



	Experiment title: Reflection mode time resolved XAS study of surface electrode reactions	Experiment number: CH-630
Beamline: ID 24	Date of experiment: from: 06-Feb-99 to: 11-Feb-99	Date of report: 13.09.1999
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Report: (preliminary)

Time resolved XAS was applied for *in situ* study of the first stages of the oxide/ hydroxide film formation on the copper surface under electrochemical conditions in the alkaline solution. The measurements were performed at grazing incidence using our home made reflexafs device. Instead of the so called moving slit method, we used the original ID24 design i.e. the dispersive mode with the position sensitive detector for the reflection mode XAFS spectra recording. This was only possible due to a significant improvement of the beamline performance during the last few months. Whereas the simultaneous $I_0(E)$ -measurement is still not possible for reflection mode measurements, the stability of the beam is now sufficient for using the first (last) spectrum as a reference. If the electrode surface structure is known for the first (last) spectrum - and this is the case for our study - all the time dependent spectra can be normalised with respect to this spectrum. Figure 1 shows a series of spectra recorded for a copper thin film electrode at grazing angle of 0.2 degrees. The solution was 0.1 M NaOH. The electrode length was 2.5 mm corresponding to the reflected beam height of only about 10 microns. The copper layer (300 nm) was vapour deposited onto a float glass substrate. At the beginning of the measurement the electrode potential was held at -0.6 V vs. SHE (standard hydrogen electrode). At this potential copper surface is known to be in its reduced, metallic state. The spectrum corresponding to the potential of -0.6 V (not shown) was therefore identified with a reflection mode copper spectrum calculated for the metallic copper at the grazing angle of 0.2 degrees. The time difference between two consecutive spectra was 3 s, the integration time for each single

spectrum was 1.5 s. The spectra 1 – 5 were recorded during the potential scan $-0.6\text{ V} \rightarrow 0.0\text{ V}$ with a scan rate of 50 mV/s . Starting with the spectrum number 5 the potential was held constant at 0.0 V . The spectrum number 5 differs already from the previous one. The following spectra show a continuous growth of the oxide/hydroxide layer on the copper surface with time despite the fixed potential value. The oscillatory fine structure above the edge (8980 eV), typical for metallic copper, disappears as well as the characteristic edge feature at about 8982 eV . The latter fact suggests that no significant amount of Cu^{+1} is formed during the oxide layer growth. Instead, Cu^{2+} seems to be the prevailing oxidation state of copper within the x-ray information depth of the method. The oxide layer growth is completed with the spectrum 18. The following spectra (not shown) do not significantly differ from it with the exception of the increasing non-statistical noise due to the changes in $I_0(E)$ with time.

Fig. 1

