



Experiment title: In-situ Surface X-ray Diffraction, Reflectivity and RAFS Studies of Oxidation/Reduction in Thin Hydrous Nickel Oxide Films

Experiment number:
28-01-139

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Report:

The aim of the experiment was to further research carried out previously on BM28 relating to electrochemical oxidation of nickel single crystal electrodes. Previously (report on Experiment #28-01-99) it was determined that electro-oxidation of Ni in alkaline solution led to the formation of a 3-layer system; the Ni substrate, a compact, thin oxide layer and a loosely-bound hydroxide. The hydroxide is amorphous and essentially invisible to x-rays, however, we have studied it in detail using a combination of AFM and STM. In this experiment we intended to probe the structural changes that occur in the compact oxide layer on the Ni surface when the amorphous hydroxide is developed upon the application of a positive potential. We also investigated the reversible changes in the compact oxide during the oxidation of the hydrous film which, depending on the applied electrode potential, undergoes a phase transition from $\text{Ni}^{\text{II}}(\text{OH})_2$ to NiOOH . Previous results from BM28 have shown that oxidation leads to a dramatic increase in both the thickness and density of the compact oxide layer at the interface between the Ni substrate and the hydroxide overlayer. Results from a Ni(110) crystal showed that the oxide was twice the thickness of the native oxide that is formed when the electrode is first contacted at open circuit potential (OCP) with the electrolyte.

To complete our measurements and understand the influence of surface atomic geometry on Ni oxidation, studies of all three low-index Ni surfaces were performed. Modelling of the x-ray reflectivity from all three crystals showed significant increases in the thickness of the compact oxide after the application of an oxidising potential. The thickness changes were accompanied by a density increase and a roughening of the Ni/compact oxide interface. This is consistent with the propagation of Ni ions from the Ni surface into the oxide layer and hydroxide layer.

There were four significant new results obtained in this experiment:

(1) A reversible change in density of the native oxide when held at -0.9 V (just into potential region of hydrogen evolution) and then returned to -0.4 V (near to the open circuit potential). This change has been analysed using a fit to the ratio of the reflectivity data sets, which is far more sensitive to changes than simply fitting each curve independently. A typical data set is shown in Figure 1 which shows the raw data at the 2 potentials along with the

ratio data set (lower panel). In each case the points correspond to the measured data and the solid line is a best fit using a 2-layer (compact oxide and Ni substrate) model of the surface-normal electron density profile.

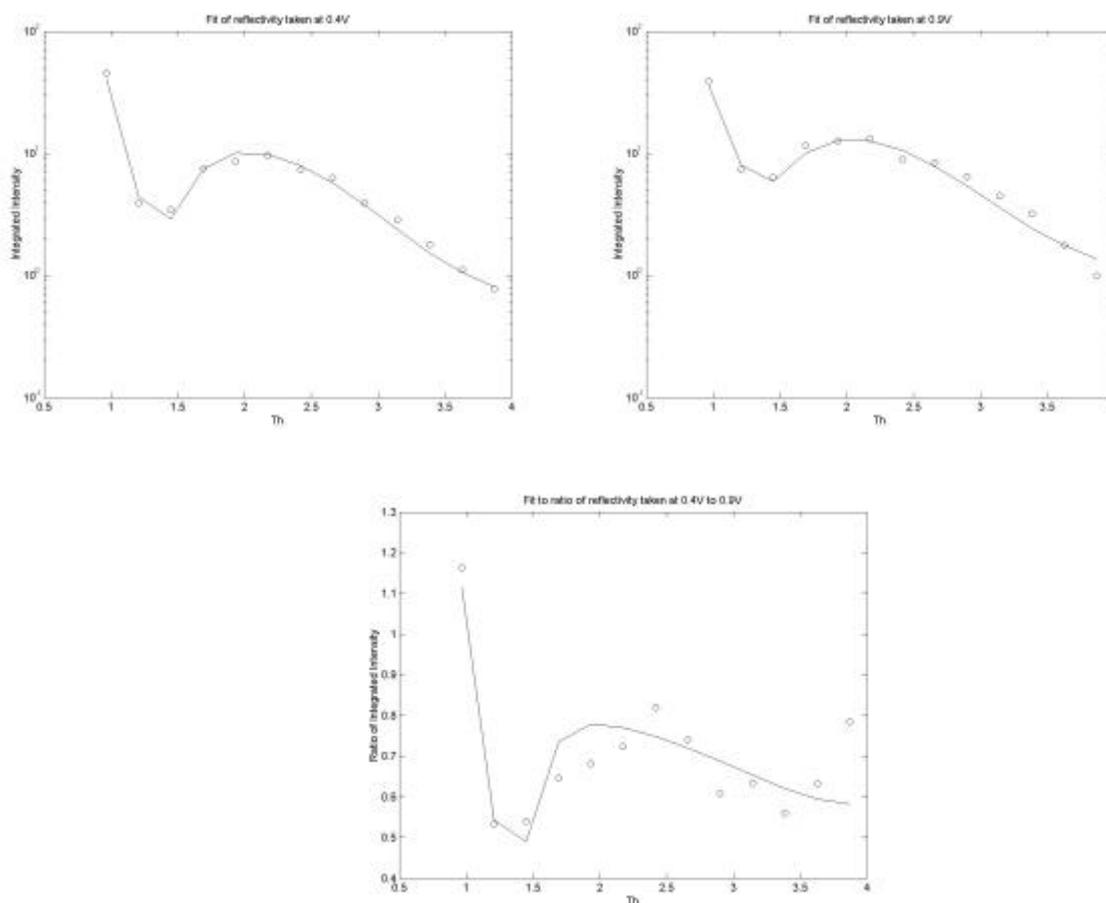


Figure 1

These measurements are currently being combined with cyclic voltammetry and galvanostatic data to correctly assign the voltammetric features to surface chemical reactions, an issue which has been subject to considerable scientific debate in the last few years.

(2) A comprehensive set of data has been obtained during the oxidation of the native oxide that accompanies formation of the Ni hydroxide overlayer. The results of fits to reflectivity data are summarised below:

	Density (g/cm ³)	Thickness (Å)	s ₁ (Å)	s ₂ (Å)
Ni(111)-native	4.7	10.0	0.1	1.8
Ni(111)-oxidised	4.9	14.5	0.1	4.0
Ni(100)-native	5.0	11.0	0.8	1.3
Ni(100)-oxidised	6.1	16.1	1.7	4.4
Ni(110)-native	5.3	10.8	1.5	1.7
Ni(110)-oxidised	5.4	21.0	4.5	5.2

These results show that the native, air-formed oxide (~10 Å in thickness) is transformed after cycling over the redox peaks to a thicker, slightly denser oxide. This, however, is not the hydroxide layer that is formed on the surface but a compact oxide layer formed at the interface between the hydroxide and the Ni substrate. The hydroxide layer is essentially invisible to the x-ray measurement due to the diffuse nature of its surface, i.e. it is granular in nature. It can also be seen that the interface roughness at the Ni-NiO interface increases after cycling due to mass transport of Ni ions through the compact oxide layer to form the hydroxide overlayer. In fact it is the formation of the compact oxide

overlayer that ultimately limits the growth of the hydroxide due to the increasing barrier for solid state diffusion of Ni ions to the hydroxide. This explains the equilibrium state that is reached during potential cycling over the redox peaks. Finally it is interesting to note that the thickness of the NiO layer increases in the sequence (111)-(100)-(110). This can be understood in terms of the atomic geometry of the low-index surfaces; the (111) surface being the most compact and the (110) surface the most open. Clearly the crystal orientation plays a role in the oxidation mechanism. A paper on this work is currently in preparation and will be submitted to the Journal of Physical Chemistry.

(3) A reversible change occurs in the x-ray reflectivity during oxidation/reduction of the hydroxide overlayer, i.e. when holding the electrode potential above and below the large peak in the cyclic voltammetry at ~ 0.6 V. The structural transformation is still being analysed, though it is most likely due to changes in thickness and density caused by the flow of ions into and out of the compact oxide layer.

(4) A detailed study of the Ni-oxide interface has been performed by crystal truncation rod (CTR) analysis. For non-specular scattering the CTR's are sensitive only to the termination of the Ni lattice and any adatoms that are commensurate with the lattice. For the specular CTR the scattering is also sensitive to incommensurate crystalline overlayers such as that formed by NiO at the interface. The specular reflectivity (shown above) is the very low-Q region of the specular CTR where crystallinity is not important. The specular CTR data indicates the presence of crystalline NiO which forms the dense oxide phase observed in the x-ray reflectivity experiments. For both Ni(100) and Ni(111) the specular CTR results are only consistent with the presence of NiO oriented with the (111) axis along the surface normal direction. These measurements are currently being modelled using a kinematic scattering theory and the results will be published in combination with the x-ray reflectivity data above. The non-specular CTR data give a precise atomic description of the truncation of the Ni lattice and this must be consistent with the electron density profile obtained via x-ray reflectivity.