



	Experiment title: In-situ surface x-ray diffraction and DAFS studies of oxidation/ reduction in hydrous nickel oxide films.	Experiment number: 28-01-99
Beamline: BM28	Date of experiment: from: 30/5/01 to: 5/6/01	Date of report: 30/10/01
Shifts: 18	Local contact(s): Dr D. Mannix	<i>Received at ESRF:</i>
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Report:

The aim of the experiment was to further research carried out previously on beamline 16-3 at Daresbury SRS relating to the electrochemical oxidation of Nickel single crystal electrodes. This beamtime was intended to probe the structural changes that occur during the oxidation of Ni^{II}(OH)₂ films to Ni(III) oxides or hydrous oxides. The change that occurs due to the electrochemical reaction is essentially the charging reaction at the positive electrode of a Ni-based battery. These changes in oxidation state are accompanied by marked structural changes and incorporation and release of electrolyte ions into and from the thin film to achieve charge electro-neutrality. Such affects modify the density of the oxide and result in dimensional changes during charge/discharge cycles. Results from Daresbury had previously shown that oxidation/reduction processes lead to dramatic changes in the x-ray diffraction spectra.

The experiment proposed for this beamtime was to probe the changes in the local atomic structure using DAFS, which accompany the transition in the long-range atomic structure as studied by x-ray diffraction and reflectivity. Unfortunately the diffraction peaks from the oxide films were extremely weak and the DAFS experiment was dominated by the fluorescent background from the bulk of the Ni crystal. In order to investigate the structural nature of the Ni oxide films, low angle reflectivity measurements were performed. These measurements were challenging due to absorption by the polypropylene film and the trapped liquid layer.

Typical results in this case for the Ni(110) surface are shown in figure 1. The first reflectivity measurements were taken with the native oxide on the surface of the crystal and the potential held (without cycling) at the OCP (open circuit potential). The native oxide was then removed by holding the potential in the hydrogen evolution region. The potential was then cycled between the oxidation region and a chosen lower limit above the hydrogen region until a stable I-V plot was produced. Reflectivity measurements were then taken at the upper and lower limits of the cycle to study the structural changes occurring on the surface.

The difference in the reflectivity curves for the native oxide and the electrochemically formed oxide can be seen in figure 1. The solid lines are fits to the data using a simple two-layer model of the electron density.

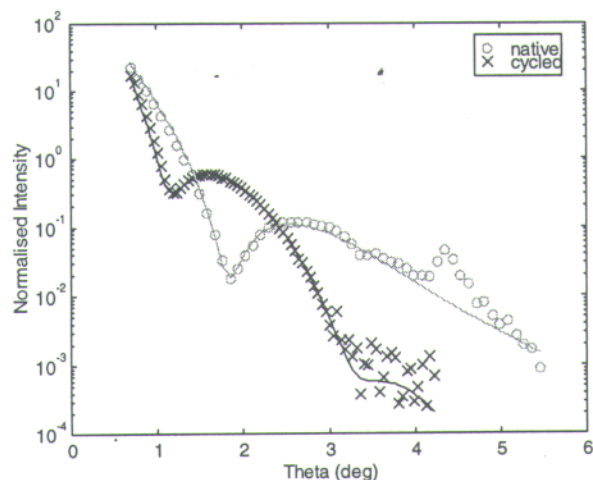


Figure 1.

The thickness of the native oxide can be seen to be much less than that of the electrochemically-formed layer. The native oxide when modelled was found to be 11.5\AA thick while the cycled layer held at the upper limit was twice as thick. The thickness of this layer was found to decrease slightly when held at the lower limit. This result not only shows that we still have potential control of the oxide for thin films but also explains why the measured diffraction peaks from the oxide were extremely weak.

DAFS

As the DAFS measurements were impossible to perform from the ultra-thin oxide films, RAFS measurements were taken at selected positions along the reflectivity curves. The RAFS shown in figure 2 were taken at the maximum and minimum of the reflectivity curve for the electrochemically formed oxide film.

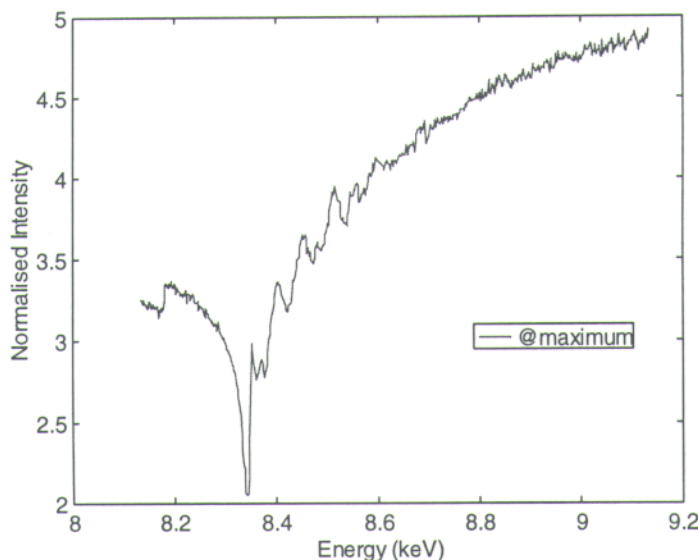


Figure 2a

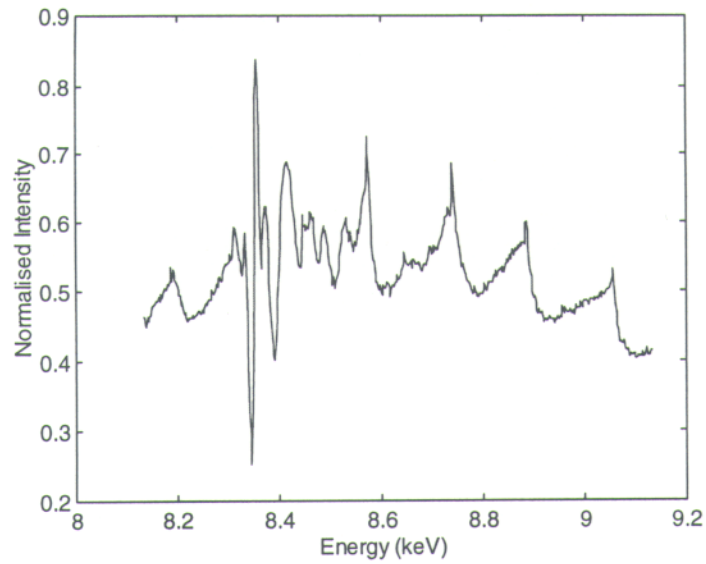


Figure 2b

Analysis of the RAFS is currently being carried out using the methodology described in reference [1].

- [1] G. M. Luo, Z. H. Mai, T. P. A. Hase, B. D. Fulthorpe, B. K. Tanner, C. H. Marrows and B. J. Hickey, *J. Mag. Mag. Mat.*, 226, 1728 (2001).