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X-RAY ABSORPTION SPECTROSCOPY STUDIES OF ELECTROCHEMICALLY DEPOSITED THIN OXIDE FILMS

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ABSTRACT

We have utilized "in situ" X-ray Absorption Fine Structure Spectroscopy to investigate the structure and composition of thin oxide films of nickel and iron that have been prepared by electrodeposition on a graphite substrate from aqueous solutions. The films are generally disordered. Structural information has been obtained from the analysis of the data. We also present initial findings on the local structure of heavy metal ions, e.g. Sr and Ce, incorporated into the electrodeposited nickel oxide films. Our results are of importance in a number of technological applications, among them, batteries, fuel cells, electrochromic and ferroelectric materials, corrosion protection, as well as environmental speciation and remediation.

INTRODUCTION

Radioactive contamination of piping systems and storage tanks generally emanates from radionuclides that have been incorporated into corrosion products and scale deposits that coat the surface of the metal alloys which constitute the materials of construction of the pipes and tanks. Knowledge of both the local structure of the corrosion scales by itself and that of the heavy metal ions that are incorporated into the corrosion scales is essential in developing cost-effective clean-up processes via chemical and electrochemical methods¹. Of particular interest are the corrosion scales on base metals such as Fe, Ni and Cr which are the main constituents of the steels used in nuclear waste storage tanks and piping systems. Corrosion processes are basically electrochemical in nature, and consequently electrochemical deposition is an excellent method to simulate the formation of scale deposits. For example, it is widely accepted that the corrosion film on nickel consists mainly of Ni(OH)₂ in the passive region and NiOOH in the transpassive region². The corrosion films can be well simulated by electrochemical deposition from an aqueous solution containing Ni²⁺ ions. Cathodic deposition results in Ni(OH)₂, while anodic deposition leads to the production of NiOOH³. Incorporation of heavy metal ions into the corrosion scales can occur by any one of the following processes: co-precipitation, lattice substitution into vacancies or interstitial sites, surface adsorption or absorption in pores that ultimately results in the co-deposition of the impurity atom with the oxide film on a surface. In this paper we report the use of X-ray Absorption Fine Structure (XAFS) to obtain structural and electronic information on both the host oxide films of Ni and Fe, as well as the incorporated heavy metal ions, Sr and Ce. The use of high energy x-rays enables the measurements to be carried out "in situ"; i.e., the films can be studied in the presence of solution and under potential control in an appropriately designed spectro-electrochemical cell. As XAFS does not rely on long range order to provide structural information, highly disordered materials (which is often the case for corrosion films) can be studied. The X-ray Absorption Near Edge Structure (XANES) contains valuable information on the oxidation state of the probed atom.

Figure 1: (a) Comparison of the XAFS $\chi(k)$ function for electrodeposited $\alpha\text{-Ni(OH)}_2$ (dotted) and chemically prepared $\beta\text{-Ni(OH)}_2$ (solid), (b) Corresponding Fourier transforms

Figure 2: (a) Comparison of XAFS $\chi(k)$ spectra of nickel oxide thin film formed by anodic deposition and taken through oxidation-reduction cycles, (b) Corresponding Fourier Transform

EXPERIMENTAL DETAILS

The host metal oxide (hydroxide) films were prepared either by cathodic or anodic deposition from aqueous solutions of the metal ion of interest onto a graphite electrode. Thus, $\text{Ni}(\text{OH})_2$ films were prepared by cathodic electrolysis of $\text{Ni}(\text{NO}_3)_2$ solution at constant current similar to that followed by Capehart et al.⁴, NiOOH films were formed by anodic deposition at positive potentials close to oxygen evolution from $\text{Ni}(\text{II})$ sulfate plus acetate solution, as was done by Chen and Noufi³; iron oxide films were prepared by constant potential electrolysis from dilute solutions of $\text{Fe}(\text{II})$ in borate buffer solution⁶. Incorporation of Sr and Ce in nickel oxide films was carried out by co-deposition from a solution containing both Ni^{2+} as well as the impurity ions. A saturated calomel electrode (SCE) was used as reference for the electrochemical experiments. The electrochemical equipment consisted of a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat, a PAR model 179 universal programmer and a Hewlett Packard model 7045 XY recorder. A specially fabricated spectro-electrochemical cell was used for simultaneous electrochemical and "in situ" XAFS measurements.

XAFS measurements were performed at beamlines X-11A, X-10C and X-23A2 of the National Synchrotron Light Source (NSLS) using a Si (111), Si (220) or Si (311) double crystal monochromator, respectively. Care was taken to minimize harmonic contamination. The monochromator was calibrated using appropriate pure metal foils. Measurements were performed either in standard transmission mode or in the fluorescence mode depending on the absorption edge step-height obtained for the various films. Care was taken to minimize thickness effect in transmission measurements and fluorescence distortion in fluorescence measurements. A suitable Z-1 filter was often used in conjunction with a Stern-Heald Soiler slit assembly to minimize the elastic and Compton scattered background components in fluorescence measurements. Alternatively, in some cases a 13-element Ge solid state detector was used. Both "in situ" (in the presence of solution at open circuit or with an applied potential) and "ex situ" (in air) measurements were carried out on the electrodeposited films.

RESULTS AND DISCUSSION

(1) Nickel Oxide Thin Films

$\text{Ni}(\text{OH})_2$ was deposited from a 0.1 M $\text{Ni}(\text{NO}_3)_2$ solution at a constant current density of 8 mA/cm^2 for a period of 5 to 15 minutes. The greenish, adherent deposit was found to be α - $\text{Ni}(\text{OH})_2$ by XAFS analysis. Ni atoms were coordinated to about 6 oxygen first near neighbors at 2.05 Å and to 6 Ni second near neighbors at 3.10 Å. The electrochemically prepared α - $\text{Ni}(\text{OH})_2$ is more disordered than β - $\text{Ni}(\text{OH})_2$ which we prepared chemically. Fig. (1) compares the XAFS $\chi(k)$ function and the corresponding Fourier Transforms (FT) for the two materials. These findings are in good agreement with the results of others⁴.

NiOOH films were prepared by anodic deposition at a constant potential of 1.10 V (vs. SCE) from a solution of 0.05 M NiSO_4 and 0.5 M Na_2SO_4 . The $\chi(k)$ functions and the corresponding FT's are illustrated in Fig. (2). The first shell of the as-deposited film can be fit using two Ni-O bond distances at 1.88 Å and 2.05 Å. In conjunction with findings on reference compounds the former distance can be associated with a Ni^{4+} species and the latter distance with a Ni^{2+} species⁵. The film was further charged in 1M KOH solution to convert more of the Ni^{2+} species to Ni^{4+} . In order to understand the electrochemistry of this system the charged film was discharged at a rate of 1 mA/cm^2 in 1M KOH. The discharged film contained only Ni^{2+} species and Ni atoms are coordinated to a first shell of 6 oxygen atoms at a distance of 2.05 Å. The conversion of Ni^{4+} to Ni^{2+} is evident in the FT, which shows that the FT peaks shift to larger r -values on discharge, as expected for a Ni^{2+} species. This discharged film can be oxidized to

Figure 3: Fe K-edge XANES of
 (a) Anodically deposited film at +0.6 V (SCE)
 (b) Sample (a) cathodically reduced at -1.05 V (SCE)
 (c) Fe foil

Figure 4: Fe K-edge $\chi(k)$ spectra of
 (a) Anodically deposited film at +0.6 V vs. SCE
 (b) Fe foil, taken at ~ 80 K (dotted) and cathodic reduction
 of anodic film at -1.05 V vs. SCE, taken at 298 K (solid)

regain some of the Ni^{2+} by recharging in KOH. Detailed data analysis and other findings such as the self-discharge behavior of anodic films are beyond the scope of this paper and will be published elsewhere⁷.

(2) Iron Oxide Thin Films

The composition and structure of the corrosion films on iron remain a subject of much debate. We report preliminary XAFS measurements performed on anodically deposited iron oxide films. Iron oxide thin films were prepared following the procedure of Markovac and Cohen⁵ using dilute solutions of Fe^{2+} in a borate buffer. Anodic deposition was carried out from a deaerated solution of 0.005 M FeSO_4 + 0.3 M H_3BO_3 + 0.075 M $\text{Na}_2\text{B}_4\text{O}_7$ borate buffer solution by holding the potential at 0.6 V (vs. SCE) for 8 hours and 10 minutes. The XANES spectrum of the film formed is shown in Fig. (3a). This film was subsequently reduced at -1.05 V (vs. SCE) and the spectrum shown in Fig. (3b) was obtained. The spectrum of bcc Fe foil is shown in Fig. (3c) for comparison. It is evident that a part of the film has been converted to bcc Fe. This can be seen more clearly in the Fig. (4), which shows the XAFS $\chi(k)$ spectra of the anodic film, the reduced film and bcc Fe foil. The $\chi(k)$ function of the anodic film diminishes very rapidly in intensity with increasing k . This indicates that the anodic film is very disordered. Preliminary fits to the data suggest that the anodic film is some form of FeOOH . More detailed experimentation and data analysis is required to elucidate the exact structure of the anodic film. The XAFS spectrum of the reduced film is distinctly different from the as-deposited anodic film. The reduced film shows spectral features that are similar to bcc Fe in the high- k region. However, the low- k region is distinctly different from bcc Fe. This difference in the low- k region indicates that some form of oxide is also present in the reduced film. Oxygen is a good backscatter of low-energy electrons but does not backscatter significantly at high- k . Consequently, the low- k region of the XAFS spectra is different from bcc Fe. Detailed electrochemistry, XAFS data collection and data analysis of the iron oxide films will be reported subsequently.

(3) Incorporation of Strontium in Nickel Oxide Thin Films

Sr was co-deposited with both NiOOH and $\text{Ni}(\text{OH})_2$ from aqueous solutions containing Ni^{2+} ions and 0.005 to 0.1 M strontium acetate. Anodically co-deposited samples were prepared at an applied potential of 1.1 V (vs. SCE) for about 8 hours while the cathodic films were prepared at a constant cathodic current density of 8 mA/cm^2 for about 15 minutes. Fig. (5) shows the Sr XAFS of an anodic film compared with a pure strontium oxide (hydroxide) which was prepared by passage of a constant cathodic current of 8 mA/cm^2 through a solution of 0.1 M strontium acetate. Both measurements were performed "ex situ". The XAFS in both cases look similar and the corresponding FT's show only one distinct peak. This shell can be fit to about 8 to 10 oxygen first near neighbors at 2.62 (2) Å. This distance is similar to the Sr-O bond distance of 2.62 Å found for Sr^{2+} in aqueous solutions⁸. Similarly, cathodically co-deposited samples of Sr and $\text{Ni}(\text{OH})_2$ also show only a single Sr-O first neighbor shell at 2.61 (2) Å. In all cases no intercalation or lattice substitution of Sr^{2+} as manifested by a Sr-Ni bond distance could be detected in the XAFS. Incorporation of Sr^{2+} into $\text{Ni}(\text{OH})_2$ and NiOOH films via electrodeposition appears to occur by a co-precipitation process that results in a separate phase. The absence of Sr-Ni bonds suggests that intercalation or lattice substitution into the nickel oxide lattice is negligible. Furthermore, the absence of higher shell peaks in Sr XAFS shows that the co-precipitated phase is very disordered. More details of the data analysis can be found in reference (7).

Figure 5: (a) Sr K-edge XAFS $\chi(k)$ function in cathodically deposited pure Sr-oxide film (dotted) and Sr anodically co-deposited with NiOOH (solid)
(b) Corresponding Fourier transforms

Figure 6: Ce L_3 - XANES of
(a) CeO_2
(b) Ce(OH)_4
(c) Ce in NiOOH
(d) Pure anodic Ce oxide film

Figure 7: Ce L_3 - XANES of
0.08 M Ce(III) nitrate solution (dotted),
and Ce in Ni(OH)_2 (solid)

(4) Incorporation of Cerium in Nickel Oxide Thin Films

The general shape of the near-edge spectra of Ce at the L_3 -edge is a good fingerprint of the valence state of Ce in its oxides/hydroxides. Ce(III) compounds exhibit an intense white line at the threshold energy while Ce(IV) compounds show a double peak structure. We have studied the incorporation of Ce in both NiOOH and Ni(OH)₂ by co-depositing Ce with the nickel oxides from solutions containing Ce³⁺ and Ni²⁺ ions. Fig. (6c) shows the "in situ" XANES spectrum of Ce incorporated into NiOOH by anodic co-deposition at 1.1 V (vs. SCE) from a solution of 0.05 M NiSO₄ + 0.5 M sodium acetate + 0.04 M cerium (III) acetate for 9 hours. The double peak indicates the presence of Ce⁴⁺ in the film by comparison with the CeO₂ and Ce(OH)₄ standards (Fig. 6a and b, respectively). We could also deposit a pure cerium oxide film by constant potential electrolysis at 1.1 V (vs. SCE) in 0.08 M Ce(III) acetate solution. The XANES of this film shown in Fig. (6d) is quite similar to Ce in NiOOH film. By using laser Raman measurements, x-ray diffraction and XAFS analysis we find that the structure of the anodic films is similar to Ce(OH)₄. We also find that Ce(OH)₄ is not really a hydroxide but rather a disordered form of hydrous cerium oxide. This material has the same medium range structure (~4 Å) as crystalline CeO₂ but has much higher structural disorder. More details can be found in references (7 and 9).

Fig. (7) shows the XANES of Ce in Ni(OH)₂ and that of 0.08 M Ce(III) acetate solution. The co-deposited film was prepared from solution containing 0.01 M Ce(III) acetate solution and 0.1 M Ni(NO₃)₂. The XANES of Ce in the co-deposited film shows a doublet at threshold. The first peak is larger and broader than in Ce(IV) compounds (Fig. 6). This indicates that the Ce in the film is a superposition of Ce³⁺ and Ce⁴⁺ components. This is a surprising result because one expects Ce to be present as Ce³⁺ on cathodic deposition. This can be explained, however, if the Ce³⁺ species cathodically co-deposited with Ni(OH)₂ is easily oxidized by dissolved oxygen. The outer parts of the film, in contact with solution, may have lost contact with the electrode and would then be oxidized to Ce⁴⁺. Further details of this investigation will be published elsewhere^{7,9}.

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