ESRF

	Experiment title: Energy Dispersive EXAFS Studies of Cu Diffusion in an Electrochemical System	**Experiment number**: CH 1062
Beamline: ID 24	**Date of experiment**: from: 2 May 2001 to: 9 May 2001	**Date of report**: 31 Aug ‘01 *Received at ESRF:*
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Report:

As the first stage of an investigation of electrogenerated intermediates, Energy Dispersive EXAFS (EDE) has been used to study the diffusion of Cu from a polycrystalline Pt working electrode (WE). Literature published to date shows that there have been few applications of XAS to the study of electrogenerated species in solution. The close proximity of reacting species to the electrode and their small local concentration makes these systems extremely challenging to investigate.[1]

Third generation sources provide x-ray beams of a size comparable to a typical reaction zone for an electrode reaction; ID24 was selected as a suitable station to initiate studies of these species, for it permits the collection of complete spectra on a millisecond timescale – matching the diffusion and reaction time of many electrochemical systems.

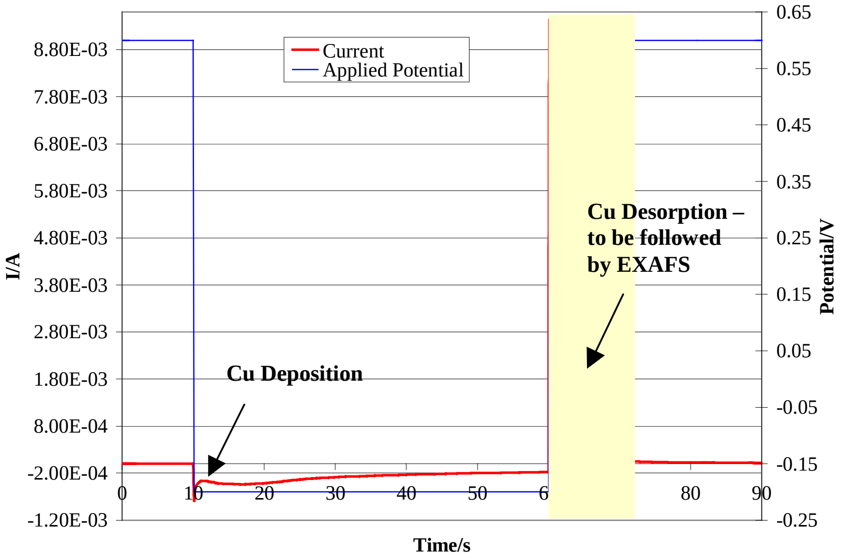


FIGURE 1: Example Cu Deposition/Desorption Plot. Blue Line = Applied Potential, Red Line = Current/Time Plot, Yellow Area = Process to be Followed by EXAFS

Appropriate experimental conditions were derived from calculations of time dependent concentration profiles using typical diffusion constants. Well-defined doses of Cu ions were injected into 0.5M H_2SO_4 aqueous solution by electrochemically stripping a layer of copper that had been previously deposited from a 5mM solution. Figure 1 give an prototypical Current/Time trace observed during deposition/desorption and highlights the process that EDE was employed to study. The CCD camera was triggered for data collection upon a change of potential from –0.2V to 0.6V, i.e. low to high.

By passing the x-ray beam at varying heights over the Pt WE, (see Figure 2) it is possible to follow the progress of copper into solution.

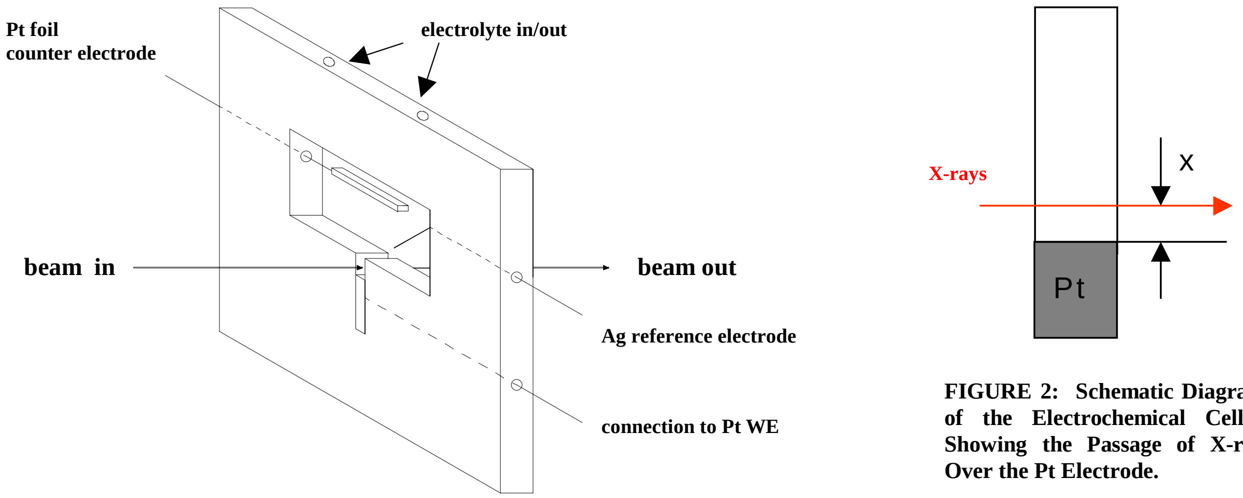
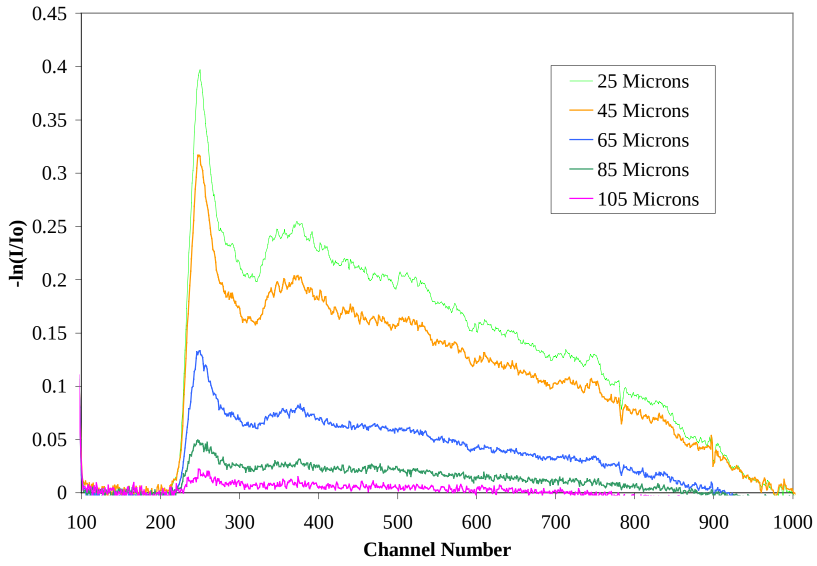


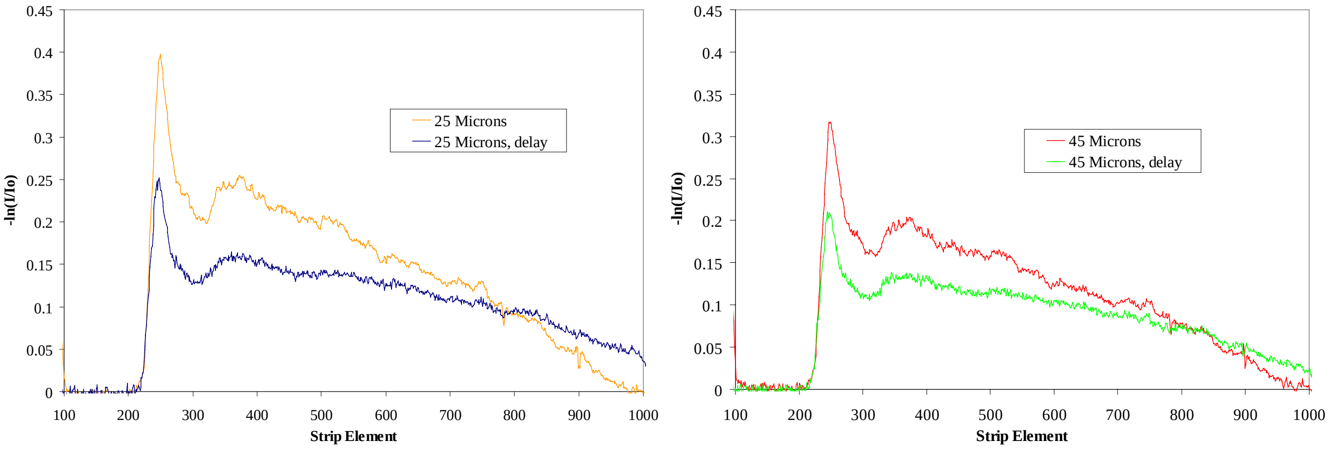
FIGURE 2: Schematic Diagrams of the Electrochemical Cell – Showing the Passage of X-rays Over the Pt Electrode.

Figure 3 shows spectra obtained in 300 msec, 500 msec after intitiating electrodesorption, for a sequence of different beam positions. There is ample data from which diffusion profiles and constants may be determined. However these data are not yet of a sufficient statistical accuracy to permit structural analysis via EXAFS.

FIGURE 3: Cu^{2+} EXAFS Spectra Obtained at Varying Heights Above the WE Surface.



The principle limitation in these experiments is data acquisition system of the CCD camera. The timescale of this experiment is such that none of the normal modes of data acquisition could be employed efficiently. The best that could be achieved via extensive modification to the data acquisition software, it was possible to collect just two continuous sets during one desorption cycle; the delay between collection periods being imposed by the CCD readout system (requiring approximately 220ms.) Results obtained by this ‘dual data collection’ at two distances from the electrode and are shown in Figures 4a and b.



FIGURES 4a/4b: Showing Results Obtained at 25 and 45 Microns Respectively from the Surface of the Pt WE. Delay Between Data Collection for Any One Height is ~ 220ms.

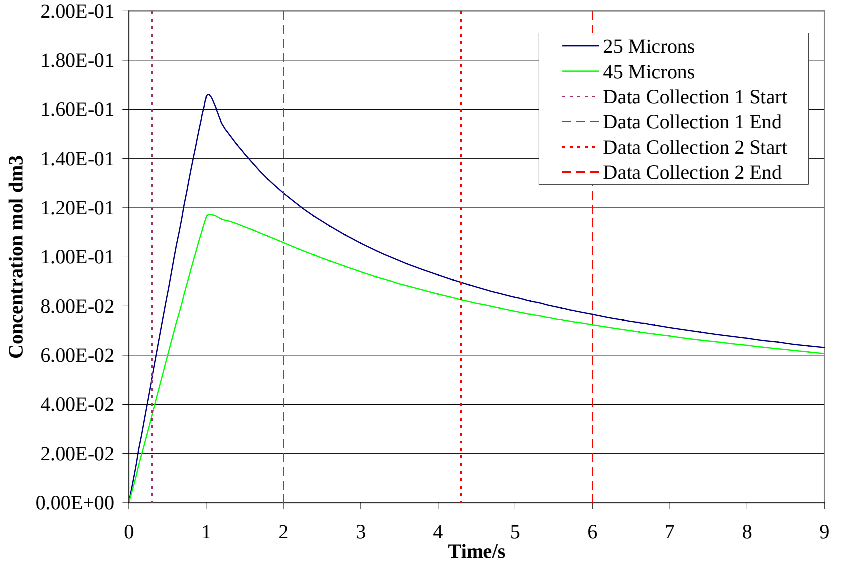


FIGURE 5: Regions for Which Data Collection is Feasible Within a Typical Cu Diffusion Profile

Figure 5 shows the solution to Fick's Second Law of Diffusion[2] based upon a representative number of Cu atoms. The regions highlighted show the two zones during which data collection was possible. Clearly, there is much of the diffusion process that can not be followed.

Initial trials of the XSTRIP detector for EDE (developed at the CLRC Laboratory) indicate that these time resolution limitations could be overcome. We are awaiting the results of the tests of this detector at the ESRF before applying to continue this work in the next round.

These experiment have shown that it is possible to follow the concentrations of species generated at an electrode surface as they diffuse into bulk solution and shown the challenges that must be overcome if the structure of intermediates is to be studied by EDE.

We wish to thank the staff of ID24 for their assistance with this experiment.

References

1. D. Lutzenkirchen-Hecht, R. Frahm, *J Synchrotron Rad.* 6 591, (1999), D. Lutzenkirchen-Hecht *Corrosion Sci.*, 40, 1037, (1998)
2. J. Bockris, A.K.N. Reddy, *Modern Electrochemistry 1* (1977) New York Plenum Press