

# IN SITU Ru L<sub>III</sub> AND L<sub>II</sub>-EDGE X-RAY ABSORPTION NEAR EDGE STRUCTURE OF ELECTRODEPOSITED RUTHENIUM DIOXIDE FILMS

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## INTRODUCTION

A detailed characterization of electronic and structural changes induced by changes in the applied potential of ruthenium dioxide is expected to provide much needed insight into the rather unique supercapacitive behavior this material displays in acid electrolytes. Analysis of *in situ* Ru K-edge extended X-ray absorption fine structure EXAFS(1) collected in our laboratory for electrodeposited RuO<sub>2</sub> films on Au was found to be consistent with a sizable decrease in the Ru-O bond distance from values characteristic of Ru(IV) for the material as prepared, to those of Ru(III) compounds as the films were polarized negative to the broad voltammetric peak. Somewhat surprisingly, only very subtle differences were observed in the corresponding 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<sub>II</sub> and L<sub>III</sub> edges revealed clearly discernable changes in both the positions and shapes of the white line, which support our early assignments.

## EXPERIMENTAL

Ruthenium dioxide films were electrodeposited on Au vapor-deposited on Melinex, using the same method employed for the Ru K-edge studies,(1) to a thickness large enough for fluorescence signals to be clearly observed. Immediately thereafter the films were rinsed with water and the cell filled with 0.5 M H<sub>2</sub>SO<sub>4</sub>. The cell was mounted in a He-purged sample chamber, with the electrode placed at an angle of 45° with respect to a He-purged Lytle detector. XANES spectra were acquired in the fluorescence mode, by scanning the X-ray energy in 0.1 eV steps in the edge region at various potentials. Analysis of the data was performed using least-square fit routines available in the WinXAS software package.

## RESULTS AND DISCUSSION

Ru L<sub>III</sub> and L<sub>II</sub>-edge XANES spectra of RuO<sub>2</sub> films at 0.40 and 1.2 V vs RHE (see arrows in the cyclic voltammetry in the inset) are shown in the upper and lower panels, Fig. 1, respectively. The symbols in this figure represent background-corrected experimental data at the two potentials, and the solid lines the best fits to the data using asymmetric pseudo-Voigt functions. As evidenced by the analysis, both the L<sub>III</sub> and L<sub>II</sub> peaks are best fit by a single function, consistent with a single electronic transition, associated with the dipole allowed  $2p_{1/2} \rightarrow 4d_{3/2}$  (L<sub>II</sub>), and  $2p_{1/2} \rightarrow 4d_{5/2}, 4d_{3/2}$  (L<sub>III</sub>) transitions. This behavior is unlike that found for many oxides (perovskites) for which the L<sub>III</sub>-edge white line is composed of two peaks,(3) as expected for transitions involving Ru sites in an octahedral geometry, and reflects the high electronic conductivity of RuO<sub>2</sub> materials, where band structure rather than a crystal field theory formalism is applicable. Moreover, the structure and properties of Ru dioxide are similar to the better studied IrO<sub>2</sub> which also has a L<sub>III</sub>-edge white line derived from a single transition. On this basis, the L<sub>III</sub> and L<sub>II</sub> white lines for RuO<sub>2</sub> may be attributed to transitions from  $2p$  orbitals to partially occupied bands at the Fermi level with large  $4d$  character, and, therefore, their intensities provide a measure of the empty density of states in those bands. Since precisely  $d$  electrons are involved in the electrochemical reactions of RuO<sub>2</sub> films, the L<sub>III</sub> and L<sub>II</sub>-edge XANES spectra will be particularly sensitive to changes in redox state. Indeed,

there is a significant shift in the peak positions of the white-line toward higher energies (ca. 1 eV, and 0.8 eV, for the L<sub>III</sub> and L<sub>II</sub>-edge, respectively) as well as an increase in the peak area, for both the L<sub>III</sub> and L<sub>II</sub> edges, between the reduced (0.4 V) and oxidized forms of the film (1.2 V). These shifts compare very well with those found for Ru perovskites,(3) indicating a change of oxidation state of the Ru sites from +3 to +4 and also for the Ir L<sub>III</sub>-edge white-line upon oxidation or reduction of IrO<sub>2</sub> films.(4) A change in the Ru oxidation state from +3 to +4, or, equivalently, from a  $d^5$  to a  $d^4$  configuration, translates in an increase in the  $d$ -character empty density of states, and, thus, in an increase in the observed intensity of the transition as the data for the oxidized compared to the reduced form of the RuO<sub>2</sub> film. Although probably fortuitous, the observed increase of the peak area, of about 22% and 16% for the L<sub>III</sub> and L<sub>II</sub> white lines, respectively, is in agreement with the removal of one  $d$  electron by oxidation.

In conclusion, electronic information derived from L<sub>III</sub> and L<sub>II</sub> white lines complements and supports structural results obtained from the corresponding K-edge EXAFS.

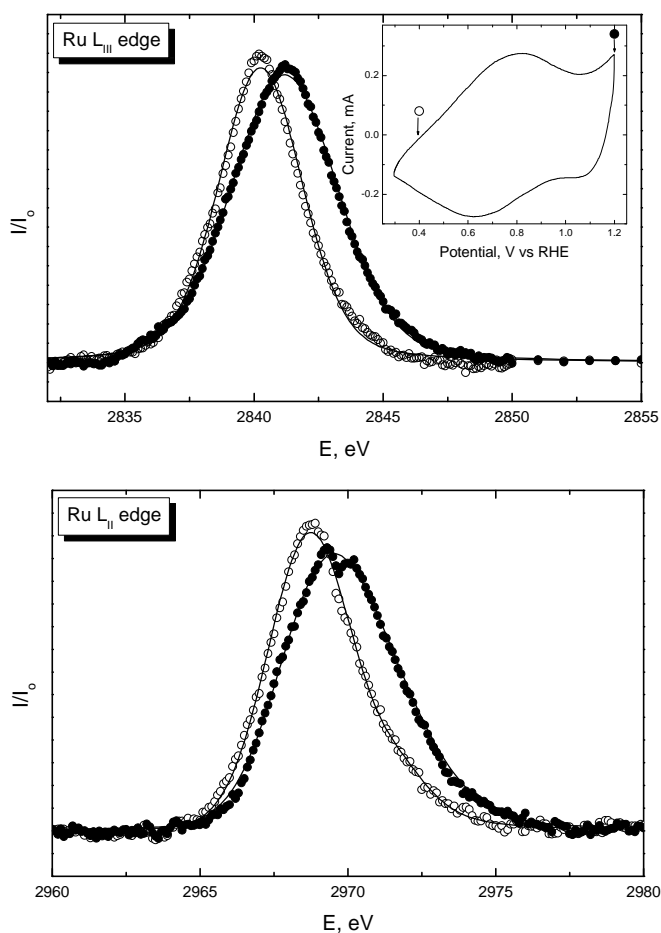


Fig. 1. Background corrected L<sub>III</sub> (upper panel) and L<sub>II</sub>-edge (lower panel) XANES of RuO<sub>2</sub> films at potentials indicated by arrows and the respective symbols on the CV in the inset.

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