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In Situ XAFS Study of Oxides Formed
on Nickel Thin Film Electrodes in KOH Solution

by

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In Situ XAFS Study of Oxides Formed on Nickel

Thin Film Electrodes in KOH Solution

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Introduction:

The composition and structure of the oxides formed on nickel are of great interest for a number of technological applications, e.g., batteries and corrosion. In spite of the considerable research that has been done, there is still much uncertainty as to the stoichiometry and structure of the various oxides (hydroxides) that are formed during the anodic oxidation of the nickel.¹ This is due largely to the highly disordered or amorphous nature of the phases formed which makes structural determination

by X-ray diffraction difficult. X-ray absorption Fine Structure (XAFS) spectroscopy is an excellent technique for the characterization of such materials which have no long range order.^{2,3,4} In this paper, we present initial results of an "in situ" study of the structure and composition of the oxides (hydroxides) formed on Ni thin film electrodes in 5M KOH solution as a function of the applied potential.

Experimental:

The in situ XAFS measurements were performed on 50 and 200 Å thin films of Ni (20 mm in diameter) deposited centrally on a 250 and 100 Å thin films of Ta (35 mm in diameter), respectively, which was in turn deposited on a 3.5 µm thick mylar support. The anodization of the Ni thin film electrodes was made in an electro-chemical cell specially designed for in situ XAFS measurements. The charging and discharging of the electrodes were made in 5M KOH solution. The X-ray absorption spectra were measured at beamline X11A of the National Synchrotron Light Source (NSLS). The room temperature X-ray absorption spectra around the Ni K-edge (8333 eV) were measured in the fluorescence mode with the storage ring operating at 2.52 GeV beam energy and beam currents of 110-220 mA.

Results and Discussion:

The XAFS spectra for the 50 and 200 Å Ni thin film electrodes are qualitatively similar in nature. Hence, only the spectra for the 50 Å Ni thin film electrode will presented and discussed here. Figure

1 shows the X-ray absorption near edge structure (XANES) spectra for the 50 Å thin film electrode cycled in 5 M KOH as a function of the applied potential along with a reference spectrum of a 4 µm thick nickel foil. A visual examination of the data clearly shows reduction in the amplitude of the shoulder at the onset of the edge (taken as the normalized absorption at 8333 eV). The amplitude of this shoulder is mainly dominated by contributions from metallic Ni while contributions from oxidized Ni are very small and can be neglected.⁵ Therefore, this amplitude can be used as an approximate measure to the fraction of oxidized Ni in the film assuming no dissolution of nickel occurs during the anodization process. This amplitude varies from 0.397 for metallic Ni to 0.340, 0.295, 0.303 and 0.240 for the 50 Å Ni thin film, electrode immersed in 5M KOH, electrode cycled between -1.10 and -0.23 V (curve d), and electrode cycled between -1.10 to 0.5 V (curve e), respectively. The anodization process also alters the intensity and position of the peaks located at ≈8346 and ≈8354 eV in the spectrum of metallic Ni (curve a). The low energy peak dominates and shifts to higher energies in the spectra of oxidized Ni thin film electrodes. This peak is located at 8347 and 8349 eV in the spectra of electrode cycled between -1.10 and -0.23 V (curve d) and electrode cycled between -1.10 to 0.5 V (curve e), respectively. Furthermore, a significant shift to higher energy in the edge position is observed for electrode cycled between -1.10 and -0.23 V relative to electrode cycled between -1.10 to 0.5 V indicating an increase in the valency of Ni at the higher potential. Detailed analysis of spectra using the technique of spectral subtraction are currently underway.

Figures 2 and 3 show the in situ Extended X-ray Absorption Fine Structure (EXAFS) and their respective Fourier transforms. The EXAFS spectra are displayed with no weighting to emphasize

the low k region of the spectra where oxygen backscattering dominates and hence is more sensitive to local structure of oxidized Ni. The Fourier transforms clearly display contributions from both oxidized and metallic Ni. The first peak located at $\approx 1.3 \text{ \AA}$ is mainly due to contributions from the first coordination sphere of oxidized Ni while the second peak at $\approx 2.15 \text{ \AA}$ is due to contributions from the first coordination sphere of metallic Ni. The amplitude of this second peak varies from 0.865 for metallic Ni to 0.577, 0.520, 0.505 and 0.391 for the 50 \AA Ni thin film, film immersed in 5M KOH, electrode cycled between -1.10 and -0.23 V (curve d), and electrode cycled between -1.10 to 0.5 V (curve e), respectively. Based on these amplitudes, 33% of nickel in the 50 \AA thin film electrode is in an oxidized state. After immersion in 5M KOH for roughly 15 minutes, the fraction of oxidized Ni increased to approximately 40%. The fraction of oxidized Ni after cycling in the potential range of -1.10 to -0.23 V for 20 cycles remained unchanged from that of electrode after immersion in the solution. Further oxidation of the electrode in the potential range of -1.10 to +0.54 increased the fraction of oxidized Ni to roughly 60 %. Quantitative analysis using non-linear least square techniques to assess the valency and structure of oxidized nickel as a function of the applied potential will be made and presented at the meeting.

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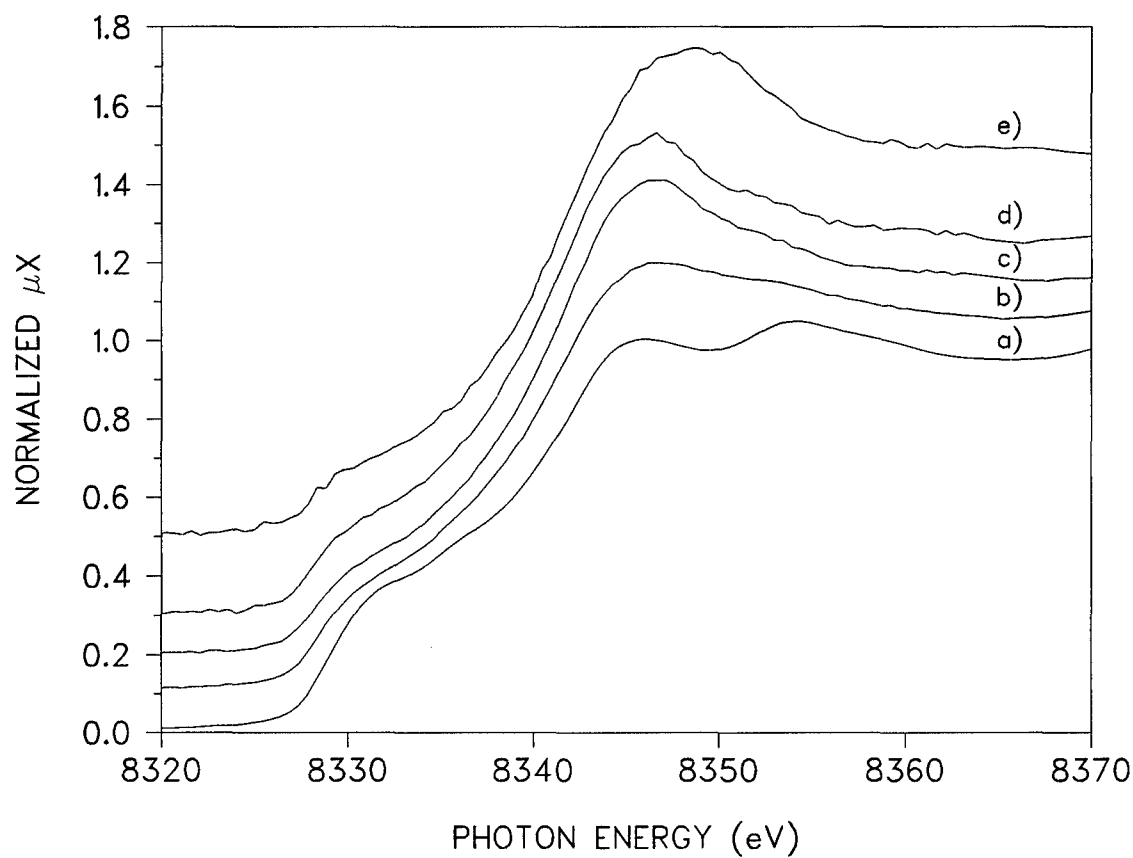


Figure 1. In situ XANES spectra of Ni K-edge for a 50 Å Ni thin film electrode cycled in 5M KOH solution. a): reference spectrum of a 4 μm thick Ni foil, b): 50 Å Ni thin film electrode, c): 50 Å Ni film immersed in 5M KOH and held at open circuit potential (OCP) of -0.31 V, d): cycled electrode, 20 cycles, -1.10 to -0.23 V, 10 mV/sec, held at -0.23 V, (Ni^{2+} region), e): d) + 15 cycles, -1.10 to +0.50 V, 100 mV/sec, held at +0.4 V.

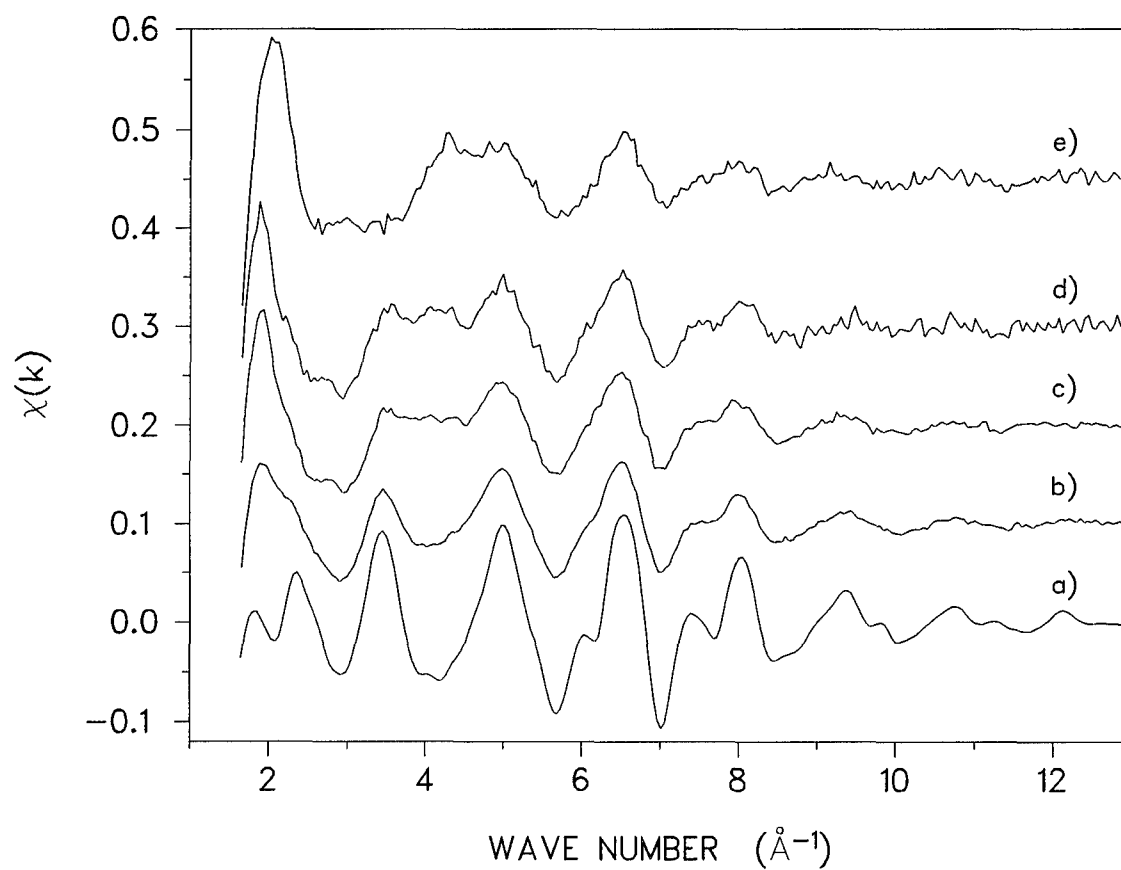


Figure 2. In situ Ni K-edge EXAFS spectra, $\chi(k)$, for a 50 Å Ni thin film electrode cycled in 5M KOH solution; conditions are the same as in Figure 1.

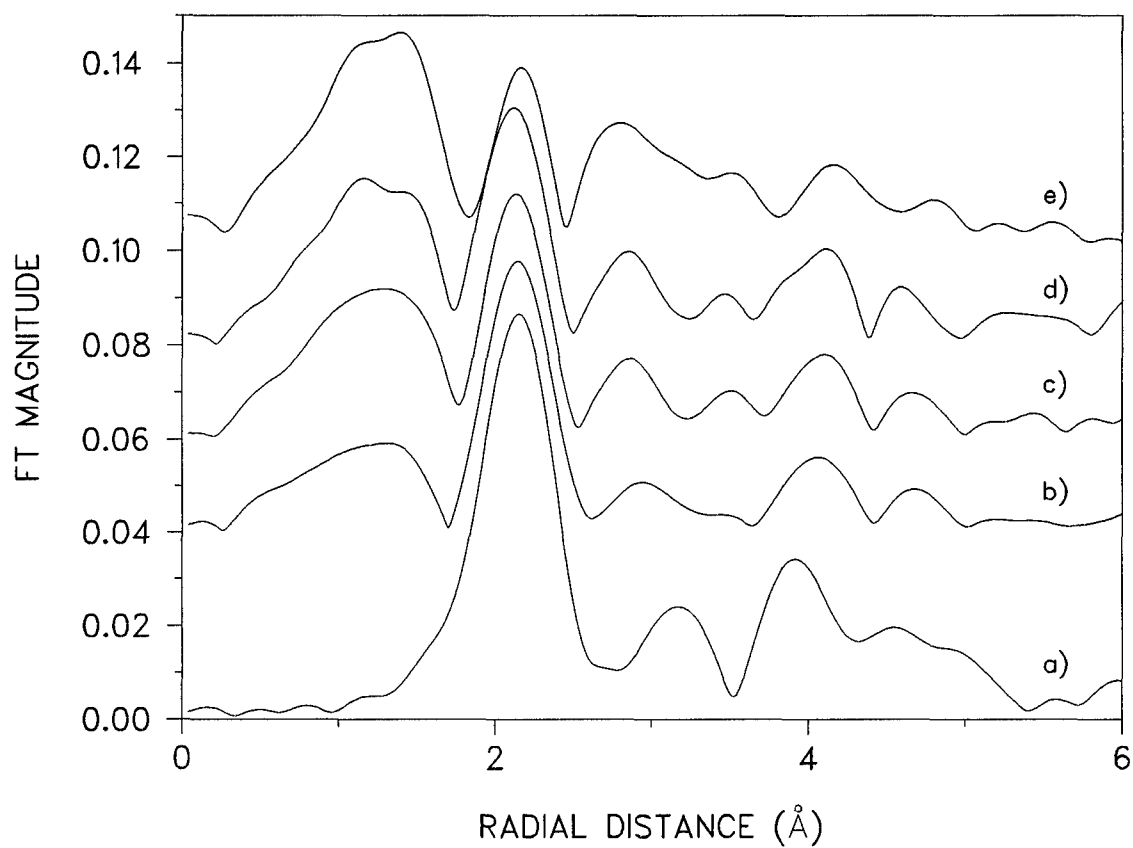


Figure 3. Fourier transforms of in situ Ni K-edge EXAFS spectra, $\chi(k)$, for a 50 Å Ni thin film electrode cycled in 5M KOH solution; conditions are the same as in Figure 1.