APPLICATIONS OF X-RAY ABSORPTION FINE STRUCTURE TO THE IN SITU
STUDY OF THE EFFECT OF COBALT IN NICKEL HYDROUS OXIDE ELECTRODES
FOR FUEL CELLS AND RECHARGEABLE BATTERIES

Sunghyun Kim, Donald A. Tryk, Daniel A. Scherson

Department of Chemistry
Case Western Reserve University
Cleveland, OH 44106-7078

Mark R. Antonio

Argonne National Laboratory
Chemistry Division
Argonne, IL 60439

ABSTRACT

Electronic and structural aspects of composite nickel-cobalt hydrous oxides have been examined in alkaline solutions using in situ X-ray absorption fine structure (XAFS). The results obtained have indicated that cobalt in this material is present as cobaltic ions regardless of the oxidation state of nickel in the lattice. Furthermore, careful analysis of the Co K-edge Extended X-ray absorption fine structure data reveals that the co-electrodeposition procedure generates a single phase, mixed metal hydrous oxide, in which cobaltic ions occupy nickel sites in the NiO₂ sheet-like layers and not two intermixed phases each consisting of a single metal hydrous oxide.

INTRODUCTION

Nickel oxide electrodes have found widespread application in a variety of energy storage and energy generation devices, including rechargeable batteries and fuel cells.¹ The addition of certain metal cations to the nickel hydrous oxide lattice can profoundly affect its electrochemical characteristics.¹ In particular, cobalt has been found to shift the potential associated with the oxidation of Ni(OH)₂ to NiOOH² and to improve the charge acceptance of nickel oxide electrodes used in alkaline batteries.¹ In contrast, composite nickel oxide films involving iron as the guest metal exhibit high electrocatalytic activity for oxygen evolution and, as such, may be of practical value in alkaline water electrolysis.³,⁴

The studies presented herein have been aimed at elucidating the structural and electronic properties of composite nickel-cobalt hydrous oxides using in situ X-ray absorption fine structure (XAFS) as a probe of the host (Ni) and guest (Co) metal sites in the lattice.

Basic aspects of XAFS as applied to the study of electrochemical interfaces have been amply reviewed in the literature⁵ and will not be discussed here. This technique can provide structural information without relying on long range order. This factor is of crucial importance, as high charge storage capacities can only be achieved by using materials in high area form, which are in many cases amorphous or consist of particles that are too small to achieve sufficient coherence for standard X-ray diffraction techniques to be very useful. Furthermore, high intensity X-rays in the energy range of interest can penetrate through thin electrolyte layers and low-Z window materials, such as organic polymers and thin aluminum sheets. This provides a means of performing measurements in situ, that is, with the electrode under potential control in an appropriately designed electrochemical cell.

13
EXPERIMENTAL

Pure metal (either nickel or cobalt) and nickel-cobalt composite hydrous oxides were prepared by cathodic (galvanostatic) electrodeposition\textsuperscript{2,6} from solutions of the corresponding metal nitrates on a solid graphite electrode. After deposition, the films were rinsed with water and characterized in the spectroelectrochemical cell first by cyclic voltammetry and subsequently by XAFS in deaerated 1.0 M KOH. The cell for \textit{in situ} fluorescence XAFS experiments employed in this study has been described elsewhere.\textsuperscript{7}

\textit{In situ} XAFS measurements for the pure Ni and Ni/Co hydrous oxide films were conducted in the discharged (i.e., reduced) and partially and nominally fully charged (i.e., oxidized) states. For the latter experiments, the potential was first scanned to a value more positive than the onset of oxygen evolution and then reversed to a value sufficiently negative for the current to drop essentially to zero but still positive with respect to the onset of NiOOH reduction. This strategy made it possible to eliminate problems associated with oxygen bubble formation during spectral acquisition. For measurements involving partially oxidized films, the potential was scanned up to a value on the rising part of the Ni(OH)\textsubscript{2} oxidation peak and then reversed to a no-current voltage condition.

All experiments were performed at beam-line IV-2 at the Stanford Synchrotron Research Laboratory. Details regarding these measurements as well as the method employed in the analysis of the EXAFS data have been given in previous work.\textsuperscript{8}

RESULTS AND DISCUSSION

I. ELECTROCHEMISTRY

The cyclic voltammogram of a composite 9:1 Ni/Co hydrous oxide in 1.0 \textit{M} KOH, shown in curve a, Figure 1, displayed characteristic oxidation and reduction peaks associated with the Ni(OH)\textsubscript{2}/NiOOH redox process. In agreement with the observations of Corrigan,\textsuperscript{2} but at variance with those of Cordoba et al.\textsuperscript{4}, the overpotential for oxygen evolution was larger for this composite oxide than for a pure nickel hydrous oxide prepared using the same procedure (see curve b, Figure 1). Also in harmony with earlier data\textsuperscript{4} are the shifts in the Ni(OH)\textsubscript{2}/NiOOH redox features in the negative direction (ca. 50 mV) induced by the presence of Co in the Ni hydrous oxide lattice. As pointed out by Corrigan and Bender,\textsuperscript{2} no voltammetry features associated with the Co(OH)\textsubscript{2}/CoOOH redox couple can be identified for this composite Ni/Co film. This is particularly interesting, as the redox peaks of pure Co hydrous oxide in this same electrolyte occur at a potential of 0.09 V and thus more negative than those observed for a pure Ni film and therefore should be clearly discernable in the voltammogram.

II. XANES

A. Nickel K-edge

The Ni K-edge XANES for the composite Ni/Co hydrous oxide film in the reduced (fully discharged) and oxidized (nominally charged) state recorded at -0.3 and +0.3 V vs. SCE, in 1.0 \textit{M} KOH are shown in Curves a and b, Fig. 2, respectively. These curves are nearly identical to those reported by Pandya et al.\textsuperscript{9} for pure Ni hydrous oxide in 1.0 \textit{M} KOH. Particularly noticeable is the shift in the overall absorption edge region toward higher X-ray energies for the oxidized (Ni\textsuperscript{3+}) film compared to the reduced (Ni\textsuperscript{2+}) film, including the peak at about 8363 eV. As discussed by Pandya et al.\textsuperscript{9} the pre-edge feature at about 8332 eV is ascribed to the 1s \rightarrow 3d electronic transition, for which the intensity is found to be larger.
for the oxidized than for the reduced state. It must be stressed that in both cases this spectral feature is relatively small and therefore consistent with a slightly distorted octahedral environment.

B. Cobalt K-edge

The Co K-edge XANES for the Ni/Co composite film in the oxidized and reduced states are very similar (see Curves a and b, Fig. 3) displaying a very small pre-edge peak. This observation provides strong evidence that the nature of the cobalt sites is not modified by the structural and electronic changes in the lattice associated with redox processes involving the nickel sites. A comparison between these curves and those obtained for pure cobalt hydrous oxide films (prepared using the same electrodeposition method: see curve c in this figure) clearly shows that the cobalt sites in the latter composite hydrous oxide can be assigned to Co$^{3+}$. This is somewhat surprising since Co$^{2+}$ in a pure cobalt hydrous oxide film undergoes oxidation at a potential only slightly more negative than that observed for the Ni(OH)$_2$/NiOOH couple. As is well known, however, the nature of the ligands can profoundly alter the redox potential of the Co$^{3+}$/Co$^{2+}$ couple, e.g., $E^0[Co(NH_2)_6]^{2+/3+} = 0.108$ V, while $E^0[Co(H_2O)_6]^{2+/3+} = 1.83$ V. It can therefore be concluded that the environment of the cobaltic ions in the hydrated nickel oxide lattice is such that the potential required for their reduction is shifted to much more negative values. Such a claim has been made earlier in the literature, although without much substantiation. Additional evidence for the presence of Co$^{3+}$ sites in these composite hydrous oxides was obtained from the in situ Co K-edge EXAFS data (vide infra).

III. EXAFS

A. Nickel K-edge

The Fourier transforms (FTs) (without phase shift correction) of the $k^3\chi(k)$ Ni K-edge EXAFS for the Ni/Co hydrous oxide films in the reduced (-0.30 V vs. SCE) and oxidized (+0.30 V) states (see Curves a and b, Fig. 4, respectively) are very similar to those reported by Pandya et al. for the oxidized and reduced forms of battery-type nickel hydrous oxide electrodes. In accordance with their observations, the Ni-O and Ni-Ni distances within the sheet-like NiO$_2$ layers (1st and 2nd major shells, respectively) were found to be somewhat smaller for the nominally oxidized film, $d$(Ni-O) = 1.92 ± 0.02 Å, $d$(Ni-Ni)$_1 = 2.82 \pm 0.02$ Å, shown in Curve b, Fig. 4, compared to its reduced counterpart, $d$(Ni-O) = 2.09 ± 0.02 Å, $d$(Ni-Ni)$_1 = 3.11 \pm 0.02$ Å. The close similarity between the results obtained for the pure and composite Ni/Co hydrous oxide films indicates that within the sensitivity of this technique, the presence of cobalt at a nominally 10 metal-atom percent does not appear to significantly affect the structure of the nickel hydrous oxide.

Unlike the behavior observed for composite Ni/Fe hydrous oxide films in the nominally fully oxidized state, for which contributions due to Ni$^{2+}$ were invariably observed, the Ni-Ni shell for a fully oxidized 9:1 composite Ni/Co film displayed a single well-defined shell attributed to Ni$^{3+}$ sites. This affords unambiguous evidence that under these conditions the nickel in Ni/Co films can be completely oxidized, leaving no residual Ni$^{2+}$ ions in the lattice.

C. Cobalt K-Edge

A number of interesting conclusions can be drawn from the analysis of the FT of the $k^3\chi(k)$ Co K-edge EXAFS spectra of these composite Ni/Co films (see Figure 5). In particular, the best fit to the Co K-edge EXAFS data yielded a value of $d$(Co-O) = 1.90 ± 0.02 Å and thus, within experimental error, is
identical to d(Co-O) in crystalline CoOOH, i.e., 1.90 Å.\textsuperscript{14} This observation is consistent with the presence of cobaltic sites in the lattice, as proposed on the basis of the XANES data. More noteworthy, however, is the fact that composite Ni/Co films purposely charged only partially (obtained at +0.32 V; see curve c, Figure 5) displayed clearly resolvable Co-Ni shells associated with Co\textsuperscript{3+}-Ni\textsuperscript{2+} and Co\textsuperscript{3+}-Ni\textsuperscript{3+} interactions. These results clearly indicate that the co-electrodeposition procedure generates a single phase, mixed metal hydrous oxide, in which cobaltic ions occupy nickel sites in the NiO\textsubscript{2} sheet-like layers and not two intermixed phases each consisting of a single metal hydrous oxide.

LITERATURE


ACKNOWLEDGEMENTS

This work was supported in part by the Department of Energy through a subcontract from Lawrence Berkeley Laboratory. Additional funding was provided by Eveready Battery Co., Westlake, Ohio.
Fig. 1 Cyclic voltammetry curves for composite 9:1 Ni/Co (curve a) and a pure Ni (curve b) hydrous oxide electrode in deaerated 1.0 M KOH.
Scan rate: 5 mV s⁻¹. Cross sectional electrode area: 0.74 cm².

Fig. 2 Ni K-edge XANES for a composite 9:1 Ni/Co hydrous oxide film in the fully discharged (Curve a) and nominally fully oxidized (Curve b) recorded at -0.3 V and +0.3 V vs SCE, respectively in 1.0 M KOH.
Fig. 3  Co K-edge XANES for a composite 9:1 Ni/Co hydrous oxide film in the oxidized (0.3V) and reduced (-0.3V) states (Curves a and b, respectively). Also shown in this figure are the corresponding spectra for a pure Co hydrous film prepared by the same electrodeposition procedure described in the Experimental Section in the reduced state (Curve c).

Fig. 4  Phase-uncorrected FT for the $k^3$($k$) Ni K-edge EXAFS for 9:1 Ni/Co hydrous oxide films in the reduced (-0.3 V vs SCE, Curve a), and oxidized (+0.30 V, Curve b) states.
Fig. 5 Phase-uncorrected FT for the $k^2\chi(k)$ Co K-edge EXAFS for 9:1 Ni/Co hydrous oxide films in the reduced (Curve a), fully oxidized (Curve b) and partially oxidized (obtained at +0.32 V, Curve c) states. Other conditions are given in the Caption Figure 2.