Electrochemical Reaction of Aqueous Iron Sulfate Solutions Studied by Fe L-Edge Soft X-ray Absorption Spectroscopy

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ABSTRACT: Change in valence of Fe ions in aqueous iron sulfate solutions at different potentials has been studied by Fe L-edge soft X-ray absorption spectroscopy (XAS) in transmission mode. Each XAS spectrum is measured at a constant potential by using a liquid cell with built-in electrodes. A nonlinear oxidation of Fe(II) ions to Fe(III) ions is observed when the potential is increased from 0.0 to 0.9 V. Two processes are found in the oxidation: one is a simple oxidation process and the other is a process involving the sulfate ions. The potential peak in the latter process is changed with different scanning rates because the sulfate ions affect electrode kinetic parameters and diffusion coefficients. The reduction of Fe(III) ions to Fe(II) ions shows a linear profile when the potential is decreased from 0.9 to −0.4 V. The mechanism of these Fe redox processes is discussed by correlating the XAS results with cyclic voltammetry results at different scanning rates.

1. INTRODUCTION

To get a better understanding of electrochemistry, it is necessary to know structures of electrolytes including electric double layers at different potentials. The structures of electric double layers were mainly studied by using electrolyte molecules adsorbed on single-crystal electrode surfaces under vacuum. For example, the structural changes of surface adsorbates at different potentials were studied by X-ray photoelectron spectroscopy.1 The surface distributions of adsorbates were investigated by scanning tunneling microscopy2 and atomic force microscopy.3 However, the structures of surface adsorbates under vacuum are different from those under atmospheric conditions. There is no information on electrolytes in bulk phase. It is important to investigate the structures of electrolyte molecules at solid–liquid interfaces of electrodes under realistic conditions.

The structures of solvent water molecules at different potentials were determined from OH stretching mode in Fourier transform infrared spectroscopy.4,5 The adsorption structures of water molecules were studied by methods focusing on solid–liquid interfaces, such as sum frequency generation,6 surface-enhanced Raman,7 and surface-enhanced infrared spectroscopy.8 The orientation of water molecules at the first layers of Ag(111) electrodes was revealed to be changed at different potentials in 0.1 M NaF by X-ray scattering. The distributions of electrodeposited nanoparticles on electrode surfaces were observed by transmission electron microscopy.9 The structures of electrolyte molecules at solid–liquid interfaces of electrodes have been studied extensively by several methods, but there are few studies by direct measurement of the change in valence and structure with element-specific spectroscopy. It is also difficult to investigate the structure of electrolytic solutes in dilute electrolyte solutions.

X-ray absorption spectroscopy (XAS) is a powerful tool to study local electronic structures and is applicable to liquids. The element-specific spectra of solutes can be observed even in dilute solutions. Nakai et al. developed a liquid cell for XAS of electrolyte solutions and revealed dynamic changes of Mn ions in solution by measuring Mn K-edge XAS.11 Endo et al. studied adsorption structures of Br ions on Ag(100) surfaces at different potentials in aqueous NaBr solutions by measuring Br K-edge XAS.12 The structures of electrodeposited Ni–B films were investigated by Ni K-edge XAS.13 Wu et al. used Cu K-edge XAS to investigate the effect of different anions on the structure of underpotential deposition of Cu on Au.14,15 All of those measurements were performed in the hard X-ray region, in which XAS spectra are easily measured in transmission or fluorescence mode due to the high transmittance of hard X-rays. However, XAS in the hard X-ray region is not applicable to electrolytes including chemically important elements such as C, N, and O. It is necessary to probe these electrolytes during electrochemical reaction.

The soft X-ray region below ~2 keV has many chemically important absorption edges such as C, N, and O K-edges. Recently, the structure of liquid water has been extensively studied by O K-edge XAS.16–18 Because the X-ray absorption...
process occurs within several femto seconds, XAS is able to investigate hydrogen-bonding networks in liquid water before reconstruction of the networks. XAS spectra of liquid samples can be measured by different methods from transmission mode:20 fluorescence yield,17 nonresonant Raman technique,18 total electron yield of liquid microjet,16 and inverse partial fluorescence yield of liquid microjet.21−24 Comparison with the transmission spectra is discussed as regards background subtraction, normalization, and saturation-correction. Note that XAS in bulk liquid phase measured by nonresonant Raman and inverse partial fluorescence yields is nearly the same as XAS in transmission mode. Because soft X-rays at the O K-edge are strongly absorbed by water itself in XAS measured in transmission mode, it is necessary to keep the thickness of the liquid layer below a few micrometers.25 Therefore, it is difficult to measure XAS of liquid samples in transmission mode. It has not been applied previously to XAS studies of electrochemical reactions of electrolytes.

Recently, we have developed a liquid cell for XAS in transmission mode.19 The liquid layer is sandwiched between two Si3N4 membranes and is kept at atmospheric pressure. The liquid sample is under realistic conditions. The thickness of the liquid layer is controllable between 20 and 2000 nm. We have studied the hydration structure of different cations in aqueous salt solutions by the O K-edge XAS and the local structure of methanol−water binary solutions at different mixing ratios by the C and O K-edge XAS. This liquid cell is also able to measure XAS of solid−liquid interfaces by depositing a solid substrate on the membrane and adjusting the thickness of the liquid layer as small as possible (<20 nm).

In the present work, we have developed an in situ XAS measurement system to study electrochemical reactions of electrolytes under realistic conditions by using a liquid cell with built-in electrodes. Change in valence of Fe ions in an aqueous iron sulfate solution at different potentials is investigated by Fe L-edge XAS spectra. The redox reaction of Fe ions is one of the most common electrochemical systems because of their importance in a variety of fields. Previously, Fe redox reactions were mainly studied by voltammetric methods,26−35 but it is difficult to know the change in valence of Fe ions at different potentials in dilute electrolyte solutions. The Fe L-edge (700 eV) is more sensitive than the Fe K-edge to the 3d valence and spin states of Fe ions.36−43 Here we report direct Fe L-edge XAS measurement of the change in valence of Fe ions induced by variation of the potential at a gold electrode.

2. EXPERIMENTAL METHODS

The experiments were performed on the soft X-ray undulator beamline BL3U at the UVSOR-III facility.44 Figure 1a shows schematics of the present liquid cell. As previously described,19 the liquid cell consists of four regions I, II, III, and IV, separated by 100 nm-thick Si3N4 membranes (NTT AT Co.). SiC membranes are used for the N K-edge. Region I is connected to the beamline under vacuum. Regions II and IV are at atmospheric pressure of helium buffer gas. The flow rate of the buffer gas is changeable by a mass flow controller, and the pressure is adjusted by a needle valve at the gas outlet. The thin liquid layer (region III) is sandwiched between two Si3N4 membranes, each with a window size of 2 mm × 2 mm. The liquid layer is under atmospheric conditions. Two 100 μm thick spacers are set between the window frames of the membranes, and the membranes are compressed by sealing o-rings to keep the thin liquid layer below 2000 nm. Liquid samples can be exchanged in situ with a tubing pumping system. The thickness of the liquid layer is controllable between 20 and 2000 nm by changing the He pressure in regions II and IV.19 The absorption of soft X-rays in regions II and IV is small due to the high transmittance of helium.25 The size of the Si3N4 membrane window between regions I and II is 0.2 mm × 0.2 mm, which is small enough to endure a large difference in pressure (>1 atm). The soft X-ray beam size on the sample is determined by orifice. Although the thickness of the liquid layer varies at different positions over the 2 mm × 2 mm membranes, it is possible to measure XAS of the liquid layer at a constant thickness because of the small beam size.19 Soft X-rays, which pass through region II and the liquid layer (region III), are detected by a photodiode (IRD AXUV100) in region IV. The photon energy resolution at the Fe L-edge was set to 0.7 eV. The XAS spectra are obtained from the measured transmission signal, by the Lambert−Beer formula ln(I0/I), in which the current I0 is measured for pure liquid water and the current I is for the liquid sample. The photon energy is calibrated by the O 1s−π* peak (530.80 eV)45 for O2 gas as mixed in a buffer gas with He gas in regions II and IV.

For the investigation of electrochemical reactions, three electrodes are included in the liquid layer (region III), as shown in Figure 1b. In the present work, the electrolyte is 0.5 M aqueous iron sulfate at pH 2.2. The working electrode is a Au
3 RESULTS AND DISCUSSION

3.1 Cyclic Voltammetry. Figure 2 shows cyclic voltammetry (CV) spectra of a 0.5 M aqueous iron sulfate solution measured by using a conventional electrochemical cell. The working, counter, and reference electrodes are Au, Pt, and Ag/AgCl with 3 M NaCl, respectively. The CV spectrum shown in Figure 2a was measured at a scanning rate of 20 mV/s. The oxidation of Fe(II) ions to Fe(III) ions with increasing potential is observed as the peak at 0.70 V. When the potential is decreased, the reduction of Fe(III) ions to Fe(II) ions is observed as the peak at 0.29 V.

Figure 2b shows a CV spectrum measured at a scanning rate of 5 mV/s. The reduction of Fe(III) ions to Fe(II) ions occurs as a single peak at 0.35 V, which is close to that obtained at 20 mV/s. The oxidation of Fe(II) ions to Fe(III) ions shows two peaks, whose positions are 0.57 and 0.72 V. The peak at 0.72 V is close to that obtained at 20 mV/s and is attributed to simple oxidation of Fe(II) to Fe(III). The oxidation process at the low potential involves the sulfate ions, which affect electrode kinetic parameters and diffusion coefficients at high concentration of aqueous iron sulfate solutions. The peak positions are summarized in Table 1.

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Oxidation of Fe(II)</th>
<th>Reduction of Fe(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08 mV/s (XAS)</td>
<td>0.72</td>
<td>0.29</td>
</tr>
<tr>
<td>5 mV/s (CV)</td>
<td>0.72</td>
<td>0.35</td>
</tr>
<tr>
<td>20 mV/s (CV)</td>
<td>0.70</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Oxidation of Fe(II) ions has two processes. One is the simple oxidation (P1) and the other involves the sulfate ions (P2). The reduction of Fe(III) ions is a single process (P1).

3.2 Fe L-edge XAS. Figure 3 shows Fe L-edge XAS spectra of aqueous iron sulfate solutions at different potentials. Each XAS spectrum is measured at a constant potential. The XAS L_3 spectra have signals from both Fe(II) and Fe(III) ions and show an isosbestic point, indicating that only two species are involved.

XAS spectrum is measured at a constant potential. The Fe L-edge XAS spectra were measured by increasing the potential from 0.00 to 0.90 V, as shown in Figure 3a. The XAS measurements continued, while the potential was decreased from 0.90 to −0.40 V, as shown in Figure 3b. The scanning rate of the potential is roughly estimated to be 0.08 mV/s, which is slower than those of the CV measurements. The XAS L_3 spectra have signals from both Fe(II) and Fe(III) ions and show an isosbestic point, indicating that only two species are involved.

Figure 4a shows reference Fe L-edge XAS spectra for Fe(II) and Fe(III) ions in aqueous iron sulfate solutions. The XAS spectrum of Fe(II) ions was measured at no applied potential, whereas that of Fe(III) ions was obtained at an applied potential.
of potential and scanning direction. The uncertainty of the measured fractions is estimated to be within ±0.02. The composition is determined from the curve fitting of the XAS spectra. The amount of Fe(II) ions decreases by oxidation of Fe(II) to Fe(III) with increasing the potential, which consists of two processes, as indicated by the change in slope of the composition curve at 0.7 and 0.4 V. The formation of Fe(II) from Fe(III) with decreasing potential is linear, indicating a single-step reduction of Fe(III) ions. The fraction of Fe(II) ions \( C_{\text{Fe(II)}} \) as a function of potential is fit to a sigmoid profile as

\[
C_{\text{Fe(II)}}(E) = C_{\text{min}} + \frac{C_{\text{max}} - C_{\text{min}}}{1 + \exp\left[\alpha (E - E_0)\right]}
\]

where \( E_0 \) is the central potential and the terms \( C_{\text{min}} \) and \( C_{\text{max}} \) are minimum and maximum fractions of Fe(II) ions in the single process, respectively. The slope of the sigmoid profile is influenced by term \( \alpha \).

Table 1 shows the central potentials of the Fe redox process obtained by the fits to sigmoid profiles, together with the results of the CV spectra at the different scanning rates. The oxidation of Fe(II) ions to Fe(III) ions has two processes which occur at potentials of 0.34 and 0.72 V. The reduction of Fe(III) ions to Fe(II) ions occurs at a potential of 0.29 V. Because each XAS spectrum is obtained at a constant potential, the scanning rate of the potential is quite slow (0.08 mV/s) in the XAS measurements as compared with the CV results (5 and 20 mV/s). As shown in Table 1, the reduction peak of Fe(III) ions obtained by XAS is close to that obtained by the CV spectra. The reduction of Fe(III) ions is a simple process that reaches an equilibrium even at a scanning rate of 20 mV/s. The profile of the reduction is deviated slightly from the sigmoid profile. It might be influenced by the sulfate ions forming some complexes with Fe(III) ions. Two processes are found in the case of oxidation of Fe(II) ions. One is a simple oxidation process of Fe(II) ions to Fe(III). This peak position is 0.72 V at 0.08 mV/s and is close to that observed in the CV spectra, suggesting that the simple oxidation process reaches equilibrium. The peak position of the other oxidation process is 0.34 V at 0.08 mV/s. In the CV spectra, the peak position is 0.57 V at 5 mV/s, and it is not observed at 20 mV/s. The reason why the peak position varies with the scanning rate is that this oxidation process does not reach equilibrium. The rate of this process is dominantly influenced by the sulfate ions, which affect electrode kinetic parameters and diffusion coefficients. The present XAS results on the change in valence of Fe ions at different scanning rates are consistent with the CV results.

4. CONCLUSIONS

The change in valence of Fe ions in aqueous iron sulfate solutions at different potentials under realistic conditions has been investigated by Fe L-edge XAS in transmission mode. Each X-ray absorption spectrum was measured at a constant potential by using a newly developed liquid cell with built-in electrodes. The Fe redox process is investigated by correlating the XAS results with the CV spectra. The scanning rate of the potential used in the XAS study is estimated to be 0.08 mV/s, which is quite slow compared with that of the CV spectra (5 and 20 mV/s). The reduction of Fe(III) ions to Fe(II) ions with decreasing potential is a single process that reaches equilibrium even at a scanning rate of 20 mV/s. The oxidation of Fe(II) ions to Fe(III) ions with increasing potential consists...
of two processes. The process at a high potential is simple oxidation of Fe(II) ions that reaches equilibrium even at a scanning rate of 20 mV/s. The oxidation process at a low potential involves the sulfate ions. The peak positions are dependent on the scanning rate because the rate of this process is dominantly influenced by the sulfate ions, which affect electrode kinetic parameters and diffusion coefficients.27,28,33–35

In the present study, the change in valence of Fe ions at different potentials leads to a drastic change in the XAS spectra. Therefore, the change in valence of Fe ions can be successfully studied by measurements of the XAS spectrum at a constant potential. However with the present method it is difficult to observe small spectral changes in the XAS spectra at different potentials. For such studies it is necessary to measure changes in soft X-ray absorption at a single photon energy while scanning the applied potential. Even a subtle spectral change in the XAS spectrum can be revealed by measurements of the absorption difference with a potential modulation as a function of photon energy. This will enable us to investigate effects of the environment of a target atom and also to determine kinetic parameters in electrochemical reactions at different potential modulation rates. An apparatus to carry out such detailed measurements has been developed and will be used in future experiments.

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**Notes**

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