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Local structure of chromium incorporated into electrodeposited nickel hydroxide films

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We have utilized X-ray Absorption Fine Structure (XAFS) spectroscopy to investigate the local structure of Cr (III) and Cr (VI) ions incorporated into α -Ni(OH)₂ films. The films were prepared by cathodic co-deposition of Cr and Ni at a constant current from aqueous solutions of nickel nitrate, chromium nitrate and potassium chromate. XAFS measurements show that in films formed from 0.1 M Ni(NO₃)₂ + 0.0005 M Cr(NO₃)₃, Cr (III) is incorporated into the Ni lattice sites of α -Ni(OH)₂. In contrast, co-deposition from a 0.1 M Ni(NO₃)₂ + 0.001 M K₂CrO₄ solution results in Cr (VI) occupying the interlamellar sites of the brucite structure.

Keywords: Oxide films, chemical speciation, hydrous nickel oxides

1. Introduction

Electrodeposited thin hydrous nickel oxide films have been studied extensively in a number of critical energy technologies such as batteries and ultracapacitors. Incorporation of additives has shown an enhancement in some of the electrical performance and cycle life of nickel oxide batteries. Knowledge of the local structure of metal ion additives in nickel oxides is of importance in advancing the technology of energy conversion devices. The structure of heavy metal ions incorporated in nickel oxides is also of interest from the standpoint of environmental remediation. Hazardous heavy metal ions are often found trapped in the corrosion scales of metals. The corrosion-passivation film on nickel metal consists mainly of Ni(OH)₂ in the passive region and NiOOH in the transpassive region (Melendres & Pankuch, 1992). It is widely accepted that the corrosion of metals and alloys takes place via "local electrochemical action". Electrochemical deposition is an excellent method to simulate these processes, e.g., cathodic deposition from Ni(NO₃)₂ solution leads to Ni(OH)₂, while anodic deposition results in the production of NiOOH (Balasubramanian, 1999). In this paper we present some results of X-ray Absorption Fine Structure (XAFS) studies of the local atomic and electronic structure of Cr(III) and Cr(VI) ions incorporated into electrodeposited α -Ni(OH)₂ films.

2. Experimental Details

Cr K-edge fluorescence XAFS experiments were carried out on films formed by cathodic co-deposition of Ni (II) with either Cr (III) or Cr (VI) from aqueous solutions. The incorporation of Cr (III) was carried out by co-deposition from a solution containing 0.0005 M Cr(NO₃)₃ and 0.1 M Ni(NO₃)₂ by applying a constant cathodic current of 5 mA/cm² for 30 minutes. This sample will be referred to as sample (A). The incorporation of Cr (VI) was carried out by co-deposition from a solution of

0.001 M K₂CrO₄ and 0.1 M Ni(NO₃)₂ at a constant cathodic current of 5.13 mA/cm² for 16 minutes. This sample will be referred to as sample (B). The deposition was carried out in a spectro-electrochemical cell that has been described before (Melendres & Mansour, 1997).

3. Results and Discussion

The near edge spectra (XANES) of Cr (III) compounds exhibit only minor pre-edge features compared to those of Cr (VI) compounds which exhibit a prominent pre-edge peak. Figure (1) shows a comparison of the XANES of sample (A) and sample (B) with those of Cr (III) and Cr (VI) reference standards. It can be seen that in sample (A) Cr exists as Cr (III) while on the other hand it exists as Cr (VI) in sample (B). The presence of Cr (VI) in sample (B) is very surprising since one expects Cr to exist as Cr (III) on cathodic deposition.

Figure (2) shows the XAFS $\chi(k)$ function of Cr absorbers in sample (A) and sample (B). It is apparent that the $\chi(k)$ spectra of the two samples are distinctly different which clearly indicates that the local environment around Cr in the two samples is not the same. Figure (3) shows the corresponding k^3 -weighted Fourier transform (FT). The general appearance of the FT of sample (A) is similar to that of Ni absorbers in α -Ni(OH)₂ which has been reported earlier in several studies (Capehart, 1991, Pandya, 1990 and Balasubramanian, 1999). This suggests that the local environment of Cr in sample (A) is similar to that of Ni in α -Ni(OH)₂. We note that the FT of sample (A) shows a peak centered at ~ 5.60 Å. This peak is also seen in FT of Ni absorbers in nickel hydroxide (Pandya, 1990). This peak arises due to scattering from Ni atoms at ~ 6.18 Å in nickel hydroxide; its intensity is enhanced due to the focusing effect of the intervening shell of Ni atoms at ~ 3.09 Å (within the brucite layers). This peak thus serves as a fingerprint which clearly indicates that Cr in sample (A) occupies Ni lattice sites. Non-linear least square fits of the data to phase and amplitude functions obtained from FEFF6 in the r -range 1.05–3.40 Å show that Cr atoms in sample (A) are coordinated to 6.0(6) oxygen first near-neighbor at 1.99(1) Å and to 5.8 (7) Ni atoms at 3.09(1) Å. The Cr–O bond distance of 1.99 Å is similar to those found in Cr (III) compounds such as Cr(OH)₃ and Cr₂O₃ (Peterson, 1997). This indicates that Cr in sample (A) is present as Cr (III). This finding is consistent with the results of the XANES measurements. The Cr–Ni distance of 3.09 Å is identical to the Ni–Ni distance found in α -Ni(OH)₂ and is further evidence of Cr occupying Ni lattice sites in α -Ni(OH)₂.

The FT of Cr absorbers in sample (B) is distinctly different from that of Ni in nickel hydroxide. Detailed fitting shows that the first major peak in the FT can be well represented by $\sim 3.8(5)$ oxygen atoms at 1.66(1) Å. This suggests that Cr is surrounded by oxygen atoms located at the corners of a symmetric tetrahedra, similar to that found for Cr in CrO₄²⁻ (Pandya, 1994). The Cr–O bond distance is consistent with what is expected for a Cr (VI) compound (Pandya, 1994 and Peterson, 1997). This finding is also in agreement with the XANES spectra which shows a prominent pre-edge peak characteristic of Cr (VI) compounds. As mentioned earlier, the presence of Cr (VI) is surprising as these films were prepared by cathodic co-deposition. In addition to the Cr–O peak the FT of Cr absorbers in sample (B) also shows a small but clear peak centered at ~ 3.10 Å. This peak indicates the presence of higher shell neighbors as well. Quantitative fitting of the data in the r -range of 0.95–3.60 Å shows that in addition to the 4 oxygen

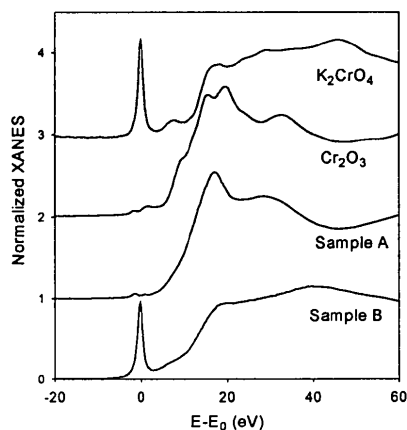


Figure 1
XANES spectra of Cr absorbers in sample (A) and sample (B) compared with those of Cr_2O_3 and K_2CrO_4 .

atoms at 1.66 Å, 1.9(8) Ni atoms at 3.41(5) Å are also present. The large uncertainty in the structural parameters of the Ni shell is due to the relatively weak contribution from this shell of atoms. As the peak at ~ 3.10 Å is relatively weak we find that this interaction can also be represented as a Cr-Cr correlation at 3.44(5) Å instead of a Cr-Ni correlation. A Cr-Ni/Cr distance of 3.41-3.44 Å is too large when compared to the Ni-Ni interaction found in $\alpha\text{-Ni}(\text{OH})_2$ (3.09 Å) or the Cr-Cr interaction found in Cr (VI) compounds such as $\text{K}_2\text{Cr}_2\text{O}_7$ or CrO_3 (3.15-3.31 Å). This shows that the Cr (VI) ions neither enter Ni lattice sites of $\alpha\text{-Ni}(\text{OH})_2$ nor form surface precipitates of pure or mixed hydroxides.

Our findings are more consistent with Cr being present as a chromate group in the interlamellar spacings. Based on a Ni-O distance of 2.05 Å in $\alpha\text{-Ni}(\text{OH})_2$ and the experimentally determined Cr-O and Cr-Ni distances in sample (B) we infer that the chromate group is bonded to $\text{-Ni}(\text{OH})_2$ with a Cr-O-Ni bond angle of $\sim 133^\circ$. This bond angle also suggests that the chromate group is bonded in a mono-dentate fashion where it shares an oxygen with the Ni-O octahedra of the $\alpha\text{-Ni}(\text{OH})_2$ lattice. The presence of a symmetric oxygen shell around Cr

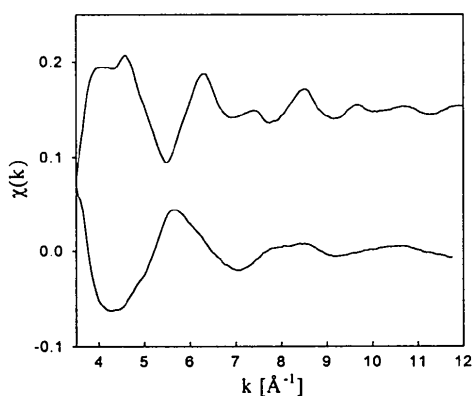


Figure 2
 $\chi(k)$ spectra of Cr absorbers in [a] sample (A) and [b] sample (B).

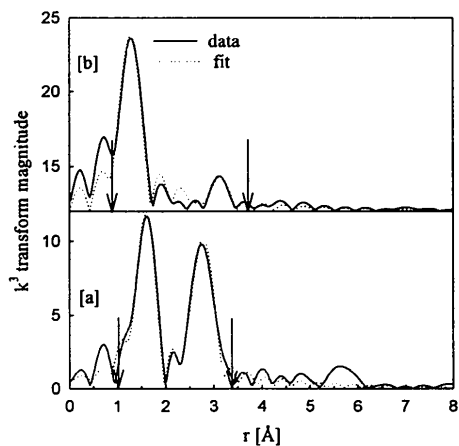


Figure 3
Fourier transform of Cr absorbers in [a] sample (A) and [b] sample (B). The fits to the data are also illustrated. The arrows indicate the fitting range covered.

and a Cr-O-Ni bond angle of 133° , excludes the possibility of bi-dentate or tri-dentate bonding as such configurations will lead to a significantly shorter Cr-Ni distance than those obtained in the experiment.

In summary, we find that Cr (III) and Cr (VI) ions exhibit selective site occupancy on co-deposition with $\alpha\text{-Ni}(\text{OH})_2$. Cathodic co-deposition of Cr (III) and Ni (II) leads to the incorporation of Cr (III) in Ni lattice sites of $\alpha\text{-Ni}(\text{OH})_2$. On the other hand in a cathodic film formed by co-depositing Cr (VI) and Ni (II), Cr surprisingly is present as Cr (VI) and occupies the interlamellar regions as a chromate group coordinated to the brucite layers of $\alpha\text{-Ni}(\text{OH})_2$ in a mono-dentate fashion.

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