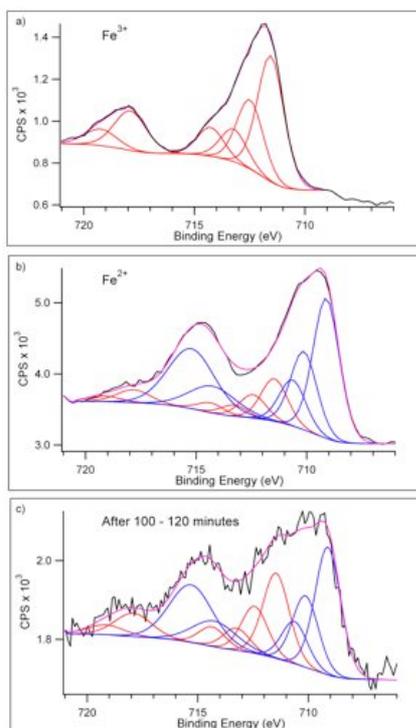


# Ionic Liquids – in-vacuo: in-situ Spectroelectrochemistry using XPS

Alasdair W. Taylor, Fulian Qiu, Ignacio J. Villar-Garcia, Men Shuang  
and Peter Licence,

School of Chemistry, The University of Nottingham, Nottingham, NG7 2RD, UK.

Spectroelectrochemistry (SEC) is a powerful tool for detecting and analysing electrochemically generated products. Traditionally, SEC uses spectroscopic techniques such as IR and UV-Vis which probe molecular vibrations or electron transfer in valence orbitals. Neither of these techniques gives information on how electrochemical processes affect the core electronic structure of the electroanalyte. To acquire this information, spectroscopic techniques that employ ionising radiation, such as XPS and X-ray absorption spectroscopy (XAS) are necessary.



This contribution will highlight our activities in the measurement of XP spectra of metal-doped systems and the development of in-situ electrochemical control. We will detail our operational system/cell and give examples of redox chemistry including a functionalised IL based Fe<sup>2+</sup> / Fe<sup>3+</sup> model system.<sup>1</sup> Samples are prepared on dedicated XPS stubs that are fitted with insulated electrodes. Once pumped into the chamber, the electrodes are connected to a circuit that allows control and sensing of the 2 electrode system by an external potentiostat. XP spectra can be recorded at any time during the experiment to monitor the progress of electrochemically driven processes. The figures (left) shows an example of the data achievable using our simple EC-XPS system, a) and b) show high resolution scans, including fitting modes, for both the starting and the new species, Fe<sup>3+</sup> / Fe<sup>2+</sup> respectively, c) illustrates an example of the XP spectrum recorded 100-120 minutes into a coulometric experiment. We will include a discussion

on sample referencing, required in systems where differential charging of the sample surface is experienced and from a brief study on copper dissolution.<sup>2</sup>

In summary, we have demonstrated for the first time the in-situ monitoring by XPS of an electrochemically induced oxidation state change. The low volatility and conductivity of ILs and the existence of redox active metal-containing ILs meant that such experiments could be performed with minimal modification of a standard XPS chamber. The power of XPS to observe changes in the electronic and chemical environment of elements in a compound opens up the possibility of identifying significant changes at the metal centre and ligand surround of organometallic compounds upon electrochemical oxidation or reduction.

1 A. W. Taylor, F. Qiu, I. J. Villar-Garcia and P. Licence, *Chem. Commun.*, 2009, 5817.

2 F. Qiu A. W. Taylor, I. J. Villar-Garcia, M. Shuang and P. Licence, *PCCP.*, 2010, DOI: 10.1039/b924985k