In Situ Ru L$_{II}$ and L$_{III}$ Edge X-ray Absorption Near Edge Structure of Electrodeposited Ruthenium Dioxide Films

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The electronic properties of electrodeposited Ru oxide films supported on Au have been examined in situ by Ru L$_{III}$ and L$_{II}$ edge X-ray absorption near edge structure (XANES) in acid media. The results obtained are consistent with the main voltammetric peak centered at 0.7 V vs RHE as being attributed to a redox couple involving formally Ru^{3+} and Ru^{4+} sites in the lattice. A linear correlation was found between the extent of oxidation of the film as derived from a deconvolution of the spectral features and the charge as determined from coulomteric analysis of the voltammetric curves. This observation suggests that only two Ru-based redox states are involved in this electrochemical process.

Introduction

A detailed characterization of electronic and structural changes of ruthenium dioxide (RuO$_x$) induced by changes in the applied potential is expected to provide much needed insight into the rather unique supercapacitive behavior this material displays in acid electrolytes.[1] Analysis of in situ Ru K edge extended X-ray absorption fine structure (EXAFS) collected in our laboratory[2] for electrodeposited RuO$_2$ films on Au was found to be consistent with a sizable increase in the Ru−O bond distance from values characteristic of Ru^{4+} for the material as prepared, to those of Ru^{3+} compounds, as the films were polarized negative to the broad voltammetric peak. Somewhat surprisingly, only subtle differences were observed in the corresponding K edge X-ray absorption near edge structure (XANES) region for Ru in the two oxidation states. As will be shown in this work, similar in situ XANES measurements at the Ru L$_{II}$ and L$_{III}$ edges revealed clearly discernible changes in both the positions and shapes of the white line, which support our initial assignments.[2] A statistical fit of data extracted from these measurements was consistent with the quantitative conversion of a single oxidation state into another over the entire potential region in which the broad voltammetric feature is observed and thus analogous to the behavior found in our laboratory for electrodeposited IrO$_2$ films in aqueous electrolytes.[3]

Experimental Section

Ruthenium dioxide films were electroprecipitated on Au vapor-deposited on Melinex (12.5 × 5.5 mm) by cycling the potential repeatedly between −0.2 and +1.0 V vs SCE at a rate of 20 mV/s in an O$_2$-saturated aqueous solution containing 2.5 mM RuCl$_3$·xH$_2$O and 0.10 M KNO$_3$, in the same cell in which in situ fluorescence X-ray absorption fine structure (XAFS) measurements were performed.[2] This film growth strategy is very similar to that described recently by Hu and

Huang,[4] who used instead a heated Ru chloride aqueous bath at a pH of 1.96. After the deposition had been completed, the films were rinsed thoroughly with pure water to remove traces of solution phase species, and the cell was then filled with 0.50 M H$_2$SO$_4$ for the spectroelectrochemical measurements. Coulometric analysis yielded film charge densities of ca. 1 mC/cm^2, which are equivalent to ca. 1.4 g of RuO$_2$/cm^2.

In situ XAFS spectra were acquired at beamline 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) operating at ring currents in the range 50−100 mA. A set of Si(111) crystals was used to monochromatize the beam, with the entire beam path purged with He. X-ray absorption spectra over the XANES and EXAFS regions were collected in the fluorescence mode, the cell being mounted in a He-purged sample chamber with the electrode placed at an angle of 45° with respect to an N$_2$-purged Lytle detector. The energy was calibrated using the first inflection point of the L$_{III}$ edge region of a metallic Ru foil, recorded also in fluorescence (Ru L$_{III}$ edge = 2838 eV). The X-ray energy was scanned in increments of 0.1 eV in the energy range ±10 eV of Ru L$_{III}$ and L$_{II}$ edges, and in 1 eV increments in the rest of the scanned range. With a 1 mm slit width, the instrumental energy resolution at 2800 eV is estimated to be 0.6 eV, which is approximately 3.5 times smaller than the natural widths of 2.00 and 2.23 eV for the Ru L$_{III}$ and L$_{II}$ levels,[5] respectively. Hence, the Ru XANES spectra shown herein are not obviously broadened by the X-ray optics.

Analysis of the spectroscopic data was performed using least squares XANES fit routines available in the WinXAS software package.[6] The white lines were isolated from the primary data by subtracting a smooth baseline using Origin 6.0, which did not correct for weak EXAFS oscillations close to the main peak (see below). As specified in a previous communication,[3] spectral decomposition of the white lines obtained at intermediate potentials was performed using the LC XANES routine of WinXAS, which relies on statistical fitting methods and spectral additivity to determine the composition of a mixture, e.g., A + B, using as input the experimentally recorded white lines of A and B, which are the pure constituent Ru^{3+} and Ru^{4+} sites in the oxide. This allows the extent of conversion of one Ru species into another as the redox reaction progresses to be determined

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TABLE 1: Heights, Positions, Full-Widths at Half-Maximum (fwhm), and Areas of the White Lines Based on the Analysis of the Ru L_{III} and L_{II} Edges of Electrodeposited RuO_2 Films in the Fully Reduced and Fully Oxidized States Recorded in Situ

RuO_2 film[a]	height	position (eV)	left fwhm (eV)	right fwhm (eV)	area
		L_{III} Edge[b]			
reduced (1)	$0.0418 \pm 1E{-}4$	2841.04 ± 0.02	4.24 ± 0.02	4.33 ± 0.02	0.192 ± 0.001
reduced (2)	$0.0278 \pm 2E{-}4$	2841.07 ± 0.02	4.31 ± 0.06	4.58 ± 0.06	0.124 ± 0.001
oxidized (1)	$0.0450 \pm 2E{-}4$	2841.95 ± 0.02	5.27 ± 0.04	5.36 ± 0.04	0.240 ± 0.001
oxidized (2)	$0.0278 \pm 2E{-}4$	2841.94 ± 0.02	5.05 ± 0.06	5.42 ± 0.06	0.148 ± 0.001
		L_{II} Edge[b]			
reduced (1)	$0.0274 \pm 1E{-}4$	2969.53 ± 0.02	3.85 ± 0.03	4.66 ± 0.03	0.124 ± 0.001
reduced (2)	$0.0154 \pm 1E{-}4$	2969.58 ± 0.03	3.80 ± 0.07	4.60 ± 0.07	0.077 ± 0.001
oxidized (1)	$0.0283 \pm 1E{-}4$	2970.27 ± 0.02	4.46 ± 0.05	6.01 ± 0.05	0.136 ± 0.001
oxidized (2)	$0.0174 \pm 1E{-}4$	2970.32 ± 0.03	4.67 ± 0.06	6.11 ± 0.07	0.086 ± 0.001

[a] The notations (1) and (2) refer to spectra recorded before and after the entire series of experiments was completed, respectively. [b] Uncertainties are those determined from the statistical analysis of each spectrum and do not necessarily reflect the actual reproducibility of the parameter measured, which, on the basis of the data presented, appears to be slightly higher.
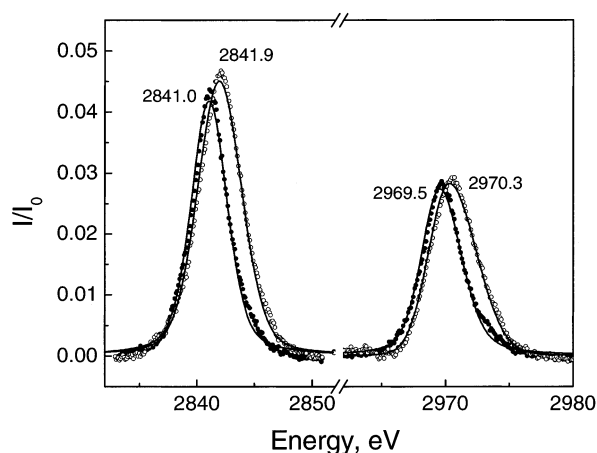

Figure 1. In situ, background-corrected, fluorescence, Ru L_{III} and L_{II} edge XANES of Ru dioxide films recorded at 0.25 V (solid circles) and 1.05 V vs RHE (open circles) in 0.5 M H_2SO_4, and fits using asymmetric pseudo-Voight functions (solid lines).

spectroscopically, and the results are then compared to those derived from coulometric analyses.

Electrochemical data were collected using a Pine RDE3 potentiostat connected to a portable PC equipped with a Keithley DAS-1000 data acquisition system. Measurements were performed in 0.50 M H_2SO_4 using a high-area carbon electrode supplied by ICET as a counter electrode and a reversible hydrogen electrode (RHE) in the same solution as a reference electrode.

Results and Discussion

Shown in Figure 1 are Ru L_{III} and L_{II} edge XANES spectra of RuO_x films at 0.25 (solid circles) and 1.05 V vs RHE (open circles), i.e., in the fully reduced and fully oxidized states (see cyclic voltammogram in the upper panel of Figure 2). The symbols in Figure 1 represent background-corrected experimental data at the two potentials, and the solid lines represent the best fits to the data using asymmetric pseudo-Voight functions. The results of the fits for spectra of the film in the reduced and oxidized state before (denoted as (1)) and after the experiments were completed (denoted as (2)) are compiled in Table 1. Better fits could be obtained by deconvolving the peaks into two Gaussians/Lorentzians with precisely the same peak energies albeit different full widths at half-heights. In view of the uncertainties associated with line shapes, it will be assumed that the peaks observed are consistent with single electronic transitions, associated with the dipole allowed $2p_{1/2} \rightarrow 4d_{3/2}$ (L_{II}) and $2p_{3/2} \rightarrow 4d_{5/2}, 4d_{3/2}$ (L_{III}) transitions,[7,8] or alternatively, final
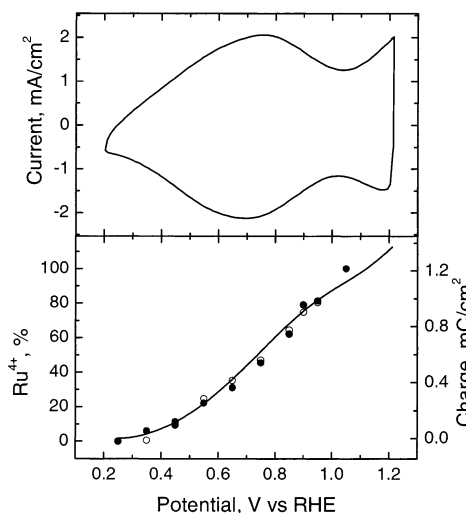
Figure 2. Cyclic voltammetry of RuO_2 films electrodeposited on Au/Melinex electrodes in 0.5 M H_2SO_4 recorded at 20 mV/s in the same cell in which the in situ XANES measurements were performed (upper panel, see text for details). Shown in the lower panel are the percent of Ru^{4+} sites, based on the analysis of the in situ Ru L_{III} (solid circles) and L_{II} (open circles) XANES data (left ordinate), and charge, obtained from coulometric analysis of the data in the upper panel in this figure (solid line, right ordinate).

states denoted as Ru$-$O (π^*, which has mostly Ru d character).[9] This behavior is unlike that found for Ru-containing perovskites, for which the L_{III} edge white line is composed of two peaks split by more than 3 eV,[10] as expected for transitions involving Ru^{4+} and Ru^{5+} sites in an octahedral crystal field. The fact that no crystal field splitting is obvious in our data of Figure 1 may reflect the high electronic conductivity of the RuO_x films, where band structure rather than a crystal field theory formalism is applicable.[11] Alternatively, the splittings for these materials may simply be less than the natural widths of the L_{III} and L_{II} core holes and, therefore, not observable by these measurements. Moreover, electrodeposited RuO_2 films are highly hydrated and amorphous, and their L edge spectral properties are expected to resemble more closely those of RuO_2 powder or vapor deposited films, rather than those of single crystals with multiplet transitions.[12] The structure and properties of electrodeposited RuO_2 films are similar to the well-studied IrO_2 films, which also have L_{III} edge white lines derived from a single electronic transition.[3,11] On this basis, the L_{III} and L_{II} white lines for RuO_2 may be attributed to transitions from 2p orbitals to partially occupied bands at the Fermi level with largely 4d character, and therefore, their intensities provide a measure of the empty density of states (or the number of 4d holes) in those bands.[13,14]

Letters

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Because 4d electrons are involved in the electrochemical reactions of RuO_2 films, the L_{III} and L_{II} edge XANES spectra are expected to be particularly sensitive to changes in redox state.

Indeed, a significant shift in the peak positions of the white-line toward higher energies (ca. 0.9 and 0.8 eV, for the L_{III} and L_{II} edges, respectively; see Figure 1 and Table 1) as well as an increase in the peak area was observed for both the L_{III} and L_{II} edges, between the reduced (0.25 V) and oxidized (1.05 V) forms of the film. These shifts compare very well with those found for Ru perovskites,[10] thereby indicating a change of oxidation state of the Ru sites from +3 to +4 or, equivalently, from a $4d^5$ to a $4d^4$ configuration. These Ru L edge shifts are similar to those found for the Ir L_{III} edge white-line upon oxidation and reduction of IrO_2 films.[3,15,16] Furthermore, a change in the Ru oxidation state from +3 to +4 leads to an increase in the d character empty density of states and, thus, to an increase in the observed intensity of the transition as revealed by the data for the oxidized (with 6 holes) compared to the reduced (with 5 holes) forms of the RuO_x film. In fact, the observed increase of the peak area, of about 22% and 12% for the L_{III} and L_{II} white lines, respectively, is in agreement with the removal of one 4d electron by oxidation of Ru^{3+}.

Additional experiments were performed in which a series of spectra were recorded at intermediate potentials within the range in which the broad voltammetric peak is observed. Each of the L_{III} and L_{II} edge spectra were deconvolved independently in terms of both experimentally observed features, and their fitted functions (not shown here), for the material in the fully reduced and fully oxidized states, i.e., at potentials immediately positive and negative to the main voltammetric peak. Virtually identical results were obtained. This overall approach is particularly advantageous, as it does not rely on the absolute peak intensities, which over long periods of time were found to vary due to changes in the He flow through the low-energy chamber assembly. The normalized spectral contributions due to Ru^{4+} (i.e., the fraction of the XANES response with 100% contribution at the potential of 1.05 V) calculated on the basis of L_{III} and L_{II} edge spectra, are shown as symbols in the lower panel of Figure 2 as a function of potential. These data correlate directly to the charge versus potential curve obtained by integration of the positive scan of the CV in the upper panel in this figure. Plots of the percent of oxidized sites, based on values of the integrated areas of each of the peaks obtained from the spectral fits, versus charge are shown in Figure 3, where different symbols correspond to data extracted from statistical analyses of each of the edges, based on two sets of reference film spectra recorded at the beginning and at the end of the experiments, denoted as (1) and (2) in Table 1, for a total of four sets of data. Excellent linear correlations ($R > 0.99$) were found for all four sets of data, the line shown in Figure 3 being obtained on the basis of all of the data collected.

We conclude that the voltammetric peaks observed in the potential region 0.25 and 1.05 V are consistent with the conversion between two distinct Ru sites in the lattice with different oxidation states and, thus, analogous to that found for IrO_2 in acid media.
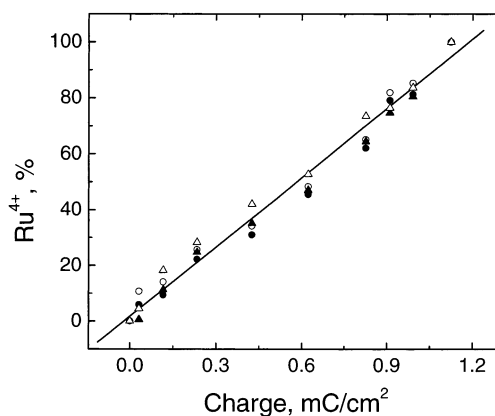
Figure 3. Percent of oxidized sites obtained by deconvolution of L_{III} (circles) and L_{II} edge (triangles) white lines using two sets of reference film spectra recorded at the beginning (solid symbols) and at the end (open symbols) of the experiments. The solid line with slope = 1.2 (± 0.02) and zero intercept represents the best fit to all experimental points.

Supporting Information Available: First and second derivatives of Ru L_{III} and L_{II} edge XANES of RuO_x films recorded at 0.25 and 1.05 V vs RHE in 0.5 M H_2SO_4, and Ru K edge XANES of RuO_x films at 0.40 and 1.20 V in 0.50 M H_2SO_4, with the Ru metal XANES used for calibration. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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