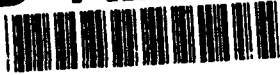


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Atomic Structure and Valency of Nickel in Some of its Oxycompounds

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Introduction:

The structure of the higher oxide forms of nickel (where Ni has a valency greater than +2) is of great interest from the standpoint of developing advanced nickel batteries for consumer applications and for electric vehicle propulsion. In spite of the considerable research work that has been published, there is still much uncertainty and confusion as to the stoichiometry and structure of the various oxides (hydroxides) that are formed during the charging (and discharging) of the nickel electrode.¹ The difficulty stems in part from the highly disordered or amorphous nature of the phases formed which makes structural determination by X-ray diffraction difficult. X-ray absorption spectroscopy (XAS) consisting of the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) is an excellent technique for the characterization of such materials which have no long range order.²⁻⁴ Preliminary to using the technique for "in-situ" structural determinations in an electrochemical cell, we have used XAS to study a number of standard samples for subsequent use as reference. We report initial XANES and EXAFS results that give the valency and structure of nickel in some compounds of interest in battery work.

EXPERIMENTAL:

The compounds studied were prepared by chemical synthesis following procedures established in the literature; others were purchased from commercial suppliers. The β -NiOOH was prepared by bromine oxidation of $\text{Ni}(\text{NO}_3)_2$ solution at low temperatures ($< 25^\circ\text{C}$) following the procedure of Glemser.⁵ The $\text{Ni}_3\text{O}_2(\text{OH})_4$ was obtained by bromine oxidation of $\text{Ni}(\text{NO}_3)_2$ in an aqueous alkaline solution at 50°C . The KNiIO_6 was synthesized following the procedure of Murthy⁶ for the peroxydisulfate oxidation of a solution of $\text{NiSO}_4 + \text{KIO}_4$. The nickel oxide (NiO) and "nickel peroxide" (NiO_2) were purchased from Aldrich

Chemical Co. (Milwaukee, WI). All samples were examined by powder X-ray diffraction (XRD). The XRD patterns indicated that both the NiO and KNiIO_6 were fairly crystalline with sharp lines while the others showed broad bands indicative of highly disordered or amorphous materials. The XRD patterns for β -NiOOH, $\text{Ni}_3\text{O}_2(\text{OH})_4$, and NiO_2 are nearly identical. X-ray absorption spectra were measured at beamline X11A of the National Synchrotron Light Source (NSLS). X-ray absorption spectra around the Ni K-edge (8333 eV) were measured in transmission with the storage ring operating at 2.52 GeV beam energy and beam currents of 110-220 mA. The spectrum of a 6 μm thick Ni foil was measured simultaneously for use as a reference in calibrating the energy scale.

Results and Discussion:

Figure 1 shows the XANES spectra at room temperature of NiO, β -NiOOH, $\text{Ni}_3\text{O}_2(\text{OH})_4$, NiO_2 and KNiIO_6 along with Ni foil used as reference. The pre-edge region from -10 to 2 eV has been expanded to display the contribution due to the transition from the 1s core level to unoccupied d-states near the Fermi level and is shown in Figure 2. The weak intensity associated with this transition is due to the fact that this transition is forbidden by dipole selection rules. It is allowed by quadrupole selection rules or as a result of hybridization between states with p and d characters. Due to the lack of unoccupied d-states near the Fermi level for metallic Ni, the pre-edge region shows no signature from d-states and, hence, its pre-edge region was omitted from Figure 2. The Ni K-edge energies are listed in Table I. As expected, the Ni K-edge energy shifts to higher energies as the oxidation state increases from Ni^0 (metallic Ni), to Ni^{+2} (NiO) and Ni^{+4} (KNiIO_6). The latter is among the few compounds where Ni has been fairly well established to be in the quadrivalent state⁷ and was chosen here as a reference because of its stability and ease of preparation. We believe that this is the first published XANES spectrum of a quadrivalent Ni compound. The observed shifts suggest that in β -NiOOH, the Ni is in the + 3 state. The compound formulated as $\text{Ni}_3\text{O}_2(\text{OH})_2$ shows a shift identical to that of β -NiOOH, although a slight difference is observed in their XRD patterns. The inflection point energy at the onset of the 1s to 3d transition (Figure 2) also shifts to higher energy with increase in valency of Ni from Ni^{+2} (NiO) to Ni^{+4} (KNiIO_6) with those of β -NiOOH and $\text{Ni}_3\text{O}_2(\text{OH})_4$ being intermediate between Ni^{+2} and Ni^{+4} indicating a Ni valency of +3 for both compounds.

We find a linear relationship between the edge energy and the Ni valency assuming a Ni valency of +3 for both β -NiOOH and $\text{Ni}_3\text{O}_2(\text{OH})_4$. Note that both NiO and KNiIO_6 display a sharp pre-edge peak characteristic of the highly ordered local structure of their first coordination sphere. The β -NiOOH and $\text{Ni}_3\text{O}_2(\text{OH})_4$, on the other hand, display a broad peak characteristic of the highly disordered structure of the first coordination sphere which consists of two NiO distances as revealed from analysis of EXAFS spectra. The nickel peroxide (NiO_2) does not have Ni in the +4 state but is most probably a Ni^{+3} compound. XANES of NiO_2 resemble more closely those of β -NiOOH and $\text{Ni}_3\text{O}_2(\text{OH})_4$ rather than that of KNiIO_6 in terms of edge energy and pre-edge peak shape.

Comparison of Fourier transforms of K^3 -weighted EXAFS spectra for β -NiOOH, $\text{Ni}_3\text{O}_2(\text{OH})_4$, and NiO_2 is shown in Figure 3. The similarity of the Ni local structure in these compounds is very clear. Quantitative Analysis of this data and others not shown here are listed in Table II.

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TABLE I. Ni K-edge Energy in Various Compounds.

Compound	Ni K-edge Energy ¹	Ni K-edge Energy ²
Ni	8336.9	N/A
NiO	8338.9	8328.9
β -NiOOH	8340.8	8329.6
Ni ₃ O ₂ (OH) ₄	8340.8	8329.6
NiO ₂	8340.2	8329.6
KNiIO ₆	8343.0	8330.6

¹Ni K-edge energy measured as the energy at which the normalized absorption (μx) is equal to 0.5.

²Ni K-edge energy measured as the energy of the inflection point at the onset of the 1s to 3d transition.

Table II. Summary Of Ni Local Structure parameters in some of its compounds as determined from XAFS spectra using theoretical phase and amplitude values calculated with the FEFF code.

Compound	X-Y Pair	N	R (Å)	$\sigma^2(10^{-3}\text{Å}^2)$
Ni	Ni-Ni	12.0	2.480(2.492)	5.5
NiO	Ni-O	6.0	2.079(2.089)	4.5
	Ni-Ni	12.0	2.946(2.954)	5.5
β -Ni(OH) ₂	Ni-O	5.8	2.06(2.073)	5.0
	Ni-Ni	6.0	3.13(3.126)	5.4
β -NiOOH	Ni-O(1)	3.7	1.89	5.8
	Ni-O(2)	2.3	2.07	5.8
	Ni-Ni(1)	3.4	2.86	7.1
	Ni-Ni(2)	2.6	3.06	7.1
Ni ₃ O ₂ (OH) ₄	Ni-O(1)	3.5	1.89	5.9
	Ni-O(2)	2.5	2.06	5.9
	Ni-Ni(1)	3.2	2.85	6.7
	Ni-Ni(2)	2.8	3.07	6.7
NiO ₂	Ni-O(1)			
	Ni-O(2)			
KNiIO ₆	Ni-O	6.0	1.88	3.5

N: coordination number,

R: bond distance (distances in parentheses correspond to the well known crystallographic distances), and

σ^2 : mean square displacement.

Figure Captions:

Figure 1 XANES of Ni K-edge in some of its compounds: Ni foil, NiO, β -NiOOH, $\text{Ni}_3\text{O}_2(\text{OH})_4$, NiO_2 , and KNiIO_6 .

Figure 2 Portion of Ni K-edge XANES displaying the 1s to 3d transition for some nickel compounds: NiO, β -NiOOH, $\text{Ni}_3\text{O}_2(\text{OH})_4$, NiO_2 , and KNiIO_6 .

Figure 3 Fourier transforms of β -NiOOH, $\text{Ni}_3\text{O}_2(\text{OH})_4$ and NiO_2 .

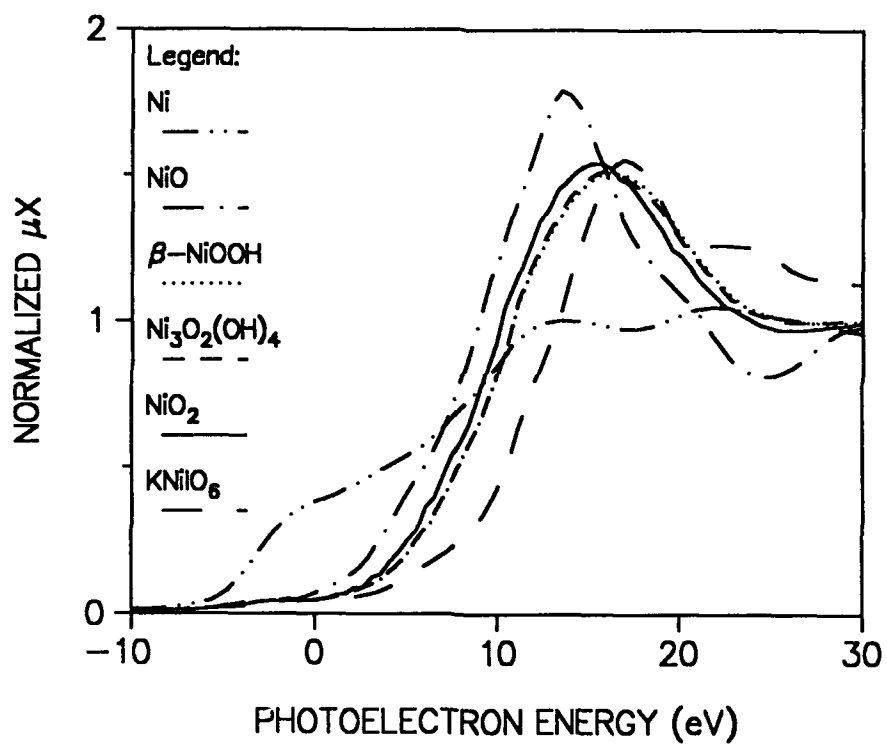


Fig. 1

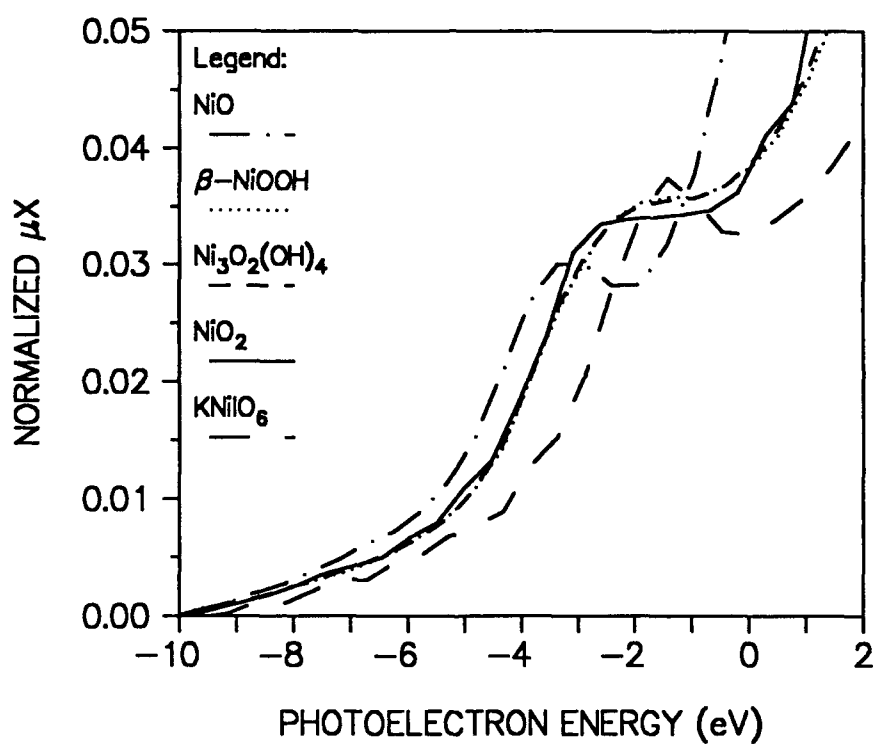


Fig. 2.

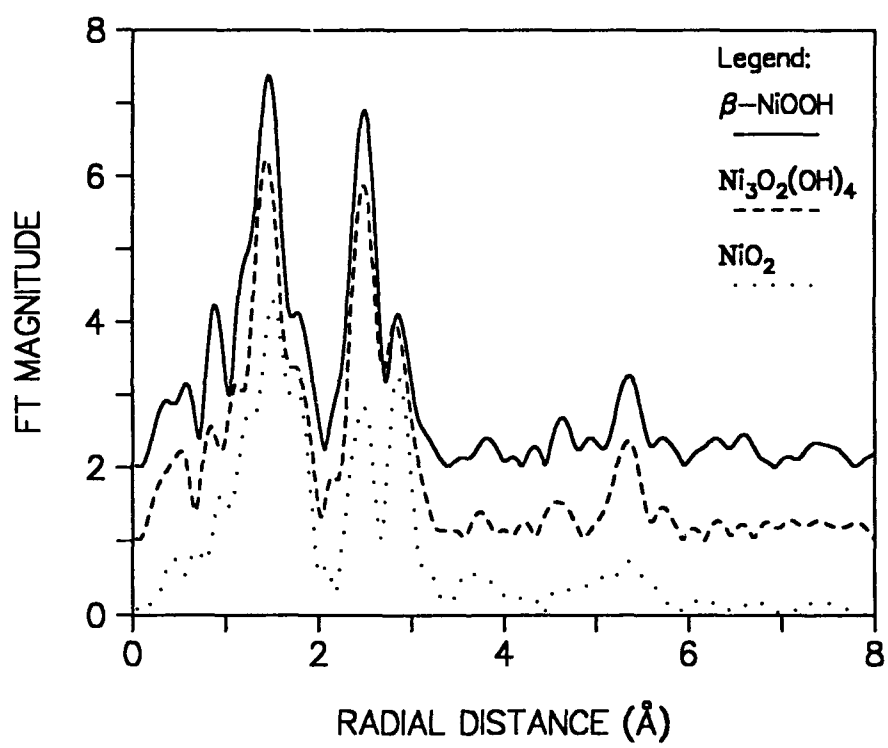


Fig. 3