In Situ Observation of Reductive Deposition of Uranium on an Electrode/Electrolyte Interface by Optical Waveguide Spectroscopy

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We report the first in situ and real-time observation of UV–vis absorption spectra of uranium electrodeposited on indium-tin-oxide (ITO) electrodes by slab optical waveguide (SOWG) spectroscopy. An absorption peak around 670 nm was distinguished after a 30-min holding period at −0.2 V (vs. Ag/AgCl). X-ray absorption near-edge structure spectroscopy confirmed the presence of uranium(IV) in the uranium electrodeposited on the ITO electrode.

Electroreduction of U(VI) has been extensively investigated because dissolved U(VI), once deposited, can be considered a recoverable resource.[1,2] Understanding the kinetics of the reduction and the production of U(IV) on electrode surfaces is important for the application of such a technique. The UV–vis absorption spectra of U(VI) and U(IV) differ, so that UV–vis absorption spectroscopy is helpful in analyzing the reduction of U(VI) in solution.[3] Unfortunately, U(IV) is removed from the solution after the reduction of U(VI), meaning that U(IV) would not be detected by monitoring the solution.

Slab optical waveguide (SOWG) spectroscopy can yield real-time molecular information at solid–liquid interfaces by evanescent waves.[4] SOWG spectroscopy detects in real time based on the adsorption of a monolayer of cytochrome *c* on indium tin oxide (ITO) attached to the SOWG.[5] This suggests that a thin layer of U electrochemically deposited on the electrode would be detected by the system. In this study, we employed SOWG spectroscopy on ITO surfaces to analyze the U deposited on the electrode/electrolyte interface.

Our use of the SOWG system followed methods described earlier.[4,5] The SOWG transmission spectra were detected with a CCD detector (PMA-11, Hamamatsu Photonics, Japan). The surface area of the ITO–SOWG plates covered with the sample solution was approximately 1.0 cm^2, and the cell length for the SOWG transmission spectra was approximately 1.0 cm.

For the electrochemical measurements, the electrode potential was controlled with a potentiostat (BAS 600C). The counter and the reference electrodes were Pt wire and Ag/AgCl, respectively. The ITO electrode was brought in contact with 0.1 M NaCl electrolyte solutions at pH 4.0, and a blank cyclic voltammogram and SOWG spectrum were obtained. Before the electrodeposition of uranium on the ITO electrode, the electrode was kept at a potential of −0.2 V for 240 min for a blank test.

Electrodeposition experiments with $UO_2(NO_3)_2$ were performed for 240 min at a potential of −0.2 V vs. Ag/AgCl. The SOWG spectra were measured at 10-min intervals. To eliminate the background, we subtracted the SOWG spectrum at the resting potential (at 0 min) from all the SOWG spectra measured after exposure to U. An X-ray absorption near-edge structure (XANES) of U electrodeposited on the ITO electrode was recorded after the reduction of U(VI) at −0.2 V for 240 min. The XANES spectra from powdered samples of precipitates of uraninite ($U^{IV}O_2$) and $U^{VI}O_3$ were used as the standards for U(IV) and U(VI), respectively. The spectra were collected at the L_{III}-edge (17166 eV) beam line 27B at the Photon Factory of the High Energy Research Organization (Tsukuba, Japan). To prevent the oxidation of U(IV) to U(VI) during transportation to the Photon Factory, the ITO electrode with its electrodeposited uranium was sealed in a plastic bag that in turn was put into an outer plastic bag containing an oxygen absorbent.

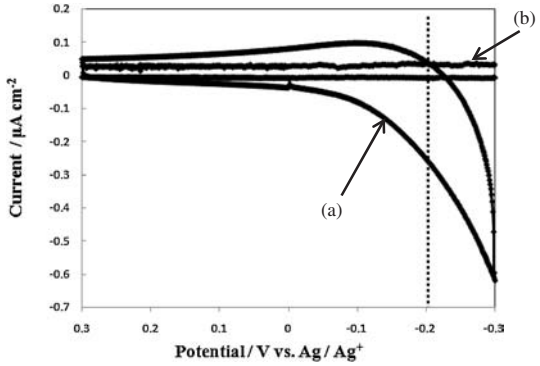

Figure 1. Cyclic voltammograms of 0.1 mM U(VI) (a) and without U(VI) (b) in pH 4.0 solution containing 0.1 M NaCl.

The CV measured after exposing the ITO electrode to 0.1 mM $U^{VI}O_2(NO_3)_2$ in a 0.1 M NaCl electrolyte solution at pH 4.0 (Figure 1a) showed a reduction current of U(VI) at a potential lower than 0 V. The measured current at −0.2 V was approximately 0.25 μA and increased with decreasing potential. Note that no peak was distinguished in the blank CV (Figure 1b) and that no absorption peak was observed in the SOWG spectrum in a 0.1 M NaCl electrolyte solution without U(VI), even though the potential was kept at −0.2 V for 240 min.

The time course of the reduction current at −0.2 V showed that the reduction current was about 0.3 μA at 0 min, sharply decreased up to 1 min, and then decreased gradually to <0.03 μA with increasing time up to 240 min. The time course of the SOWG spectra measured concurrently with the reduction current after exposure of the ITO electrode to the U(VI) solution at the potential of −0.2 V (vs. Ag/AgCl) for 240 min (Figure 2) showed that no distinct peak appeared immediately after exposure (0 min) of the ITO electrode to the U solution. A peak around 670 nm was distinguished at about 30 min. The intensity of the peak increased with the increase in reduction time. The peak wavelength did not shift even with increased exposure time. On the contrary, no distinct absorption was obtained in

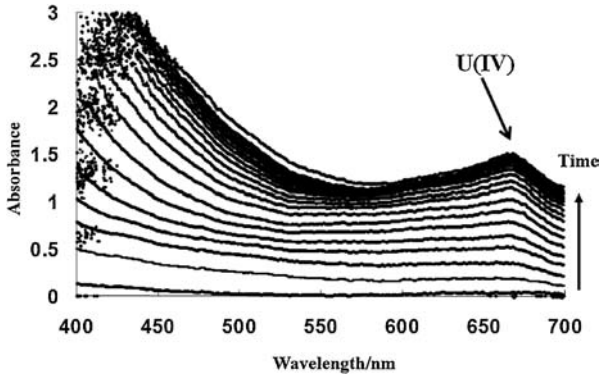

Figure 2. Time course of absorption spectrum of the ITO surface observed by the reduction of U(VI) at a potential of −0.2 V vs. Ag/Ag^+. The spectrum was measured every 10 min from 0 (background) to 240 min.

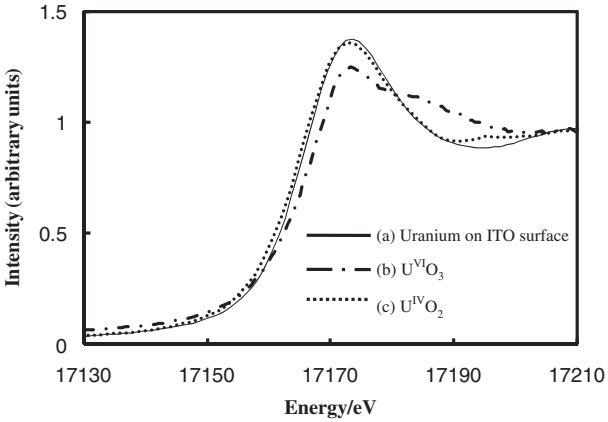

Figure 3. The U-L_{III} XANES spectra of (a) uranium on ITO surface, (b) $U^{VI}O_3$, and (c) $U^{IV}O_2$. The fluorescence intensities of spectra were normalized by the intensities around 17210 eV, and the energy was normalized by the absorption peak of white line.

the SOWG spectrum in a U(VI)-free solution at −0.2 V, indicating that the ITO was unaffected by this action.

The U L_{III}-edge XANES spectrum of the uranium electrodeposited on the ITO electrode at −0.2 V for 240 min (Figure 3) was nearly the same as the U(IV) standard, indicating that the uranium electrodeposited on the ITO electrode was U(IV).[6]

According to the literature concerning reduction of U(VI) measured at pH 4.0, U(VI) is reduced to U(V) and then to U(IV),[2,7] thereby indicating that the current detected at the potential between −0.1 and −0.4 V (Figure 1a) could be assigned to the reduction current of U(VI) to U(V). U(V) then is reduced to U(IV) by disproportionation, as expressed by the following equation:

$$2U^{V}O_2^{+} + 4H^{+} \rightarrow U^{4+} + U^{VI}O_2^{2+} + 2H_2O \qquad (1)$$

U^{4+} is precipitated as $U^{IV}O_2$ under neutral or weakly acidic conditions.[7] The XANES spectrum of the precipitates electrodeposited on the ITO electrode showed the presence of U(IV). These facts indicate the presence of $U^{IV}O_2$ in the precipitates electrodeposited on the ITO electrode after holding the potential at −0.2 V.

Gruen described the UV–vis spectrum from $U^{IV}O_2$ diluted with $Th^{IV}O_2$, derived by reflectance spectroscopy.[8] The spectrum of the $U^{IV}O_2$ alone exhibited an absorption peak around 670 nm and a broad absorption band (absorption edge is around 600 nm) in the UV–vis region. The edge of the broad absorption band in the UV–vis region gradually shifted to a lower wavelength (from 600 to 450 nm), and the intensity of the absorption band became weak with decreasing content of $U^{IV}O_2$ in the mixture of $U^{IV}O_2$ (electron configuration of $5f^2$) and $Th^{IV}O_2$ (electron configuration of $5f^0$), in response to the decrease of the f-electron interaction between U(IV) cores.

In the SOWG spectrum of electrodeposited uranium (Figure 2), an absorption peak appeared at 670 nm, indicating that $U^{IV}O_2$ was contained in the electrodeposited uranium. The edge of the broad absorption peak in the UV–vis region was located around 450–550 nm. The intensity of the absorption gradually became strong with increased reduction time. This change may be caused by the increase of eletrodeposited U(IV).

Xu et al. showed that the uranium electrodeposited on a carbon fiber electrode was U(VI); they could not detect U(IV), even though they reduced uranium at a reduction potential range of −0.45 to −0.9 V.[2] Our results showed that the oxidation state of electrodeposited uranium was IV at a reduction potential of −0.2 V, indicating that the oxidation state of electrodeposited uranium can be controlled by reducing conditions.

These results indicate that SOWG spectroscopy is useful for real-time monitoring of the uranium oxidation state, which is hard to achieve by other methods.

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