

# New Energy Sources: in-situ Characterisation of Fuel Cell and Supercapacitor Components. Complementary Studies using Transmission, Fluorescence and Photoelectron Microscopy and Imaging

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**Abstract.** Fuel cells and supercapacitors are electrochemical devices providing efficient and pollution-free production and transformation of electricity. Notwithstanding their environmental appeal, a host of materials-science problems – chiefly related to the limited durability of crucial functional components – are hindering their widespread application. The present knowledge of the relevant materials-science notion is mostly at the macroscopic and empirical trial-and-error level and the answers to many questions require much deeper scientific understanding of the origin of degradation processes. In this regard, the development and the implementation of appropriate methods for in-situ characterization of cell components at the functionally relevant length scales is highly required. Soft X-ray spectroscopies, such as X-ray absorption spectroscopy, X-ray emission (fluorescence) spectroscopy, resonant inelastic X-ray spectroscopy and X-ray photoelectron spectroscopy have been extensively employed for ex-situ characterization of materials used in electrochemical systems. Furthermore, adding spatial resolution capabilities by implementing proper optical solutions has opened unique opportunities for monitoring material changes and mass transport events occurring at submicron length scales. The input from these methods is providing correlative information about the status of the electrode surface and of the electrode/electrolyte interface and also of the processes occurring under operation conditions.

## 1. Introduction

This paper is focussed on “in operando” X-ray microspectroscopy investigations of materials-science aspects of devices for the electrochemical generation and storage of electrical energy - also denominated “electrochemical energetics” - such as fuel cells and supercapacitors. This work summarises some achievements of the collaboration between the TwinMic and ESCAMicroscopy beamlines of the Elettra synchrotron, Trieste (Italy) and the electrochemistry group of University of Salento, Lecce (Italy) [1-20]. The unicity of electrochemical energetics is twofold: (i) it enables the



direct conversion of chemical energy to electricity, allowing the so called “thermodynamic advantage” of getting rid of the Carnot efficiency, as well as the virtual elimination of emissions; (ii) it renders electrical energy storage feasible, impacting a major concern for the rational exploitation of the intrinsically localised and intermittent renewable energies. Electrochemical energetics devices rely on: (i) reversible chemical/electrical conversion processes - open (FC) or closed (batteries) to chemical fluxes – and (ii) electrostatic or faradaic charge storage (SC). In terms of the well-known trade-off between power density and energy density - often represented in Ragone-type plots - FCs cover the high energy density zone, while SCs allow to jointly optimise power and energy densities. It is worth noting that batteries lie between FCs and SCs and that conventional capacitors exhibit very high power densities, but dramatically low energy densities. In this paper we shall set forth three points: (i) offer some introductory concepts on FCs and SCs and the relevance of XRM methods for their investigation; (ii) provide details on the design and fabrication of the electrochemical cells developed for in situ XRM work; (iii) discuss a selection of examples.

## **2. Fuel cell (FC) and supercapacitor (SC) concepts, operating principles and typical problems; prospects of XRM tools for their investigation**

An FC is a device directly converting the electrons exchanged in a redox reaction (such as a combustion, most commonly of H<sub>2</sub> and O<sub>2</sub>) into a usable electric current. In order to implement this functionality, FCs feature – in an essentially symmetric way –: (i) two gas distribution systems, (ii) individual catalysts for the red and ox semi-reactions and (iii) an ionic-conduction pathway (electrolyte) allowing simultaneously electronic insulation of the red- and ox-catalysts and electrical continuity through an ionic pathway. This general concept can materialise in several ways, among which the principal ones are a room- or low temperature (<120 °C) version using a polymeric electrolyte (typically Nafion, conducting protons) and a high-T one (generally in the range 650-1000 °C) using a ceramic electrolyte (typically YSZ, conducting O<sup>2-</sup>). Since a single cell yields a typical voltage of less than 1 V, for practical applications several single cells have to be stacked and connected in series. Of course, the electronic pathways connecting the cells, distributing the gases, supporting the catalysts and in chemical contact with both catalyst and electrolyte – denominated interconnects or bipolar plates - play a key role, as detailed in Section 4.

An SC is a peculiar capacitor with ultra-high capacitance values, achieved by the implementation of the peculiar charge-separation modes that are allowed by electrochemical processes, chiefly: (i) electrostatic charge storage in ultra-high surface area electrodes; (ii) charge storage through faradaic reactions of immobilised species, such as multivalent transition metal oxides; (iii) ultra-thin dielectrics and electrochemical double layers.

From the previous descriptions of the working principles of FCs and SCs, it is obvious that electrochemical devices – thriving on subtle combinations of surface processes coupled with ionic and electronic conductance pathways – are complex systems with challenging materials-science problems on several lengthscales. In particular, special material combinations are required – not found in other technologies –, practically relevant processes are out of equilibrium and transient changes in material properties occur: these characteristics lead to the fact that these devices are daunted by durability problems, that typically impact the practical operation of these systems. For these reasons, the availability of analytical tools exhibiting chemical and structural sensitivity with space and time resolution are obviously highly desirable: hence tackling the painstaking job of setting up in situ microspectroscopy studies of these devices is expected to be highly rewarding. In the recent literature several papers have appeared, reporting mainly hard X-ray based studies of electrochemical energetics systems, centred on XANES, XRD, SAXS, radiography and tomography. The chief topics addressed have been: (i) fine chemical analysis of catalysts, generally ex situ, and (ii) imaging of water and gas flow; space constraints do not permit to review this work more in detail. The authors, instead, have concentrated on the development of soft X-ray based methods aimed at the detailed, space dependent analysis of the single, operating components of FCs and SCs. Notwithstanding the operative

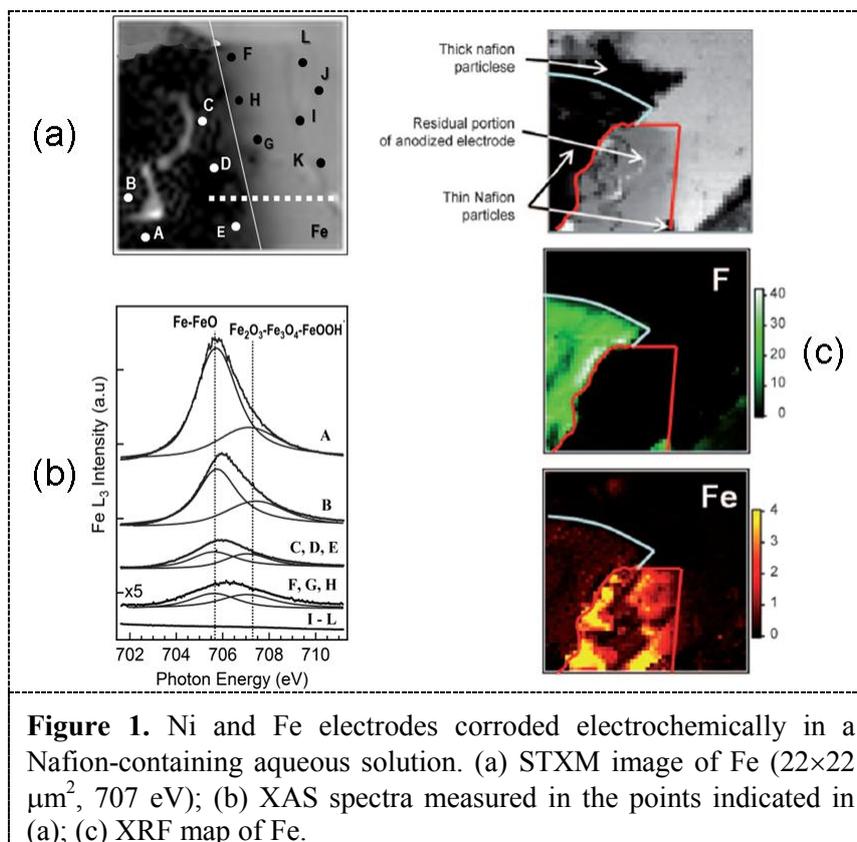
drawbacks due to absorption, soft X-ray offer the unique advantage of utmost space resolution with minimal bulk effects.

### 3. Cell fabrication and experimental details

Our microspectroscopy investigations have been carried out the TwinMic (STXM) and ESCA microscopy (SPEM) beamlines at Elettra: instrumental insight can be found in the beamline websites ([www.elettra.trieste.it/experiments/beamlines](http://www.elettra.trieste.it/experiments/beamlines)). The main interest here is to emphasise in situ electrochemical work and to this aim instrumental requirements are crucial. The TwinMic sample stage has the following constraints: (i) limited space, (ii) vacuum and (iii) work in transmission. For this reason, we have developed a three-electrode transmission electrochemical cell, fabricated along the following conceptual lines (for details, see [1-9,17,18]): we have used a  $\text{Si}_3\text{N}_4$  film as the cell support, onto which we have grown the electrode system by lithography. On top of the electrode system, an electrolyte reservoir is built by lithographic deposition of a resist frame. After the electrolyte is applied by drop-casting or dipping, a second Si-supported  $\text{Si}_3\text{N}_4$  frame is overlaid in order to close the cell that is eventually vacuum-sealed. We have developed two versions of the cell: (i) sealed for work with aqueous solution [1,4-6,8,9] and (ii) open, for studies using as the electrolyte a vacuum-stable ionic liquid [2,3,7,17]. As far as SPEM experiments are concerned, the electrochemical cells consist in electrolyte-supported, planar systems with metallic electrodes grown by lithography: the cell geometry allows access of both electrodes as well as of the electrolyte to analysis [10-16,18,19].

### 4. Results and discussion

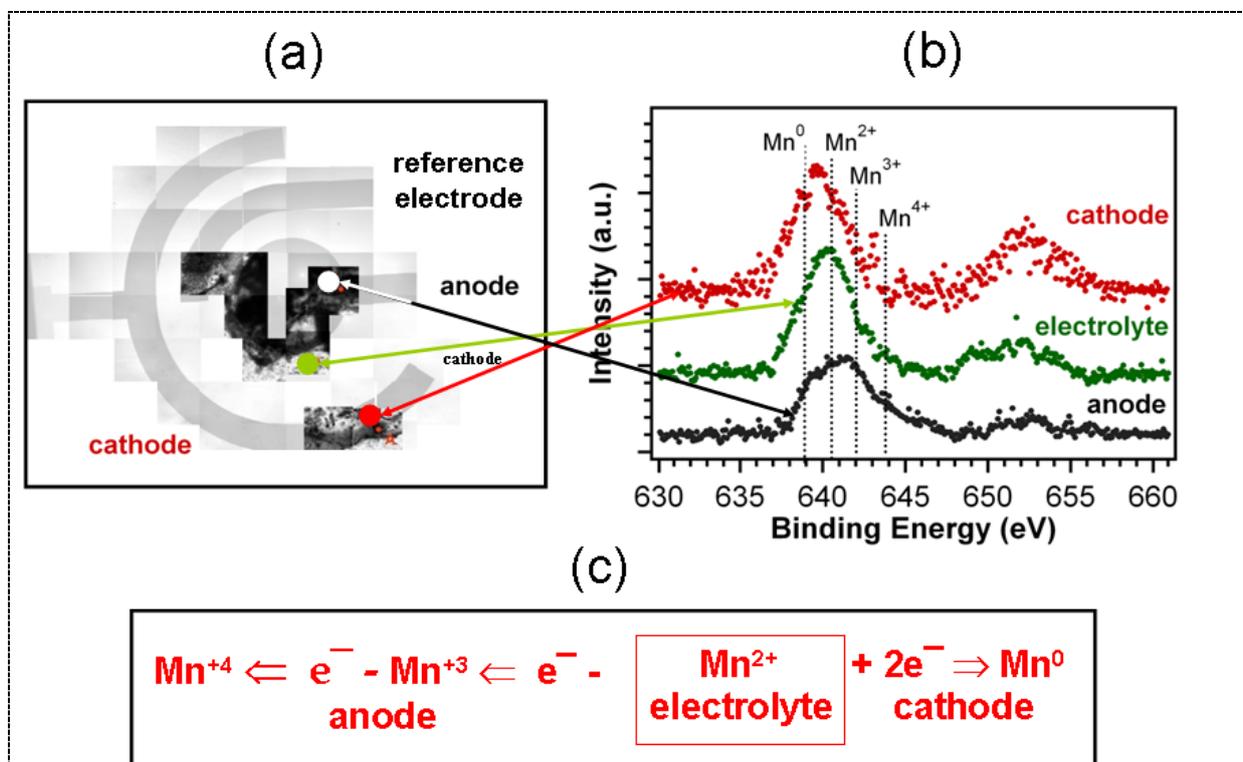
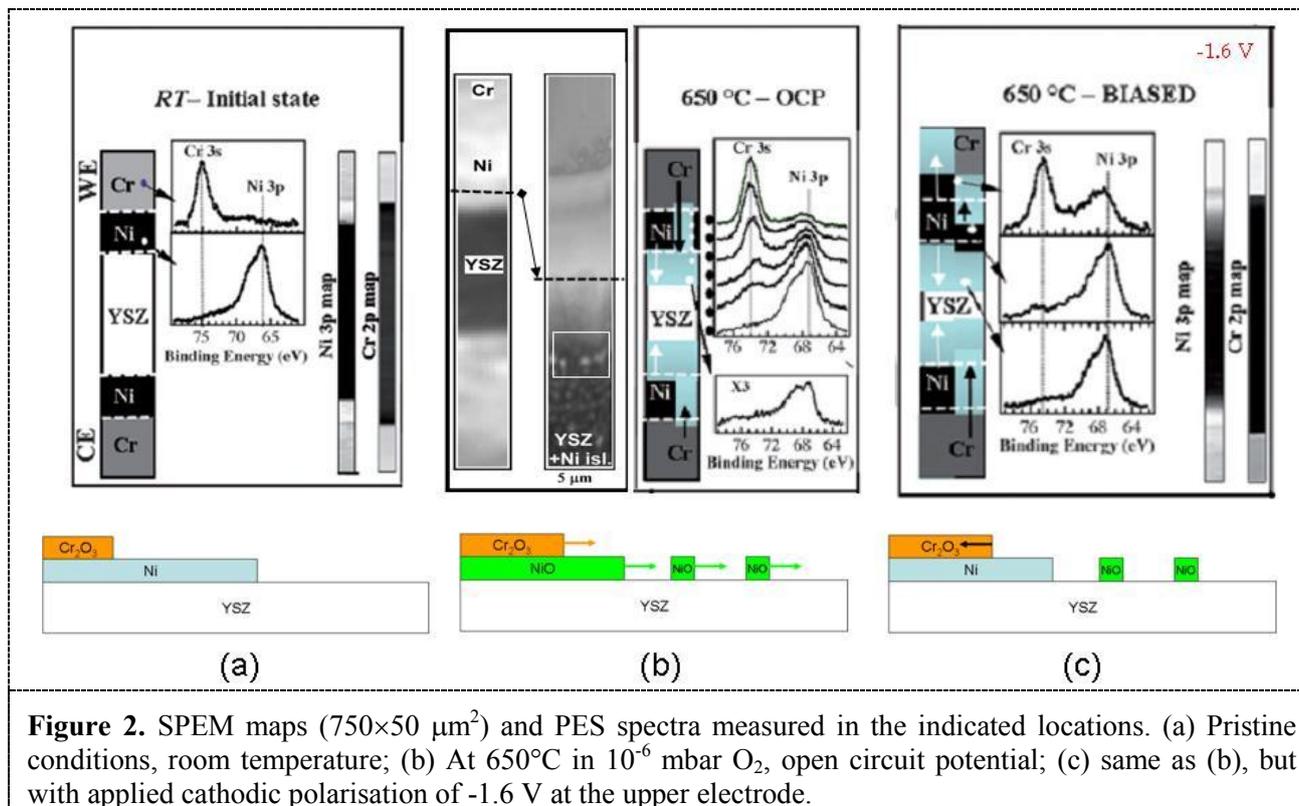
As far as STXM is concerned, our recent work included: (i) cell development and demonstrative work [1,5,17]; (ii) studies of catalyst electrodeposition [8,9]; (iii) corrosion of PEM interconnects [2-6] and (iv) electrochemical growth of materials for supercapacitors [7]. Our SPEM-based studies encompass: (i) corrosion of SOFC interconnects [11,12]; (ii) electrocatalyst degradation [13,14,20]; (iii) electroodic deposition of C in hydrocarbon-fuelled SOFCs [10], (iv) electrodeposition of catalyst-support alloys [15], (v) study of full SOFCs in single-chamber configuration [19]. As representative examples here we have chosen: (i) the corrosion of interconnects in low- and high- temperature fuel cells and (ii) the electrochemical growth of nanostructured electrode materials for supercapacitors. FC interconnects are critical components because, in the quest for durable, low cost devices, metals have proved the material of choice. Unfortunately, they exhibit corrosion problems, causing a series of problems: (i) increase of ohmic drops due to the build-up of corrosion products; (ii) clogging of the porous, gas-transfer zones; (iii) catalyst poisoning due to the deposition of corrosion products; (iv) electrolyte poisoning, again due to the fixation of corrosion products. In one of our STXM-based studies, we have investigated the release of Ni and Fe from PEM interconnects into aqueous solutions in contact with a Nafion membrane [6]. In this work, we have run single-cell experiments by driving the oxidising current through an auxiliary electrode. In Figure 1 we report absorption images of the interfaces between the Fe (a) electrode and the electrolyte, local XAS spectra (b) and XRF maps (c). From panels (a, c) it is straightforward to note that the Fe electrode develops a complex morphology related to the progress of the corrosion reaction. Local XAS spectra (b) and XRF maps (c) pinpoint the Fe space distribution. Moreover, different oxidation states are found in different positions within the area originally occupied by the electrolyte, that can be correlated with the local electrochemical potential. Furthermore, Fe corrosion products are injected into the liquid phase and end up fixed in the Nafion membrane (c), a mechanism related to the PEM electrolyte deterioration.



While STXM is suited for room-temperature studies, SPEM lends itself ideally to high-temperature work. We used this method for the investigation of interconnect stability in SOFC environment in  $\text{O}_2$   $10^{-5}$  mbar at  $650^\circ\text{C}$  [12]. In particular, we have concentrated on the interaction between the Ni electrocatalyst and the Cr-based interconnects. Figure 2 shows that the initially well defined electrode geometry and flat electrode morphology (a) - where Ni is present in the elemental state, while Cr is environmentally oxidised -, is deeply altered at high temperature in  $\text{O}_2$  ambient (b). In addition to the expected oxidation of Ni, this element diffuses onto the electrolyte patch, forming islands, while oxidised Cr spreads over the Ni electrode. Upon applying a cathodic polarisation (panel c, upper electrode), notwithstanding the oxidising gas environment, Ni can be easily reduced, while Cr requires a cathodic potential exceeding -3 V. Moreover, we found that oxidised Cr retracts from the reduced Ni patch. This type of behaviour offers mechanistic insight into the empirically observed Cr contamination problems in SOFCs implementing Cr-based interconnects.

Figure 3 reports STXM and XAS results regarding the electrodeposition of Mn from a choline-chloride/urea ionic liquid spun on top of an open electrochemical cell. This metal electrodeposition system is important for the fabrication of advanced supercapacitor electrodes, in view of the formation of  $\text{MnO}_2$ -decorated Au NPG, yielding exceptionally high capacitance values, due to a pseudocapacitance effect [7,21]. STXM allowed to analyse simultaneously the morphology development and the localisation of the Mn valence types generated by the applied electrochemical conditions.

Typical globular electrodeposition morphologies, controlled by the local current density distribution, were found on the cathode, while fibrous structures grow at the anode. Localised XAS demonstrates that elemental Mn is obtained at the cathode, Mn(III) dominates at the anode, while outside the electrode patches the Mn(II) spectra corresponding to the electrodeposition bath are found.



## 5. Conclusions

In situ electrochemical microspectroscopy has been proved capable of following morphological and chemical effects of electrochemistry. In the studies reviewed in this paper, we have developed three types of microfabricated cells with nm-thick electrodes: (i) sealed cells for SXTM with aqueous electrolytes; (ii) open cells for STXM with spun IL-based electrolytes; (iii) solid electrolyte-supported cells for high-temperature SPEM analyses. Moreover, we have shown the possibility of dosing electroactive gases in the analysis chamber: a first step towards environmental in situ X-ray microspectroscopies. We have thus demonstrated that SXTM and SPEM can contribute unique information to electrochemical materials science, in particular for energy-conversion devices, in terms of: (i) assessment of localisation processes (chemical and overvoltage); (ii) rationalisation of growth/damaging mechanisms; (iii) acquisition of mechanistic information on coupling of materials.

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