Bridging the material and pressure gap in synchrotron based photoelectron in situ/operando studies

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Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). For instance to monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones is of crucial importance to shed light on the running processes. But the possibility to investigate chemical reactions with X-ray photoelectron spectro-microscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. The graphene sealed cells, combined for the first time with XPS by A. Kolmakov [1], allow the possibility to investigate systems which require an ambient pressure regime (e.g. liquid/solid interfaces). Despite the huge ongoing progress in the development and performance of these cells several crucial issues are unsolved and will be addressed by this presentation.

Another recent development is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200 µm diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

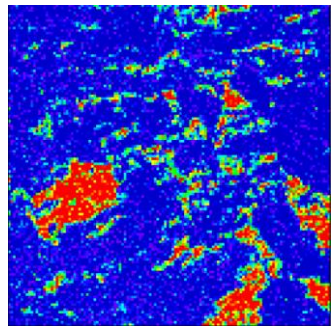

Figure 1. A processed 100x100 µm^2 SPEM Cu LMM map obtained during the reduction of a Cu(I) surface under 0.2 mbar H_2 at 723 K. The processed map has been obtained by the division of the Cu(I) and Cu(0) correspondent energy maps to emphasize the chemical contrast between the two oxidation states. The blue color code indicates a fully reduced state, and red color surface areas still having fully +1 oxidation state of Cu domains. However, the green and yellowish colors represent partially reduced intermediated oxidation state and/or much smaller (<<100 nm) mixture of metallic and +1 oxidation state regions.

[0] A. Kolmakov et al., *Nature Nanotechnology* **(**2011) 6-10, 651-657.
[1] H. Sezen et al., *Chem. Cat. Chem.* (2015), 7(22), 3665-3673.