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XAFS Investigation of Structure and Valency of Nickel in Some Oxycompounds

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(e) Abstract

We report on the Ni valency and local structure in α-$Ni(OH)_2$, β-$Ni(OH)_2$, Ni_2O_3, $Ni_3O_2(OH)_4$, β-NiOOH, γ-NiOOH, NiO_2 and $NiKIO_6$.

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Preliminary to using XAFS spectroscopy for "in-situ" structural determinations in an electrochemical cell, we have used it to study a number of standard samples for subsequent use as references for the identification of electrochemically prepared (ECP) phases. Namely, we have examined the Ni valency and local atomic structure in chemically prepared (CP) α-$Ni(OH)_2$, β-$Ni(OH)_2$, Ni_2O_3, $Ni_3O_2(OH)_4$, β-NiOOH, γ-NiOOH, NiO_2 and $NiKIO_6$ and ECP γ-NiOOH. Most of the compounds investigated were prepared by chemical synthesis following procedures established in the literature; others were purchased from commercial sources.[1,2] Room temperature XAFS spectra of the Ni K-edge were measured in transmission on beamline X11A at NSLS. Figure 1 shows XANES spectra of Ni K-edge in some oxycompounds. 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) to Ni^{+4} ($NiKIO_6$). The observed shifts suggest that the average valency of Ni increases in the order α-$Ni(OH)_2$, Ni_2O_3, β-NiOOH, ECP γ-NiOOH, CP γ-NiOOH, and $NiKIO_6$. The shift in edge energy, measured at half-height the edge step, is roughly 2 eV per unit change in valency assuming that the average valency of Ni in β-NiOOH is +3. The pre-edge structure (not shown here) due to the transition from the 1s core level to unoccupied d-states has an intensity of roughly 3.5% of the edge step and shifts at a rate of 1 eV per unit change in oxidation state. Figure 2 shows a comparison of Fourier transforms of Ni K-edge k^3-weighted EXAFS spectra in some oxycompounds (Δk of 2.6-16.1 $Å^{-1}$). The first and second shells of atoms were filtered, backtransformed to k-space and quantitatively analyzed using non-linear least square fitting methods. The data was fitted using theoretical

standards calculated with the FEFF Code (version 4.06).[3] Single shell fits were sufficient in analyzing the first and second shells for β-$Ni(OH)_2$ and $NiKIO_6$. However, a two shells fit was necessary for analyzing each of the first and second shells of atoms for all other samples. The sum of the coordination numbers for each of the Ni-O first and Ni-Ni second coordination spheres was constrained to be equal to 6. In addition, we assumed that all atoms within a specific shell have the same disorder. A summary of local structure parameters are listed in Table I. All reported distances are low by 0.01 Å which is very common when theoretical standards are used. The local structure parameters for β-$Ni(OH)_2$ are more consistent with the brucite C6 type structure published by Greaves and Thomas[4] than those reported by McEwen.[5] The $NiKIO_6$ first shell distance of 1.89 Å differs significantly from the 2.00 Å distance reported by Vannerberg and Blockhammar[6] but is more consistent with what one expects for Ni^{+4}.[7] The first and second shells for all other samples consist of a short and long distances characteristic of Ni^{+4}/Ni^{+2} with varying fractions depending on preparation methods.

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Table I. Summary of Ni local structure in some oxycompounds.

Compound	X-Y Pair	N	R (Å)	σ^2 (10^{-3}Å^2)
β-$Ni(OH)_2$	Ni-O	5.8	2.06	5.0
	Ni-Ni	6.0	3.13	5.4
α-$Ni(OH)_2$	Ni-O(1)	1.0	1.90	3.7
	Ni-O(2)	5.0	2.05	3.7
	Ni-Ni(1)	0.4	2.85	8.3
	Ni-Ni(2)	5.6	3.12	8.3
$Ni_3O_2(OH)_4$	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
Ni_2O_3	Ni-O(1)	2.2	1.87	7.8
	Ni-O(2)	3.8	2.03	7.8
	Ni-Ni(1)	2.5	2.88	8.1
	Ni-Ni(2)	3.5	3.07	8.1

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
γ-NiOOH	Ni-O(1)	4.6	1.89	5.1
(CP)	Ni-O(2)	1.4	2.12	5.1
	Ni-Ni(1)	4.7	2.84	4.2
	Ni-Ni(2)	1.3	3.08	4.2
γ-NiOOH	Ni-O(1)	4.0	1.89	7.0
(ECP)	Ni-O(2)	2.0	2.08	7.0
	Ni-Ni(1)	3.9	2.84	6.4
	Ni-Ni(2)	2.1	3.07	6.4
NiO_2	Ni-O(1)	2.7	1.91	8.1
	Ni-O(2)	3.3	2.06	8.1
	Ni-Ni(1)	2.6	2.88	7.8
	Ni-Ni(2)	3.4	3.07	7.8
$NiKIO_6$	Ni-O	6.0	1.88	3.5

Figure Captions:

Fig. 1 XANES spectra of Ni K-edge in some oxycompounds.

Fig. 2 Fourier transforms of k^3-weighted Ni K-edge EXAFS in some oxycompounds.

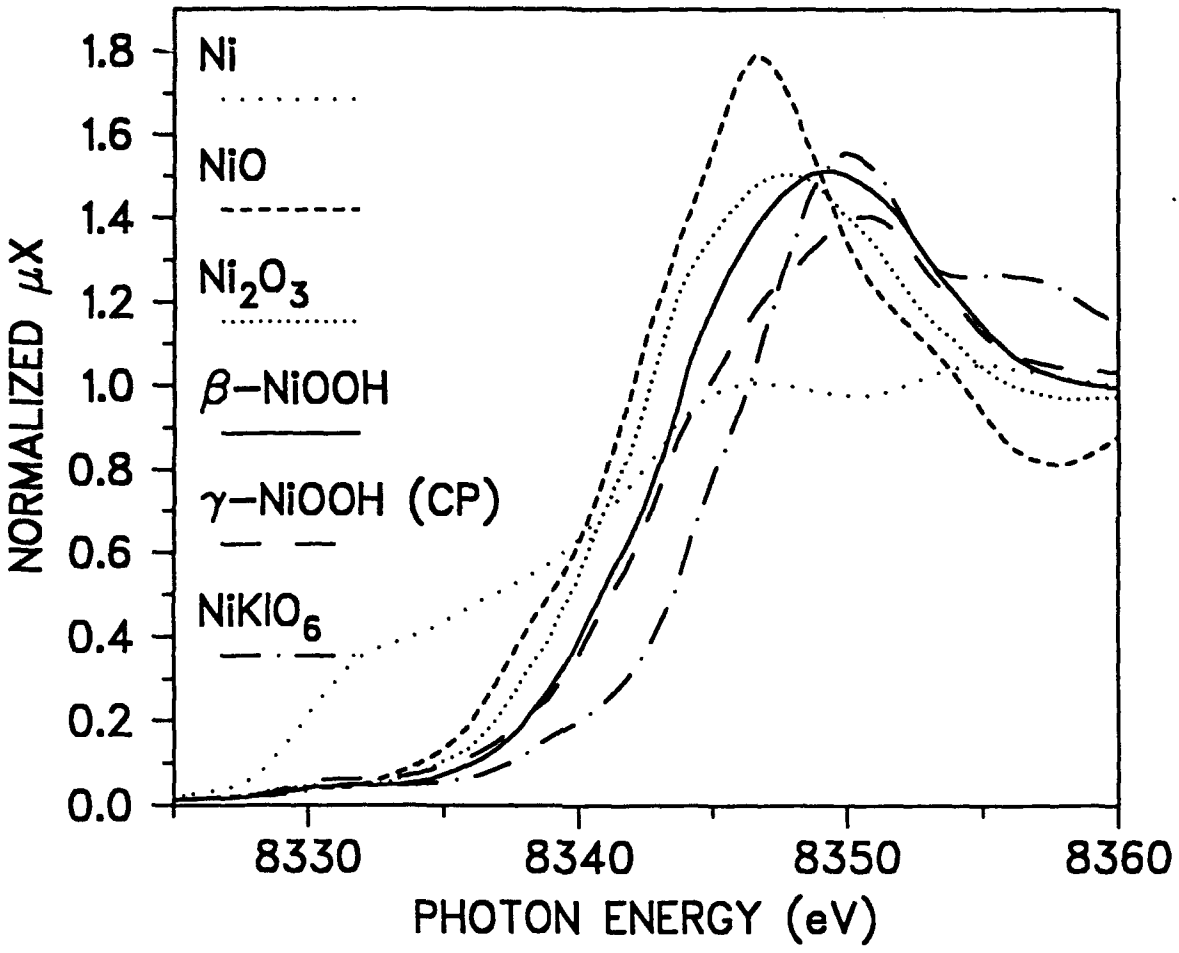
Ni
NiO
Ni_2O_3
β–NiOOH
γ–NiOOH (CP)
$NiKIO_6$
NORMALIZED μX
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
8330
8340
8350
8360
PHOTON ENERGY (eV)

Fig. 1

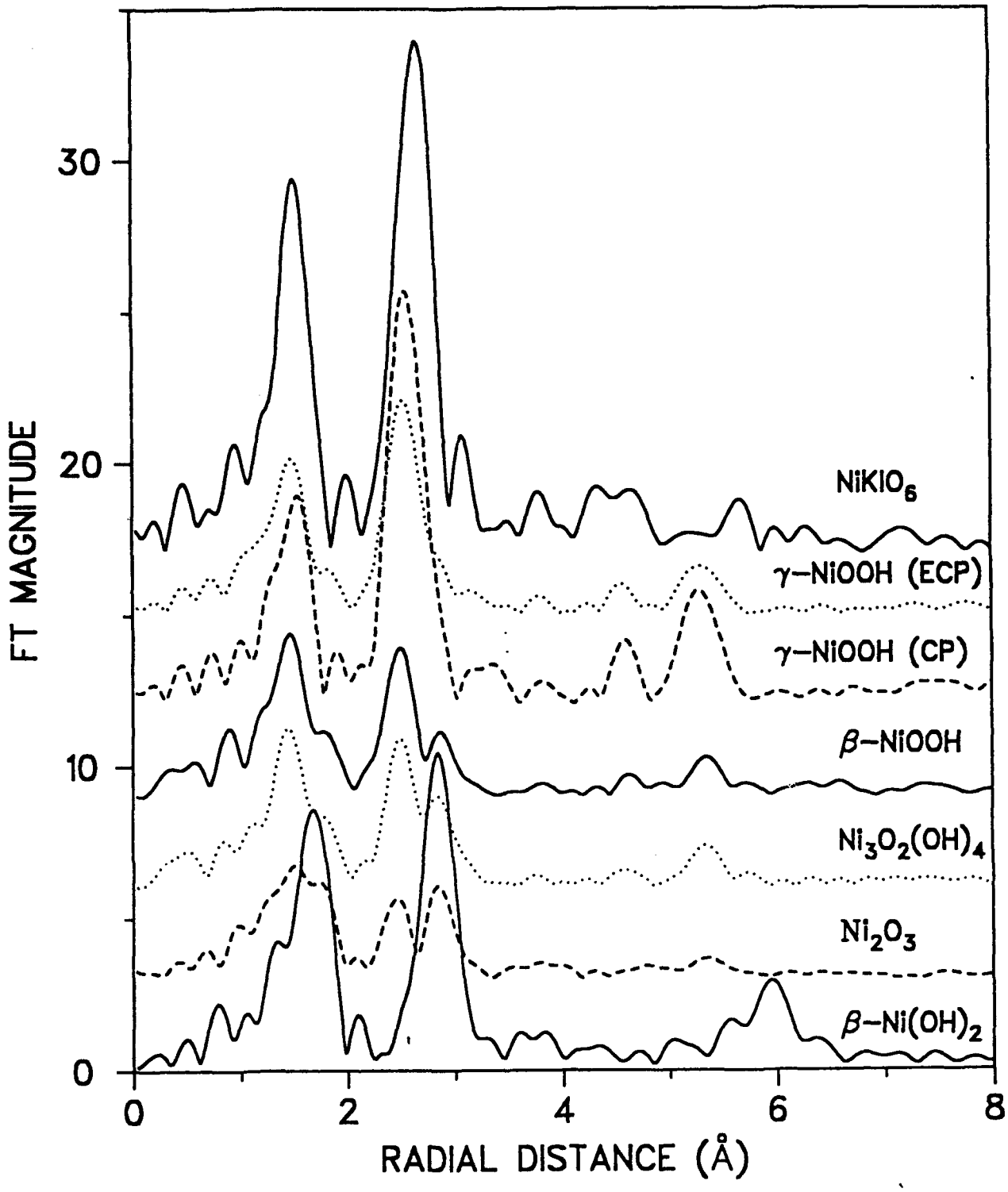
30
20
10
0
FT MAGNITUDE
NiKIO6
γ–NiOOH (ECP)
γ–NiOOH (CP)
β–NiOOH
Ni3O2(OH)4
Ni2O3
β–Ni(OH)2
0
2
4
6
8
RADIAL DISTANCE (Å)

Fig. 2