and cathodic BPs

1- Proving in situ electrochemical STXM with aqueous el-lyte & sealed cell



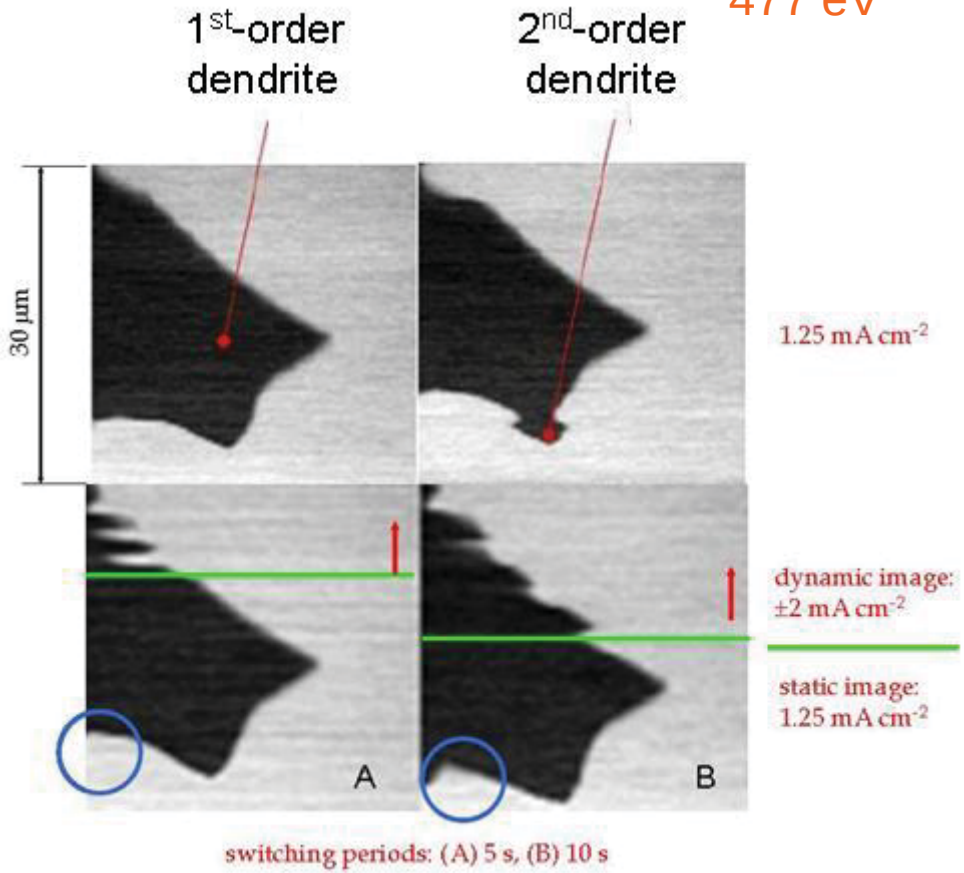
Cell reactions: Ag $\rightleftharpoons$ Ag^+-e^-



-34 mA cm^{-2}, 1′ -5 mA cm^{-2}, 60′

NH_4^+

477 eV



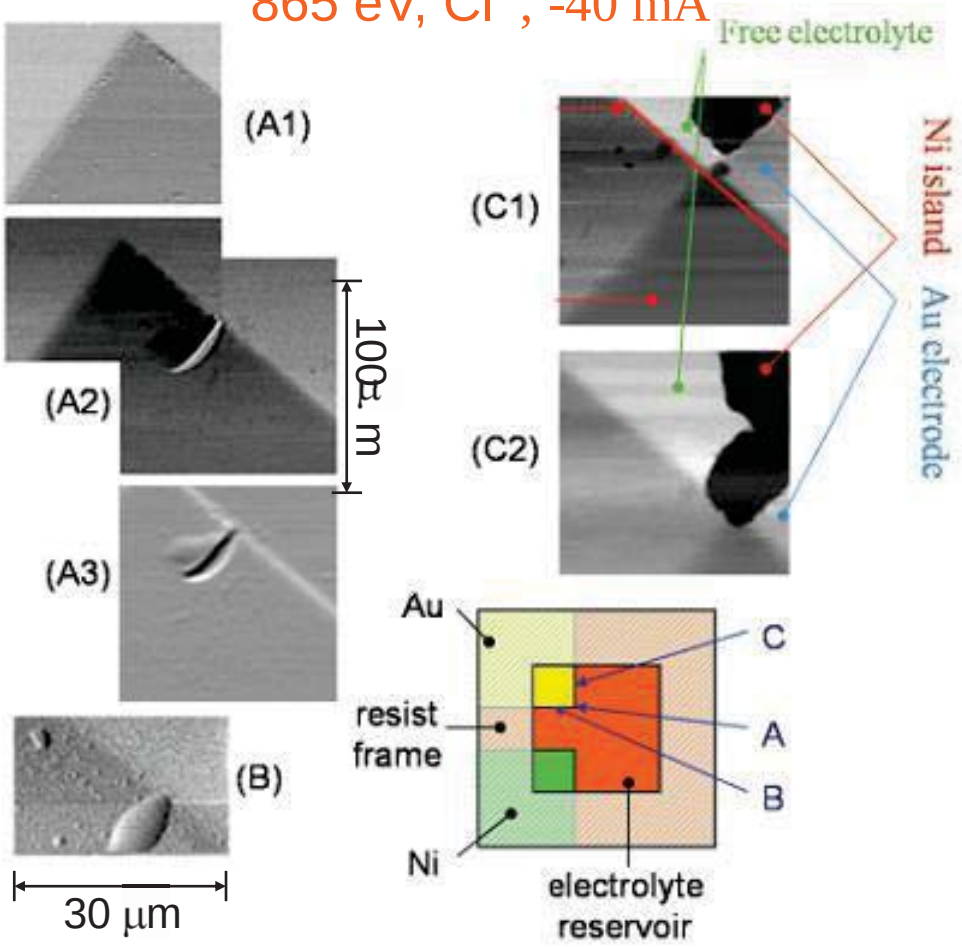
Cl^-

Bozzini et al. Electrochem. Comm. 10 (2008) 1680

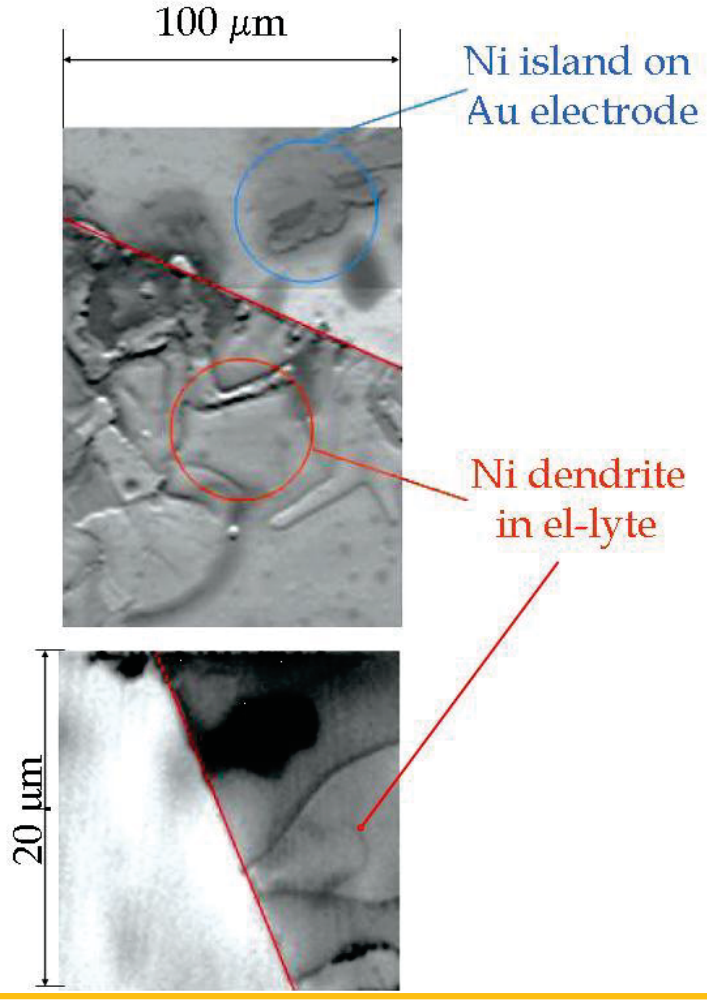
2 - In situ dissolution and redeposition of Ni STXM with aqueous el-lytes

Homogeneous dissolution, heterogeneous redeposition

865 eV, Cl^-, -40 mA

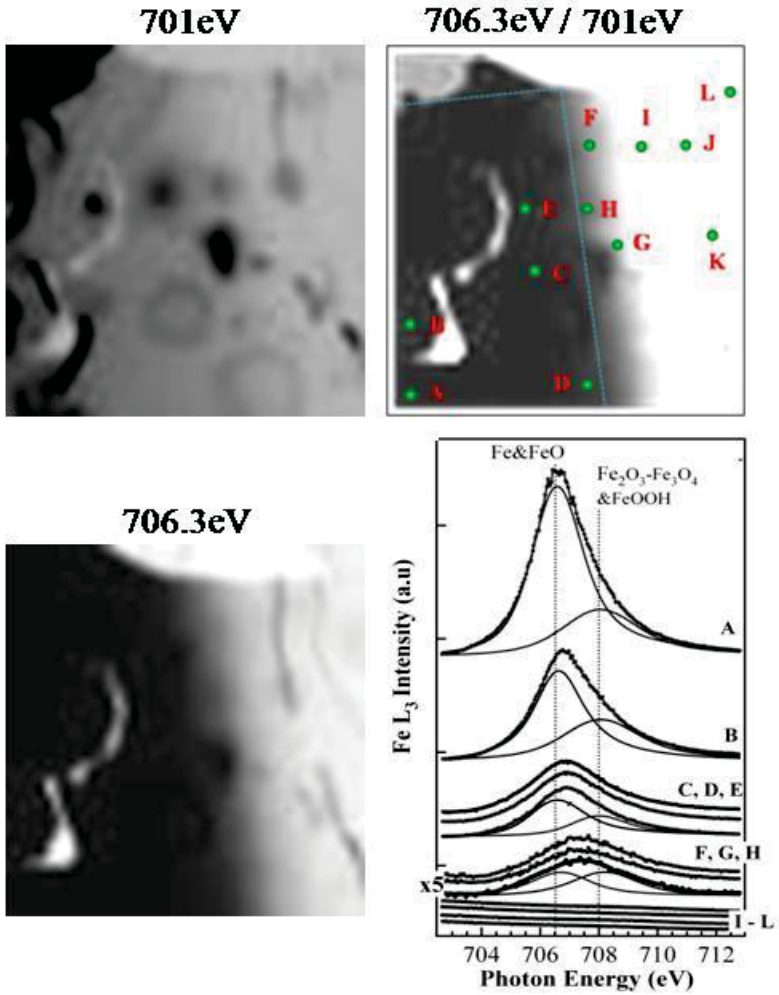


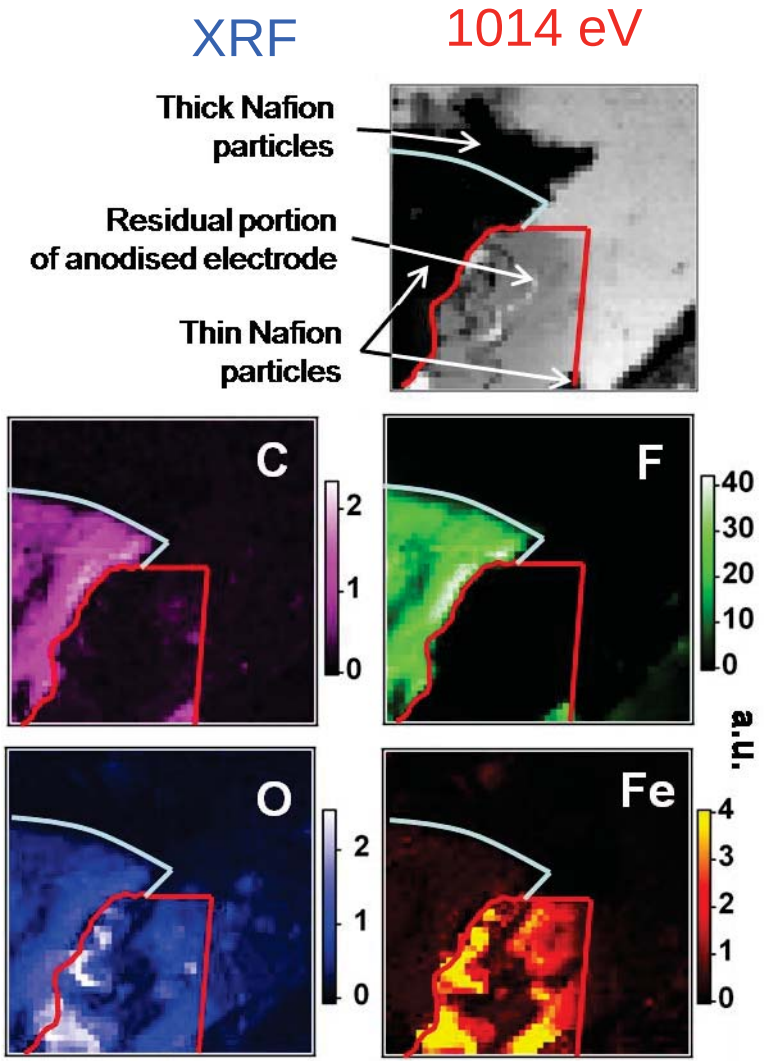
865 eV, NH_4^+, -0.5 mA



Bozzini et al. J. Phys. Chem. C 113 (2009) 9783

3 - Release of Fe BP corrosion products to aqueous el-lyte and fixation in Nafion

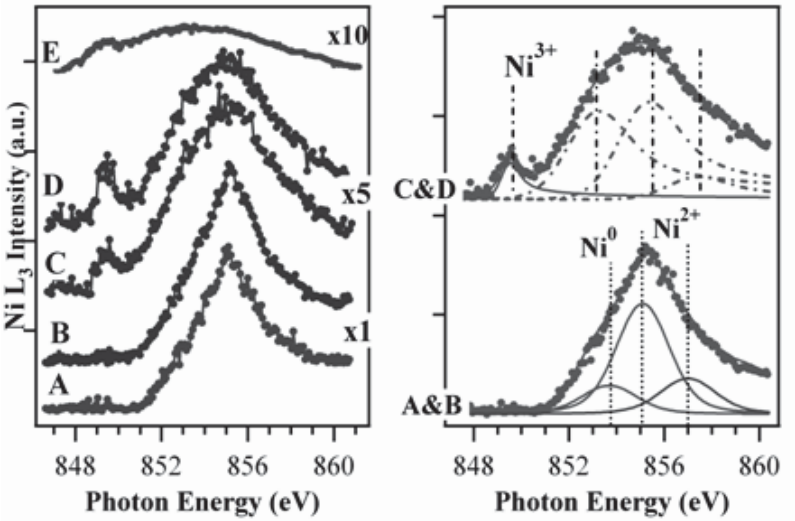


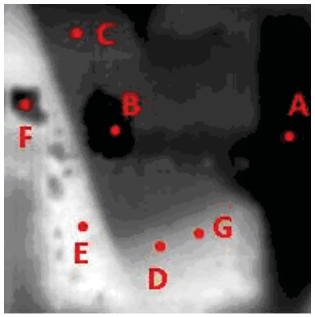


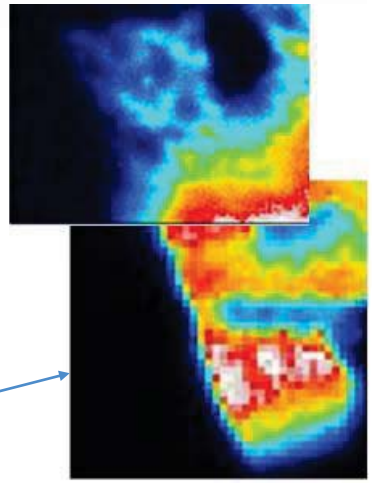
Bozzini et al. ChemSusChem 7 (2010) 864

4 - In situ dissolution of Ni: STXM, XANEF & XRF in [BMP][TFSI] IL

Ni XANES spectra



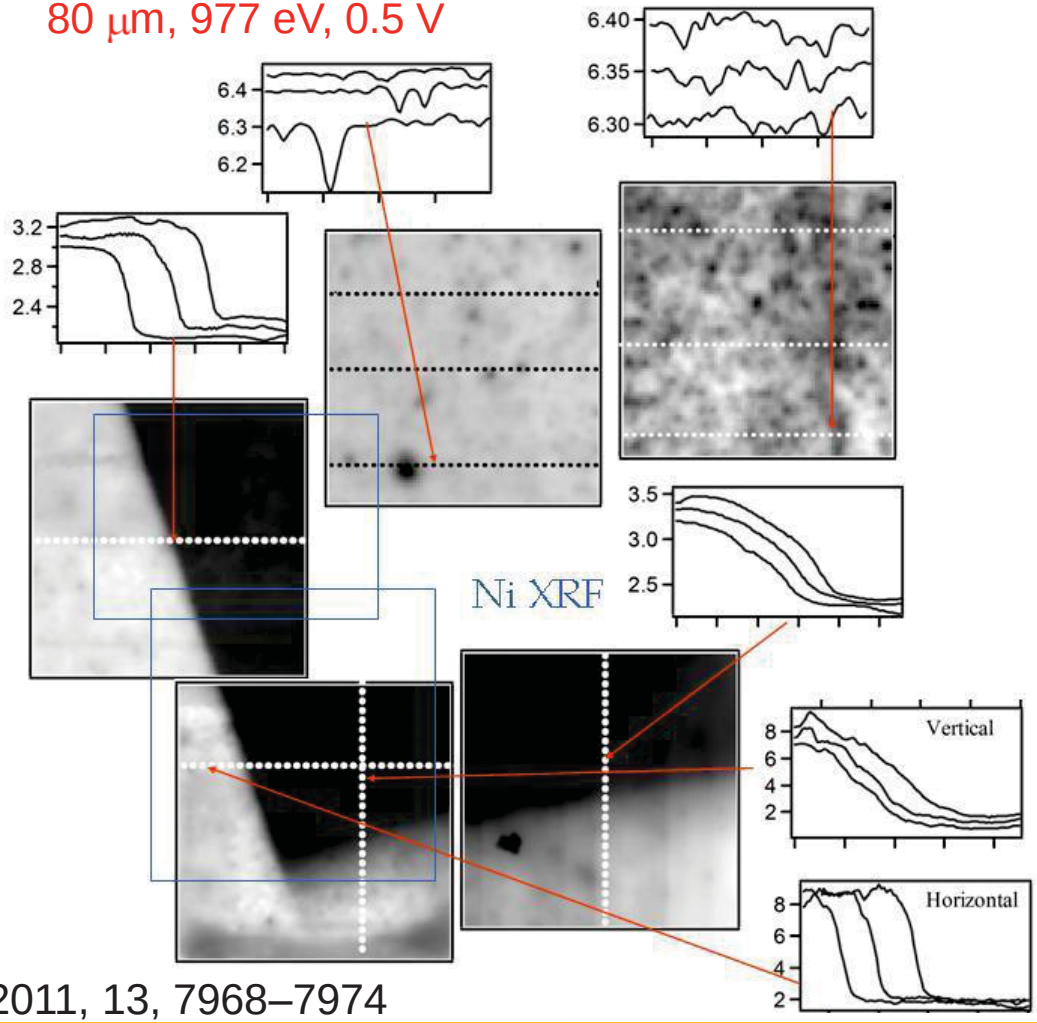




Ni XRF map

Ni XRF profiles

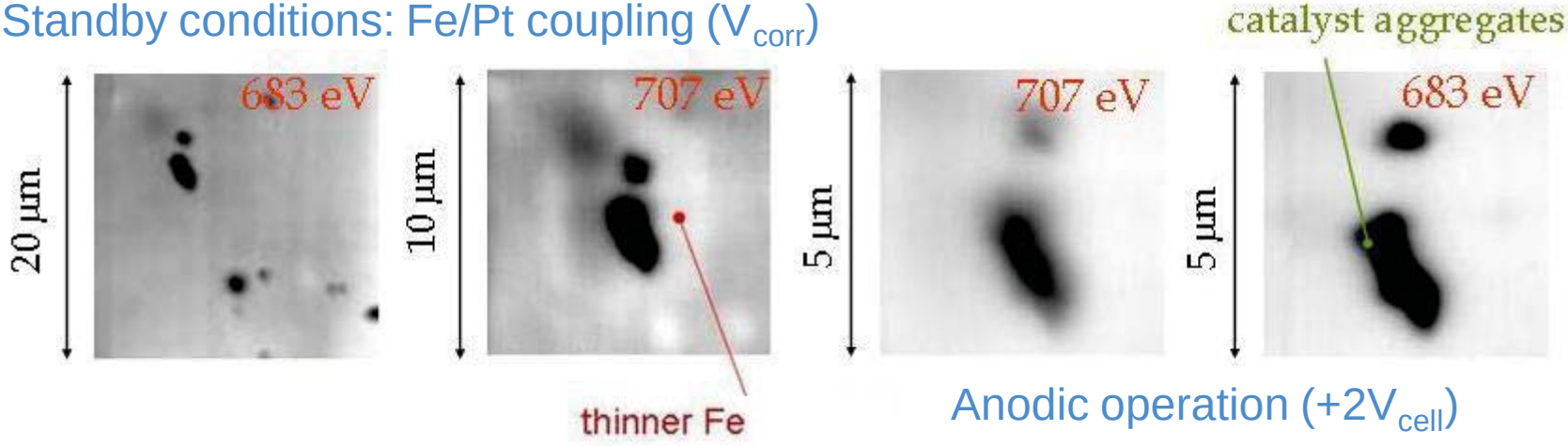
80 μm, 977 eV, 0.5 V



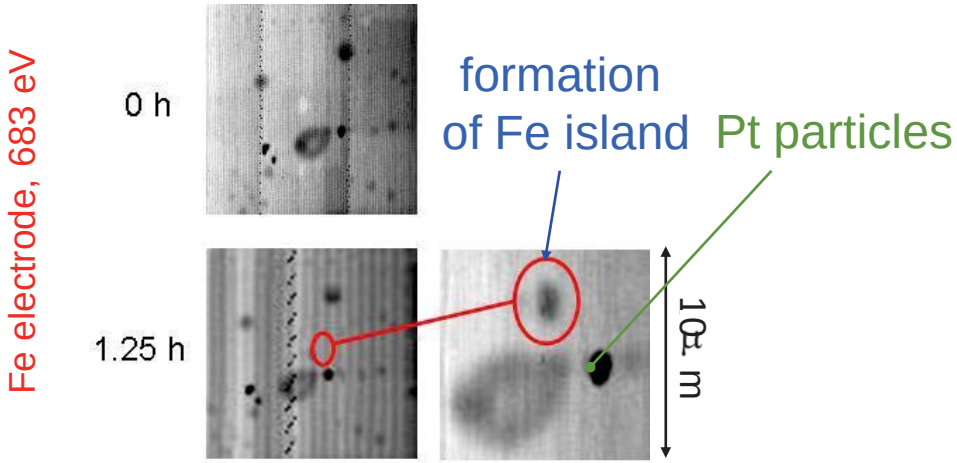
Bozzini et al. Phys. Chem. Chem. Phys., 2011, 13, 7968–7974

5 - In situ study of the cathodic half-cell (Fe/Pt/O_2)

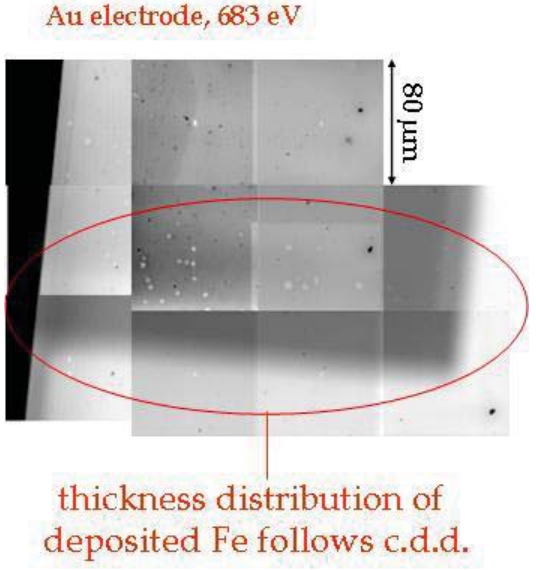
Standby conditions: Fe/Pt coupling (V_{corr})



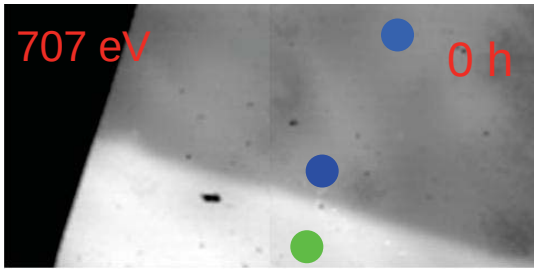
Cathodic operation (-2V_{cell})

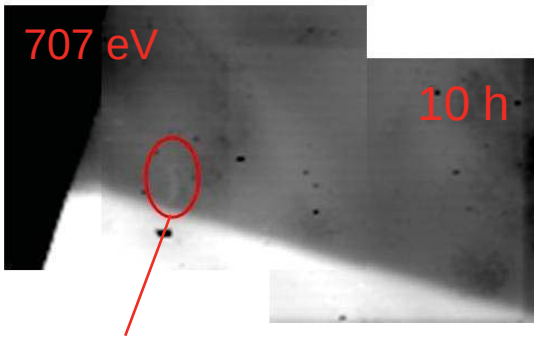


Anodic operation (+2V_{cell})



5 - In situ study of the anodic half-cell (Fe/Pt/$NaBH_4$)

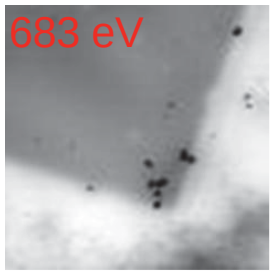




minor thinning & localised attack

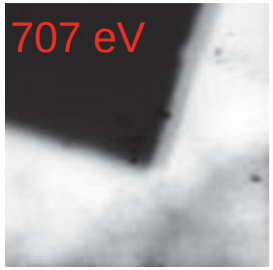
Anodic operation (+2V_{cell})

80 μm

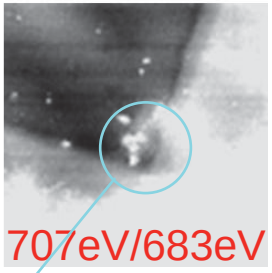


Au/Fe shorting

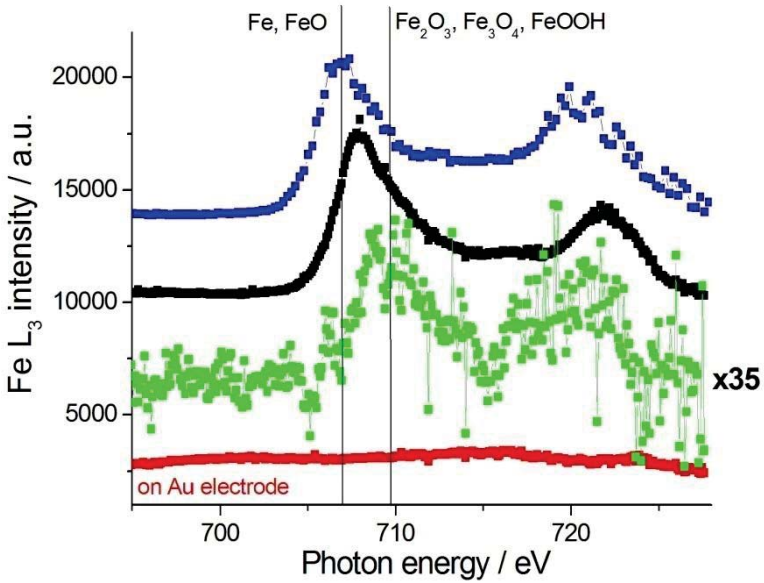
10h at 2V



10h at 2V



10h at 2V



No preferential attack at Pt/Fe interface

protective action of BH_4^-

Standby conditions and cathodic (-2V_{cell}) polarisation for 5 h: no measurable effects

Conclusions

In situ electrochemical dynamic spectromicroscopy with resolution 50 nm

Microfabricated vacuum-tight cells: nm thick electrodes and electrolyte

Morphological, chemical and structural effects of electrochemistry

Completed actions: stability of BP matarials under FC conditions in: (i) a range of aqueous systems, (ii) Nafion, (iii) IL, (iv) IL-Nafion composite.

Next action: in situ dynamical analysis of a complete FC combining the described half-cells with a microfluidic approach.

In addition to FC and electrochemical energetics (LIB, supercapacitors) this approach is also expected to impact all fields of electrochemical materials science and bioelectrochemistry