Time-Resolved Studies of Electrochemical Processes Using Energy Dispersive X-Ray Absorption Spectroscopy

R. O'Malley[1], T. Rayment[1,*] A.Vollmer[1], J. Headspith[2], I. Harvey[2], S. Fiddy[3]

[1]Department of Chemistry, Lensfield Road, Cambridge CB2 1EW
[2]CLRC Daresbury Laboratories, Daresbury, Cheshire, WA4 4AD
[3]European Synchrotron Radiation Facility, ESRF, BP 220, F-38043 Grenoble Cedex, France

In the field of electrochemistry, X-Ray Absorption Spectroscopy (XAS) has been used extensively in the study of electrode materials and their surfaces.[1,2] However, in many electrochemical systems, the process of electron transfer at an electrode is simply the start of a complex sequence of chemical processes that occur in solution. Many of these involve transient intermediates.

XAS would be a valuable tool for elucidating the structure of electrogenerated intermediates since it yields information such as interatomic distances, oxidation states and co-ordination numbers. However, its application to electrochemical processes has been very limited to date due to challenges which must be overcome in order to study such systems. The concentration of intermediates is only significant in the immediate vicinity of the surface and hence, high spatial resolution is required. In addition, temporal resolution defined both by the reaction rate and by diffusion into bulk solution.

The study of transient species resulting from redox reactions at electrodes necessitates use of a focussed x-ray beam and fast measurements. These requirements are met by the use of energy dispersive XAS in which synchrotron radiation is focussed via a bent dispersive monochromator crystal onto the sample (i.e. solution above the working electrode.) The intensity of the radiation is measured by a position sensitive detector whereby a complete absorption spectrum is measured simultaneously. The development of parallel detection methods (XSTRIP detector, CLRC[3]) now make it possible to monitor reactions with a time resolution > 10μs. By designing an electrochemical cell suited to the geometrical demands of a transmission experiment (Figure 1), it has been possible to couple these techniques for the first time.

We describe two studies utilising XAS in time-resolved processes.

Known quantities of Cu were electroplated onto a Pt electrode and then desorbed into solution by applying a step change of potential. Diffusion of Cu^{2+} ions away from the electrode has been measured as a function of time and distance from the electrode surface; the results of which have been modelled by Fick's Second Law (Figure 2). Whilst the diffusion constants of simple ions in aqueous solution are already well known, the technique could already find use in the study of redox processes and charge transport of ions in complex membranes such as those found in batteries or fuel cells.

Traditionally, electrochemical methods are applied to probe the rate and mechanism of reactions in solution. Cyclic voltammetry (CV) is one of the most popular techniques for studying electrochemical behaviour and in particular, provides kinetic and oxidation state information, but structural changes associated with changes in oxidation state cannot be determined. Simultaneous XAS and CV data will be presented that show how time-resolved XAS offers the potential for direct structural interpretation of complex electrochemical behaviour.

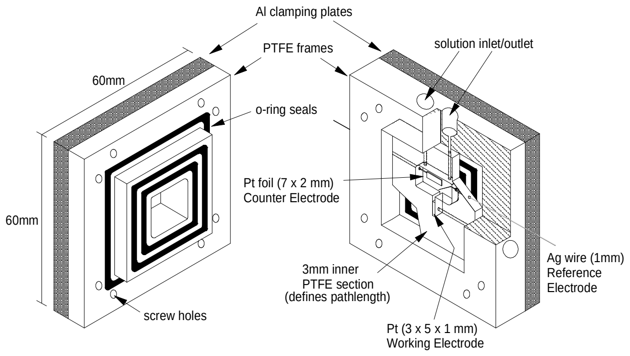

Figure 1: Schematic of the XAS cell

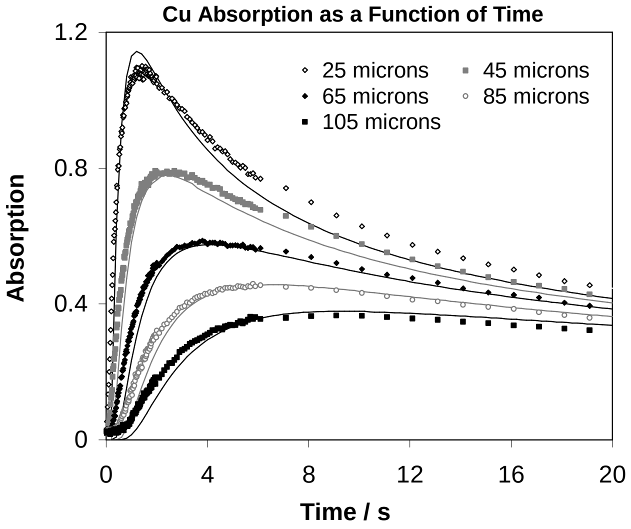

Figure 2: A plot of the edge step as a function of time and distance of the x-ray beam above the electrode surface. (Points = data, line = model.)

References:

1. S. Wu, Z. Shi, J. Lipkowski, A.P. Hitchcock, T. Tyliszczak, J. Phys.Chem B., 101 (1997) 10310
2. A.N. Mansour, P.H. Smith, W.M. Baker, M. Balasubramanian, J. McBreen, Electrochimica Acta, 47 (2002) 3151
3. J. Headspith, G. Salvini, S.L. Thomas, G. Derbyshire, A. Dent, T. Rayment, J. Evans, R. Farrow, C. Anderson, J. Cliche, B.R. Dobson, Computer Physics Comm., submitted 2002