# X-ray Absorption Spectroscopy above, below and at electrodes

R. O'Malley,[2] B Abbey, [2] A Vollmer,[3] H. Weiss,[4] J. Lipp,[5] S. Fiddy,[5] T. Rayment[1]

[1]*School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.;* [2]*Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK;* [3]*Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany;* [3]*CCLRC Rutherford Appleton Laboratory, Oxon, OX11 0QX UK;* [5]*CCLRC Daresbury Laboratory, Warrington WA4 4AD, UK*
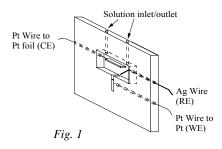
## Introduction

X-ray absorption spectroscopy (XAS) is a well-established technique in the field of electrochemistry that has been used extensively for the characterisation of electrode materials, particularly in the fields of fuel cells, energy storage and electrocatalysis. However, the activities of electrochemists span much wider areas that include both electroanalysis and electrochemical surface science: in these fields there have been comparatively few applications of XAS.

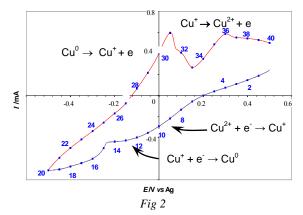## Time-resolved studies above an electrode

Electron-transfer (e.t.) is crucial to a large number of synthetic and biological processes and, in the study of this phenomenon, electroanalysis is the simplest and most commonly used analytical tool. Electroanalysis gives insights into reaction mechanisms and molecular energy levels, but it does not inherently carry structural information. Where transition metal complexes are involved, the starting point for understanding the e.t. mechanism would be knowledge of the number and types of atoms coordinated to the metal. XAS is thus an obvious technique to apply but there are a number of formidable obstacles to overcome that include low concentrations of transient electrogenerated species whose concentrations vary as functions of time and position relative to the electrode surface. We summarise here progress towards this goal. Studies of copper containing solutions show that diffusion constants may be readily obtained by direct measurements of concentrations near an electrode following pulsed electrodesorption [1]. The next step is the study of a multicomponent system that contains a transient species. $Cu^{2+}$ / $Cu^+$ redox are ideal candidates since Cu (I) species are unstable in aqueous solution with respect to disproportionation to Cu(II) and Cu(0), but Cu(I) is stabilised by complex formation with halide ions. Time-resolved XAS studies of this system are described below.

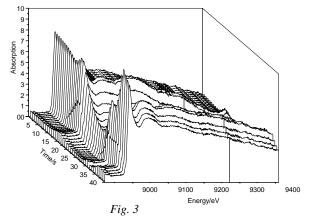## Experimental Method and Results

Fig. 1 shows the central part of an electrochemical cell for transmission XAS studies of species in solution near an electrode. A polished platinum electrode is pressed into a 1mm wide slot in a 3mm thick ptfe holder sealed within between polyimide windows thereby ensuring approximately 1D diffusional behavior.
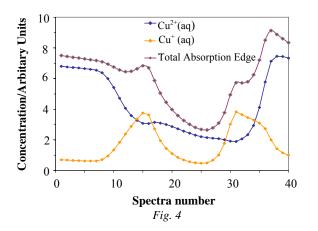


*Fig. 1*

Experiments were carried out on the energy dispersive XAS Beamline ID24 at the ESRF. An X-ray beam of 20μm diameter was positioned 50 μm above the electrode. Fig. 2 shows a cyclic voltammogram (CV) of 30mM $CuCl_2$ in 0.2 M KCl obtained in the XAS electrochemical cell. Features attributed to reduction to $Cu^+$ and $Cu^0$ are marked on the figure. The scan rate for the CV was 50 mV s⁻¹.



*Fig 2*

Spectra were collected at 50 mV intervals and data from 26 CVs were combined to improve statistics. Fig. 3 gives a plot of XAS spectra collected at the potentials indicated on the CV. The intensity of the white line tracks the concentration of copper species in solution above the electrode. During the cathodic



*Fig. 3*

sweep of the CV and before electrodeposition of copper occurs on the electrode, a pre-edge feature can be seen to emerge. This is indicative of the presence of Cu(I) species in solution. (closer examination of the data shows that the position of the absorption also changes over the course of the oxidation / reduction cycle). Factor analysis of these datasets shows that the data can be fully described in terms of just two species whose concentrations vary with potential as shown in Fig. 4 [2].

*Fig. 4*

Preliminary digital simulations of the CV give good qualitative agreement with the results in Fig. 4 [3].

Electrochemical channel flow cells have been constructed for use with transmission and fluorescence detection; these reduce the effects of beam damage associated with the need for focused X-ray beams.

The most suitable electrochemical systems that we have identified for early studies of intermediates are dimeric iron complexes in which two sequential one-electron oxidations lead to a drastic shortening of the Fe-Fe distance and folding of the $Fe_2S_2$ ring about the S…S vector[4].

## Electrode Structure below the Surface

Most applications of XAS to electrochemistry focus upon the bulk structure of electrode materials but, it is recognised that in many systems the structure of the surface region may be different from that of the bulk. Surface sensitive analytical probes are highly desirable, but most of those in common use rely upon the low mean free path of electrons in materials and operate under high vacuum conditions that are far from those under which the material functions. There are few structural depth profiling tools applicable to rough polycrystalline materials that operate in the presence of water. Energy-resolved Auger electron detection of XAS is emerging as a tool for ths purpose.

The underlying concept of the technique is that Auger electrons lose energy by various inelastic processes as they propagate to a surface, and therefore the emergent electron energy profile contains information about the structure as a function of depth from the surface. Put simply, electrons emitted with energies close to the Auger energy must have originated from close to the surface, and conversely those emerging with low energy most probably originated from deep within the material. This idea has been utilised for many years in XPS and Auger electron studies of surfaces under UHV conditions. Gas microstrip detectors give modest energy resolution but operate at ambient pressures [5]. Experiments have been carried out in reactive gases at elevated temperatures and in a water vapour containing detector gas [6,7]. It has been demonstrated for model Ni/NiO samples that the the thickness of overlayers can be dervied by a combination of XAS and electron-trajectory simulations [8]. Results are largely immune to effects of surface roughness. This offers the possibility that emersed, but still wet, electrodes will be amenable to study. A critical feature is the design of electrochemical cells compatible with the electrical requirements of the detector. Prototype models have been tested and a preliminary data has been collected on nickel hydroxide which is an important battery material [9].

[1] R. O'Malley,A. Vollmer, J.R.I. Lee, I. Harvey, J. Headspith, S. Diaz-Moreno, T. Rayment, Electrochem Commun. 5 1-5, (2003)
[2] R. O'Malley, PhD Thesis, University of Cambridge, (2004)
[3] A. Fisher, University of Cambridge, private communication
[4] N.G. Connelly, L.F. Dahl, J. Am. Chem. Soc. 92, 7472, (1970)
[5] T. Rayment, S.L.M. Schroeder, G.D. Moggridge, J.E. Bateman, G.E. Derbyshire, R. Stephenson, Rev. Sci. Instrum., 71, 3640, (2000)
[6] A. Vollmer, J.D. Lipp, J.R.I. Lee, G.E. Derbyshire, T. Rayment, Analytical Chemistry, *75*, 6571, (2003)
[7] A. Vollmer, J.D. Lipp, H. Weiss. R. O'Malley, T. Rayment, Angewandte Chemie-International Edition, 43, 3691, (2004)
[8] B Abbey, J.D. Lipp, Z.H. Barber, T.Rayment, J. Appl. Phys. In press, 2006
[9] B. Abbey PhD Thesis, Cambridge University, (2006)