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X-Ray Absorption Spectra and the Local Structure of Nickel in Some Oxycompounds and Fluorides

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Abstract: X-ray absorption spectra were measured for a number of nickel oxycompounds and fluorides which contain nickel with valencies in the range of 2 to 4. Information on the local structure and nature of bonding of nickel were derived using theoretical standards generated with the FEFF code. The energies of the main Ni K-edge and the pre-edge peak were found to shift to higher values by about 1.5 and 0.6 eV, respectively, per unit increase in the valency of nickel. The average Ni-O and Ni-F bond length within the octahedron decreased linearly with increase in nickel valency from 2 to 4. The local structure parameters for the higher valency nickel oxycompounds are consistent with a multi-phase model in which up to three phases corresponding to Ni^{2+} , Ni^{3+} , and Ni^{4+} could be present in different proportions depending on preparation procedures.

1. INTRODUCTION

The structure and composition of the higher oxide forms of nickel where nickel has a valency greater than 2 are of great interest from the standpoint of developing materials for energy conversion and storage devices (e.g., advanced nickel batteries, fuel cells, and supercapacitors) as well as understanding the corrosion-passivation behavior of nickel and its alloys in aqueous solution environments. The various phases that are formed during the charging and discharging of the nickel oxide electrode (NOE) have been the subject of extensive studies since the Edison cell was invented about 100 years ago.[1] While there seems to be a general agreement that the divalent oxide and hydroxide forms of nickel could be well represented by the stoichiometric formulae NiO and $\text{Ni}(\text{OH})_2$ (α and β modifications), respectively, various formulations of trivalent nickel oxides and hydroxides have been given in the literature. Thus, stoichiometric formulae like β - and γ - NiOOH , Ni_2O_3 , Ni_3O_4 , $\text{Ni}_3\text{O}_2(\text{OH})_4$ have been proposed. A quadrivalent form, NiO_2 , has also been claimed amid much controversy. The confusion stems mainly 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) is uniquely suited for studying the local structure of such materials and have been used to characterize the structure of the NOE. McBreen et al.[2] carried out XAS studies in situ in electrochemical cells during the charging and discharging cycles. Capehart et al.,[3] using thin films of $\text{Ni}(\text{OH})_2$, claimed to have charged the nickel electrode to a state where the average nickel valency was 3.67 and thus postulating the formation of a $\text{K}(\text{NiO}_2)_3$ phase. Our objective was to determine if simple relationships exist between (i) the Ni x-ray absorption edge energy and valency of nickel and (ii) the Ni-O and Ni-F bond lengths and the valency of nickel. Subsequently, this information will be used to aid in the determination of the valency of nickel in various oxyhydroxides and electrochemically formed nickel phases. Therefore, we have measured and analyzed the x-ray absorption spectra of structurally well defined nickel oxides, hydroxides, and fluorides such as NiO , β - $\text{Ni}(\text{OH})_2$, LiNiO_2 , KNiFO_6 , NiF_2 , K_2NiF_6 , and K_2NiF_6 as well as other compounds such as α - $\text{Ni}(\text{OH})_2$, $\text{Ni}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}_3\text{O}_2(\text{OH})_4$, NiO_2 , β - and γ - NiOOH whose structures are not as well established.

2. EXPERIMENTAL

Most of the compounds studied were prepared by chemical synthesis following procedures established in the literature; others were purchased from commercial suppliers.[4] Three samples of γ - NiOOH were prepared following the procedures described by Bartl et al.,[5] Cotton and Wilkinson,[6] and Capehart et al.[3]; they will be referred to hereafter as γ - NiOOH (1), γ - NiOOH (2), and γ - NiOOH (3), respectively. The X-ray absorption experiments were performed on beamline X-11A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) with the electron storage ring operating at an electron energy of 2.5 GeV and a stored current in the range of 110 to 220 mA. Spectra of the Ni K-edge (8333 eV) were obtained in the transmission mode at room temperature (300 K). The energy calibration of the monochromator was monitored using a Ni foil employing a third ion chamber. To minimize the effect of particle size on EXAFS amplitudes, powdered samples were prepared by grinding and sieving through a 20- μm -size nylon screen. The sieved powder was then spread on Kapton tape or mixed with BN and pressed into pellets. The x-ray absorption edge jump for each sample was kept below 1.5 in order to minimize the thickness effect.

3. RESULTS

The Ni K-edge absorption and the EXAFS spectra were extracted from the raw data using procedures described elsewhere.[7] Local structure parameters were obtained using ab initio theoretical backscattering amplitude and phase values based on the curve-wave single scattering formalism. These were generated with the FEFF Code[8] employing x-ray diffraction structural data for NiO and/or β -Ni(OH)₂. As expected, the Ni K-edge shifted to higher energies as the oxidation state increased from Ni⁰ (metallic Ni), to Ni²⁺ (NiO, Ni(OH)₂ or NiF₂) and Ni⁴⁺ (KNiO₂ or K₂NiF₆). Variations in the Ni K-edge energy (measured as the energy at which the normalized absorption intensity is equal to 0.5) as a function of nickel valency are shown in Figure 1a. It shows that the nickel K-edge energy shifts by 1.5 eV per unit change in valency of nickel. The pre-edge peak energy which corresponds to the transition from the 1s core level to bound unoccupied states near the Fermi level also shifts to higher energy with increase in nickel valency. Variations in the pre-edge peak energy (measured as the energy at which the absorption intensity is half the pre-edge peak intensity) as a function of valency of nickel are shown in Figure 1b which shows a shift of 0.6 eV per unit change in valency of nickel. Based on these results, the x-ray absorption edge energies for other compounds indicate that the average valency of nickel increases in the order NiO < NiO₂ = Ni₂O₃·6H₂O < γ -NiOOH (3) < β -NiOOH = Ni₃O₂(OH)₄ = γ -NiOOH (3) < γ -NiOOH (2) < KNiO₂. Results of local structure analysis indicate that the Ni-O bond length for divalent nickel with an octahedral coordination is in the range of 2.06 to 2.08 Å. The structure of the first coordination sphere for LiNiO₂ consists of a distorted octahedron with 4 oxygens at 1.91 Å and two oxygens at 2.06 Å rather than 6 oxygens at 2.04 Å as predicted by the x-ray diffraction data. The Ni-O bond length for quadrivalent Ni in KNiO₂ is 1.88 Å. Variations in the average Ni-O (for oxides) and Ni-F (for fluorides) first shell distance as a function of nickel valency are shown in Figure 1c indicating that the first shell distance is inversely proportional to nickel valency in the range of 2 to 4. Local structure results for the higher valency nickel oxycompounds reveal that the first coordination sphere consists of two different Ni-O bond lengths. One Ni-O bond length near 1.90 Å is similar to that for Ni⁴⁺ or the short distance for Ni³⁺ in LiNiO₂. The other Ni-O bond length near 2.07 Å is similar to that for Ni²⁺ or the long distance for Ni³⁺ in LiNiO₂. The distribution of these Ni-O bond lengths varies from sample to sample and in some cases differs significantly from that observed for LiNiO₂ (i.e., 4 short and 2 long distances). The x-ray absorption edge energies and local structure results suggest that the higher valency nickel oxycompounds may consist of up to three phases corresponding to Ni⁴⁺, Ni³⁺, and Ni²⁺ in different proportions depending on preparation procedures.

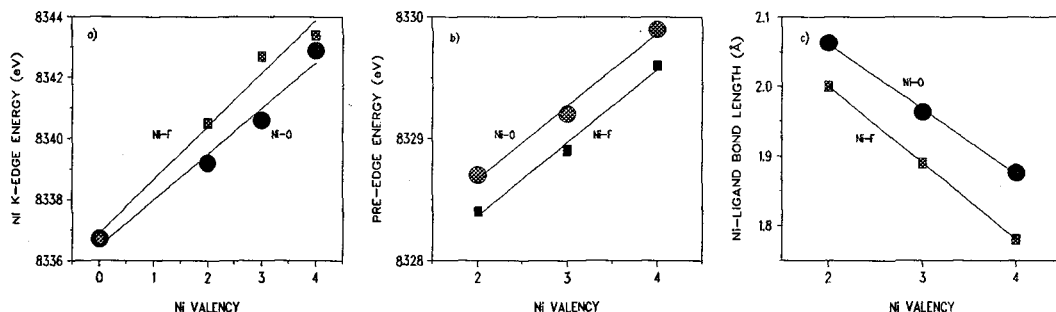


Figure 1: Ni K-edge energy (a), pre-edge peak energy (b), and the average Ni-Ligand bond length (Ni-O for oxides and Ni-F for fluorides) as a function of Ni Valency obtained from structurally well defined nickel oxides and fluorides.

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