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In Situ XANES Study of the Cathodic Reduction Behavior of the Passive Film on Iron and Artificial Passive Films

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The objective of the present work is to compare the behavior of the passive film on iron with artificial passive films (thin sputter-deposited films of iron oxides on inert substrates). In situ XANES measurements were used to monitor both dissolution and changes in the valence state of passive films on iron during cathodic reduction in borate buffer and in NaOH. Reductive dissolution of the passive film on iron proceeds by a very similar mechanism as has been found for artificial passive films (thin, sputter-deposited films of iron oxides on inert substrates) - i.e. including a conversion step of the passive film to a lower-valent oxide. With low reduction current densities, the dissolution process does not stop when the metal is exposed but can proceed as active metal dissolution. In NaOH, no or very minor material loss takes place during reduction due to the insolubility of Fe(2+) species in the alkaline solution. By potential stepping of a thin film iron sample between reduction and oxidation range of the passive film, a conversion of the whole sample from metallic film into an oxide film can be achieved.

INTRODUCTION

In previous work, in situ x-ray absorption near edge structure (XANES) investigations on the cathodic reduction behavior of "artificial iron passive films" (thin, sputter-deposited iron oxide films of Fe_3O_4 and Fe_2O_3) were carried out (1) . The results showed that the reduction mechanism of Fe_2O_3 depends strongly on the electrolyte. In borate buffer, reduction of Fe_2O_3 proceeds via a two step consecutive reaction (Fe_2O_3 --> Fe_3O_4 --> Fe^{2+}(aq)) and leads to complete dissolution of the oxide film. In an alkaline solution, no dissolution of Fe_2O_3 is found but a reductive a solid state conversion into ferrous hydroxide/oxide takes place.

The objective of the present work, is to compare above findings from artificial passive films with passive films on Fe. Similar to the studies on artificial passive film, in situ XANES measurements were used to monitor both dissolution and changes in the valence state of passive films on iron during cathodic reduction in borate buffer and in NaOH.

EXPERIMENTAL

Thin iron films (100 Å) were evaporated on Mylar (6 μm), onto which a thin layer of Ti ($\approx$ 200 Å) had previously been evaporated to establish a back contact to the samples. The base pressure in the chamber before evaporation was $<10^{-8}$ Torr which was achieved with a titanium sublimation pump.

Thin iron oxide films were prepared by r.f. sputter deposition using a Fe_2O_3 target. Also in this case the films were deposited on a Mylar (6 μm) / Ta ($\approx$200 Å) structure. The r.f. sputtering system has been described elsewhere (2) . Before each deposition, the sputter chamber was evacuated to a pressure of 4 to 7 x 10^{-4} Pa. The deposition was carried out in pure Ar (99.998%). The oxide films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and analytical transmission electron microscopy (TEM). Details of the characterization of the samples are given elsewhere (3) .

The electrochemical cell has been described previously (4, 5) . XANES measurements were carried out *in situ* during the electrochemical treatment of the samples. The electrolyte solutions were continuously deaerated with a stream of Ar bubbles. The potentials were measured and are reported against a saturated mercury sulfate reference electrode (MSE, $\approx$ +0.4 V (SCE)). A platinum wire was used as a counter electrode. The solutions were prepared from reagent grade chemicals and distilled water.

XANES measurements were carried out at Beamline X10C at the National Synchrotron Light Source at Brookhaven National Laboratory. The energy scale was calibrated by taking the peak in the first derivative of a spectrum from an iron foil to be the position of the Fe K edge at 7112 eV. The monochromator energy was periodically checked and was found to be very stable during the measurements. The edge position was defined as the energy value at the half-height of the peak after background subtraction. The edge height was determined at an energy 100 eV above the edge after the background was subtracted out of each spectrum by extrapolating the curve fitted to the signal below the edge. *In situ* measurements on the electrochemically controlled samples were made using fluorescence detection set up with a Canberra 13-element solid-state detector. Further details of the geometry are given in reference (5) .

RESULTS AND DISCUSSION

Measurements in air

Figure 1a) shows normalized reference spectra for an Fe foil and different Fe oxide powder standards. Apart from changes in the shape of the spectra, clearly an increase in the oxidation state leads to a shift of the edge position to more positive energies. In Fig. 1b) normalized spectra for the thin film samples used in this study are shown (evaporated Fe film and sputter-deposited Fe_2O_3 film). The spectra of these thin film samples agree very well with the corresponding reference materials in Fig. 1a.

Borate buffer

DISCLAIMER

Figure 2 shows spectra obtained with Fe after a series of potential steps at open-circuit potential, -1.6 V MSE, +200 mV MSE, and after return to -1.6 V MSE. The spectra were measured after 5 min polarization at each potential. From the spectra, both material loss (drop of edge height) and changes in the valency (shift in the edge position) during an electrochemical experiment can be determined. The edge height (which was determined 100 eV above the edge position) corresponds to the total amount of iron in the sample. During the first potential step to -1.6 V MSE, dissolution of the air-formed oxide film takes place which leads to a drop of the edge height. During the formation of the passive film at +200 mV, no material loss is observed as has been shown previously (6, 7) . This passive film can be dissolved by a subsequent step to -1.6 V as indicated by a drop of edge height. In Fig. 2b) the spectra are normalized after background subtraction to unity edge height, and are shown with an expanded energy scale near to edge position. It is clear that a potential step to -1.6 V leads to reduction of the average valency (negative edge shift), resulting from the removal of the oxidized part of the sample. By polarizing at +200 mV MSE, a passive film is formed, which leads to an increase of the averagy valency of the Fe in the sample (positive edge shift). The changes in the edge position are not very large, due to the fact that compared with signal from the underlying metallic iron the the contribution from the thin passive film is relatively small.

Figure 3 shows the behavior of a thin (20 nm) film of Fe_2O_3 during potential steps in borate buffer. The 1st spectrum measured at -1.6 V MSE was started immediately after stepping to this potential. The time to acquire the spectra of Fig. 3 is 5 min. Due to the thickness of the film (20 nm as compared to $\approx$ 3 nm of the native passive film on Fe), no complete loss of the oxide film takes place during the first measurement. However, after 5 min at -1.6 V MSE, the second spectrum shows that the sample has completely dissolved.

A main drawback of acquiring entire spectra is that the time for collecting one spectrum is in the range of a few minutes. In the case of reductive dissolution experiments of passive films this means that to adequetly follow the thinning of the passive film, these type of experiments can only be performed with a low current density (to allow an acquisition of several spectra during the reduction experiment). This type of experiments was carried out in an earlier XANES study on galvanostatic reduction of the passive film on Fe (8) . A possibility to achieve higher data acquisition rates is to determine the edge height at a single energy above the iron edge and hence the drop in height - due to reductive dissolution of the oxide film - can be monitored as a function of time. Thus, acquisition rates in the range of seconds can be achieved, which allow reduction experiments up to current densities of 50 $\mu A/cm^2$. In a similar way - by fixing the energy at the steepest slope of the edge - qualitative information on chemical modifications of the film can be obtained.

Figure 4 shows the XANES edge height as a function of charge density (4a), the intensity measured at an energy corresponding to the edge position (4b), as well as the corresponding potential/charge curve (4c) during galvanostatic reduction (-10 $\mu A/cm^2$) of Fe passivated for 20 min at +200 mV MSE in borate buffer, pH 8.4. Clearly, the drop of the edge height corresponds to the plateau observed in the potential/charge behavior. After the steep potential drop at the end of the experiment, no further dissolution takes place. A comparison of the spectra measured before and after the reduction show that the edge position of the sample reduced by a step to -1.6 V MSE and after galvanostatic reduction is identical; hence no oxidized iron is present in the sample after galvanostatic reduction.

In earlier work on the galvanostatic reduction of thin Fe_2O_3 films (1) it was found that the reduction proceeds in two stages: The first stage is a consecutive reaction of a solid state conversion of the oxide to a lower valent oxide, followed by dissolution (Fe_2O_3 --> Fe_3O_4 --> Fe^{2+} (aq)); in the second stage, after the conversion of the whole oxide film to the lower valent oxide, this suboxide dissolves with an increased rate. Figure 4a) shows that also in the case of the passive film on Fe the drop of the edge height is accelerated after a short time (see insert in Fig. 4a showing a magnification of the beginning of the reduction). However, the break in the slope occurs at a very low charge density and hence the first stage of reduction is much less significant than in the case of the sputter-deposited Fe_2O_3 film. This can be explained by the fact that the passive film on Fe formed at -200 mV MSE is not a pure Fe_2O_3 film, but contains a remarkable amount of Fe(2+), as has been shown by other authors (7, 9) . Hence, less charge is needed to convert the passive film with a stoichiometry similar to Fe_3O_4.

Figure 4b) shows the intensity measured at a fixed energy in the region of the edge. In the beginning of the reduction, a slight increase of intensity is found (see the insert in Fig. 4b). This can be explained by a shift of the edge position to lower energies, hence this is a strong indication that a conversion of the passive film to a lower valent oxide takes place. The decrease in the intensity after the maximum is due to dissolution, which reduces the measured intensity in the whole energy region. The inserts of Figs. 4a,b show that the acceleration of dissolution (faster drop of the edge height) occurs in the same region of charge density as the drop of intensity due to dissolution in Fig. 4b. Therefore we can conclude that in the beginning of reduction conversion of the passive film to a lower-valent oxide takes place with a slow dissolution rate, and this stage is followed by accelerated dissolution of the lower-valent oxide. Hence, it can be deduced that reductive dissolution proceeds by a very similar mechanism for the native passive film on iron and for artificial passive films.

If the galvanostatic reduction is carried out with a much lower current density, metal dissolution can contribute to the observed material loss. An example of this type of behavior is shown in Figure 5, with galvanostatic reduction density of -0.5 $\mu A/cm^2$. Clearly, the dissolution continues with an increased rate after the potential has reached its final value. With this low current density, the end potential of reduction (Fig. 5b) of the passive film on iron is in the active range of iron dissolution, as shown by the cyclic voltammogram of Fe in borate buffer (Fig. 6). Hence, material loss continues after reductive dissolution of the passive film (Fig. 4a). The XANES data indicate that this is due to active dissolution of the film-free iron surface (edge position corresponds to metallic iron).

0.1 M NaOH

A cyclic voltammogram of Fe in 0.1 M NaOH (scan rate = 10 mV/s) is shown in Fig. 7. It is clear that a distinct oxidative peak (I, at $\approx$ -0.7 V) during anodic cycles and a distinct reductive peak (II, at $\approx$ -1.05 V) during cathodic cycles appear. Both of the peaks increase steadily with each cycle. This in contrast to the cyclic voltammogram in borate buffer (Fig. 6), where a reversible behavior of film oxidation and reduction was found. It has been shown in previous work by a LASER absorption technique that no or only very minor dissolution of the iron passive film takes place during reduction in an alkaline solution (10).

To elucidate this behavior further, in situ XANES measurements were performed with a thin film Fe sample. In order to keep the experiments within a reasonable time frame, in XANES experiments potential steps were used instead of potential cycling. I.e., a cycle in the XANES experiments is defined as: a potential step to -1.6 V for 5 min. followed by a step to -0.2 V MSE. Spectra were acquired after 5 min at the corresponding potential.

Figure 8 shows the spectra taken at open circuit potential after immersion into the electrolyte, and the spectra taken after 6, 9, 12, and 15 cycles (potential step sequences). From the almost constant edge height in Fig. 8a it is evident that during potential stepping only a minor amount of material is lost. Figs. 8b and 8c show the region of the main edge for the measurements at -1.6 V (Fig. 8b) and 0.2 V (Fig. 8c) with an expanded energy scale. From Fig. 8c it can be seen that with an increasing number of cathodic/anodic potential steps, the position of the Fe edge is shifted to higher energies. Since the XANES spectra are a sum of the signal of the metallic Fe film (original thickness 100Å) and the passive film, this indicates that with continuous potential stepping an increasing amount of Fe is present as Fe(III), i.e. a successive conversion of Fe(0) to an Fe(III)-film is obtained. At -1.6 V (Fig. 8b), a shift can also be observed but it is less distinct because the Fe(II) edge position is closer to Fe(0) - but from the shape of the main edge peak the conversion from a metallic to an oxide response is apparent. The results indicate that after 15 cycles most of the original 100 Å Fe is converted to an oxide.

After the 15 cycles the sample was studied while stepping the potenial incrementally from -1.6V in the anodic direction or from 0.2V in the cathodic direction, respectively. Fig. 9a shows the spectra starting from -1.6 V, i.e. all Fe is present as Fe(II), during anodic steps (+100 mV / 10 min). Clearly, a significant shift of the edge position to more positive values takes place at -1.1 V MSE (≈-0.7 V SCE), which is in very good agreement with the oxidation peak in the CV. In Fig. 9b the Fe edge is shown now starting from -200 mV after 15 cycles, i.e. in this case the whole Fe film is converted into an Fe(III) oxide, during cathodic potential steps. The significant edge shift now takes place at a potential of -1.4 V MSE (≈-1.0 V SCE), which is again in very good agreement with the cathodic reduction peak in the CV.

Fig. 10 shows as a comparison the behavior of a sputter-deposited Fe_2O_3 film during galvanostatic reduction in 0.1 M NaOH. The constant edge height indicates that no reductive dissolution takes place. A strong peak shift towards lower energies indicates a conversion into an Fe(II) film. The total edge shift during the experiment is 3.4 eV, which is similar to the shift in the experiment on pure Fe after converting the Fe metal film into an oxide film (Figs. 9a,b). This further confirms that the Fe film had been converted almost completely into an oxide film by potential cycling.

CONCLUSIONS

1. Reductive dissolution of the passive film on iron proceeds by a very similar mechanism as has been found for artificial passive films (thin, sputter-deposited films of iron oxides on inert substrates).
2. In borate buffer, in the beginning of reduction, conversion of the passive film to a lower-valent oxide takes place with a slow dissolution rate, and this stage is followed by accelerated dissolution of the lower-valent oxide leading to a complete dissolution of

the passive film. With low current densities, metal dissolution can contribute to mnaterial loss, if the end potential of reduction lies in the active dissolution range of iron.

3. In NaOH, no or very minor material loss takes place during reduction due to the insolubility of Fe(2+) species in the alkaline solution. By potential cycling a thick oxide layer can be grown which is electrochemically active - i.e. during a potential cycle the red-ox reactions Fe(II) --> Fe (III) and Fe(III) --> Fe (II) take place over the entire layer.

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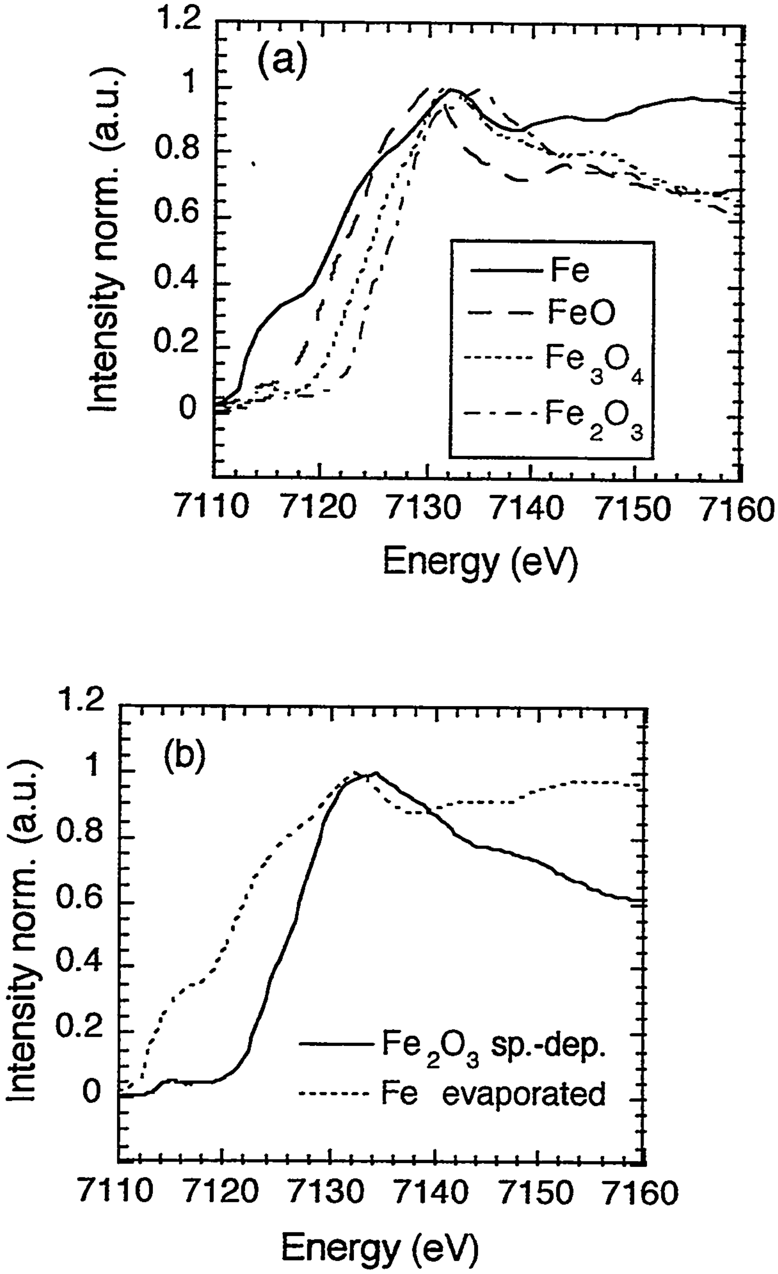

Fig. 1 Normalized reference XANES spectra measured in air
a) Fe foil and Fe oxide powder standards
b) evaporated 100 Å Fe film and sputter-deposited 20 nm Fe_2O_3 film

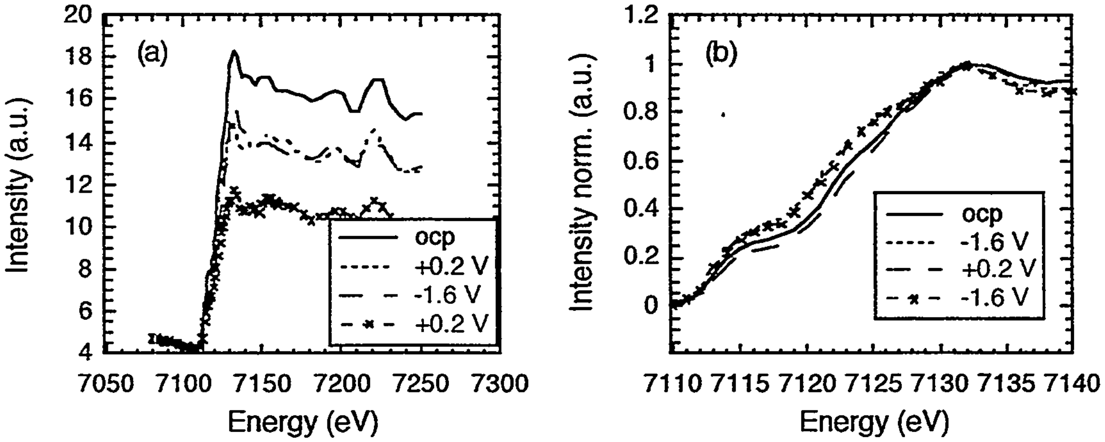

Fig. 2 XANES spectra of an Fe foil in borate buffer, pH 8.4. Measurements were taken after 5 min at the potential shown in the Fig.
a) raw data
b) normalized data

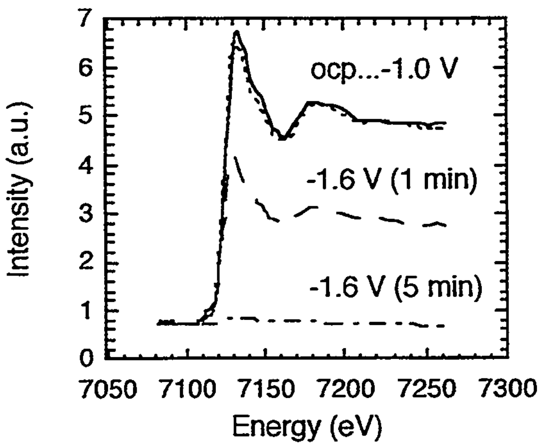

Fig. 3 XANES spectra of sputter-deposited film of Fe_2O_3 (20 nm) during cathodic potential steps in borate buffer, pH 8.4.

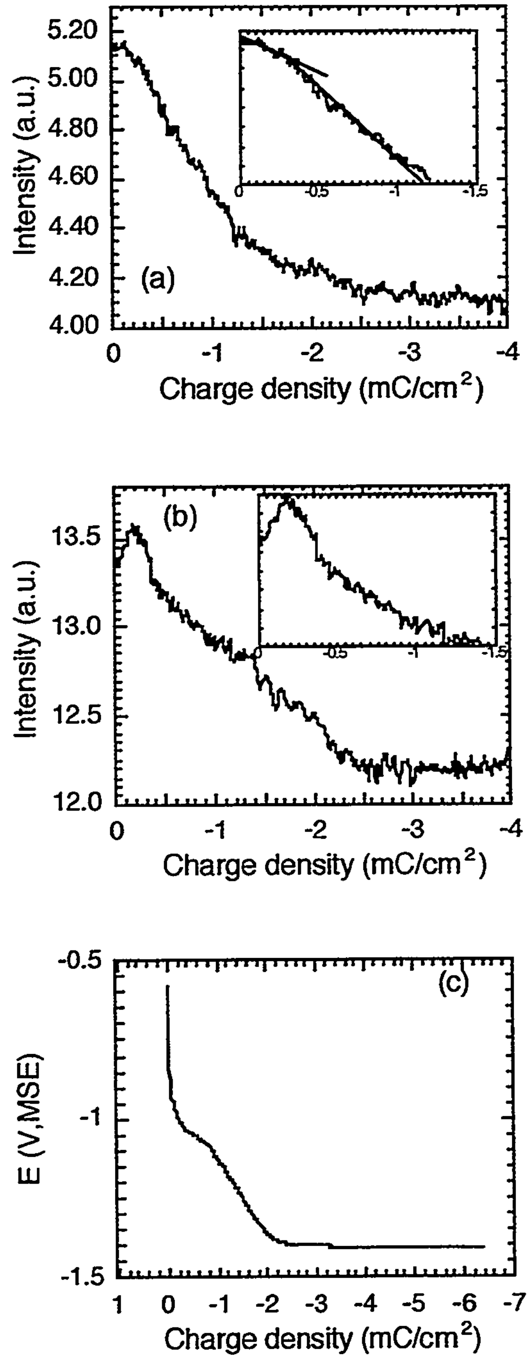

Fig. 4 Galvanostatic reduction with -10 μA/cm^2 of Fe passivated at +200 mV MSE in borate buffer, pH 8.4. Insert in Figs. 4a,b show the data between 0...-0.7 mC/cm^2

a) Intensity corresponding to the edge height (at 7250 eV)

b) Intensity corresponding to the edge position (at 7124 eV)

c) Potential decay

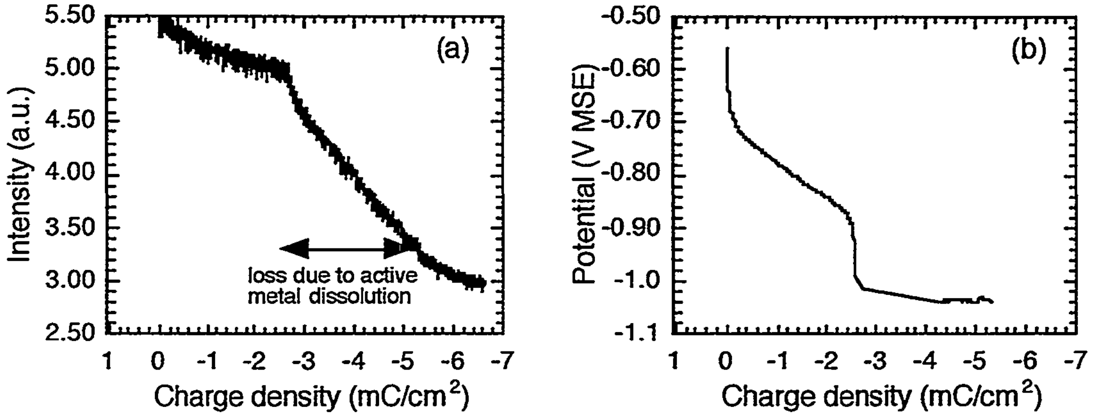

Fig. 5 Galvanostatic reduction of Fe passivated at +200 mV MSE with -0.5 μA/cm^2 in borate buffer, pH 8.4

a) Intensity corresponding to the edge height (at 7250 eV)

c) Potential decay

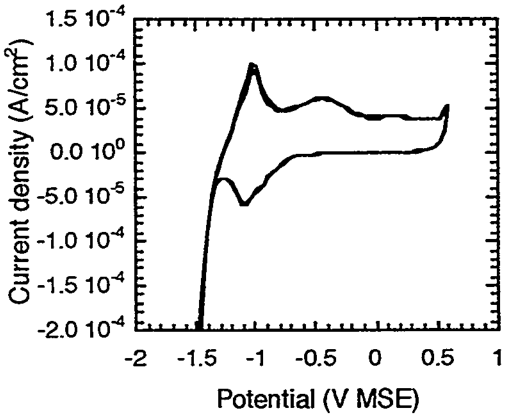

Fig. 6 Cyclic voltammograms for Fe in borate buffer (10 mV / s)

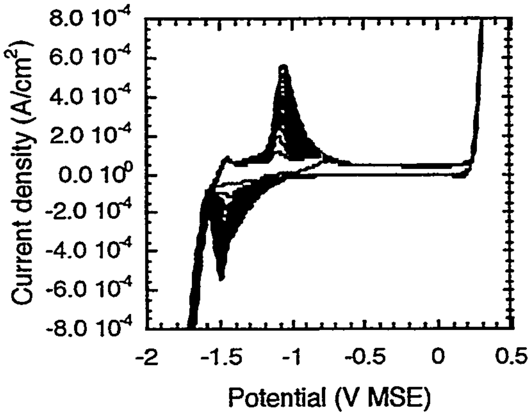

Fig. 7 Cyclic voltammograms for Fe in 0.1 M NaOH (10 mV / s)

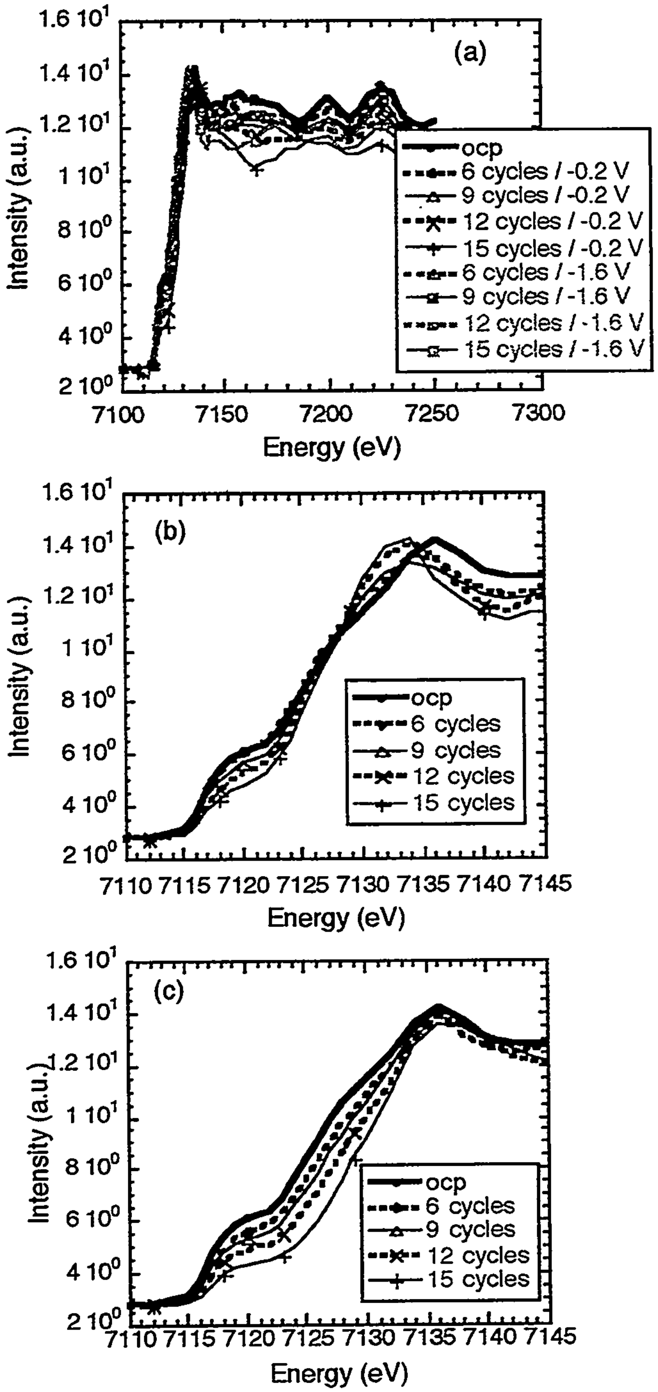

Fig. 8 XANES spectra of Fe in 0.1 M NaOH measured after potential stepping between -0.2 V and -1.6 V MSE
a) all measurements
b) measurements at -1.6 V MSE
c) measurements at -0.2 V MSE

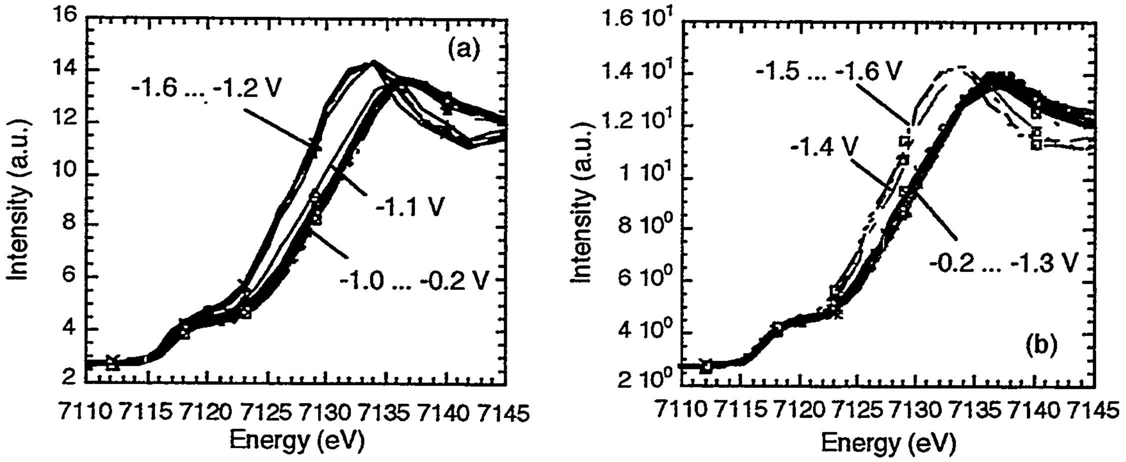

Fig. 9 XANES spectra of Fe film converted into oxide by potential stepping in 0.1 M NaOH according to Fig. 8a
a) during anodic potential stepping starting from -1.6 V MSE
b) during cathodic potential stepping starting from -0.2 V MSE

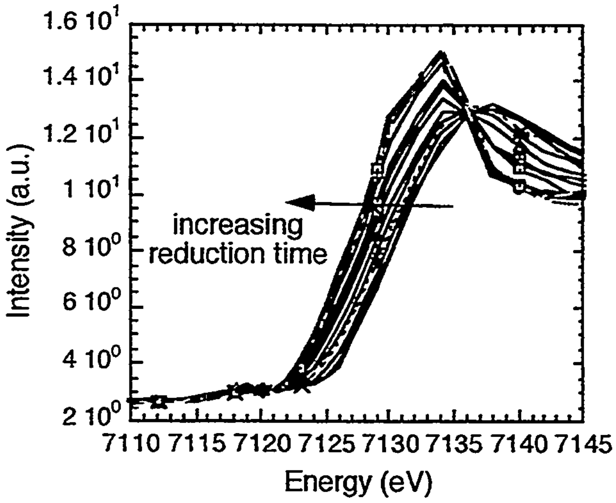

Fig. 10 XANES spectra of a sputter-deposited film of Fe_2O_3 in 0.1 M NaOH during galvanostatic reduction (-10 μA/cm^2)