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In situ Ru K-edge X-ray absorption spectroscopy of a high-area ruthenium dioxide electrode in a Nafion-based supercapacitor environment

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Abstract Changes in the state of charge of a high-area RuO_x electrode in an operating $\text{RuO}_x|\text{Nafion}|\text{IrO}_x$ supercapacitor were monitored in situ by time-resolved, transmission Ru K-edge X-ray absorption spectroscopy (XAS). Linear and reversible variations in the intensity of the transmitted X-ray beam as a function of time were found by fixing the energy of the incident X-ray beam, E_i , at judiciously selected values within the Ru K-edge X-ray near edge structure (XANES), while the supercapacitor was charged and discharged at constant current. The sign of the slope of these temporal signals was found to vary, depending on the value of E_i . This behavior could be rationalized based on the spectral differences between the Ru K-edge XANES of RuO_x in the fully oxidized and fully reduced states, recorded in situ from films of the material electrodeposited on a gold substrate in the fluorescence mode.

Keywords Ruthenium dioxide · Supercapacitor · X-ray absorption spectroscopy

Dedicated to Prof. Wolf Vielstich on the occasion of his 80th birthday in recognition of his numerous contributions to interfacial electrochemistry

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Introduction

Ruthenium oxide (RuO_x)-based supercapacitors incorporating Nafion-type ionomeric membranes have been shown to display promising characteristics in terms of specific capacities ($0.8\text{--}1.0\text{ F/cm}^2$) and energy densities (ca. 5.5 J/cm^3) [1]. Considerable insight into the nature of the interfacial and bulk processes responsible for the unique properties of highly dispersed RuO_2 was recently gained from in situ fluorescent Ru K-edge X-ray absorption spectroscopy (XAS) of films of this material electrodeposited onto Au in aqueous $0.50\text{ M H}_2\text{SO}_4$ [2, 3]. Based on the results obtained, it was concluded that films in the reduced state contain Ru^{3+} sites in a phase with apparently less order beyond the Ru–O coordination sphere than films in the oxidized state, which contain only Ru^{4+} sites in a hydrous RuO_2 -type environment. Careful inspection of the Ru K-edge X-ray absorption near edge structure (XANES) for the film in the two oxidation states revealed only a very minute change in the slope of the absorption edge, without detectable differences in the energy at the inflection point. This behavior is unlike that found for certain transition metal oxides of the first row, for which changes in the formal oxidation state can lead to shifts in the absorption edge energy as large as $2\text{--}2.5\text{ eV/electron}$ [4, 5].

This paper illustrates the use of transmission Ru K-edge XAS for monitoring in situ changes in the electronic properties of a RuO_x electrode in a judiciously designed $\text{RuO}_x|\text{Nafion}|\text{IrO}_x$ supercapacitor during charge and discharge. Initial efforts were met with unexpected difficulties, as the subtle differences between the spectral properties of RuO_x in its two oxidation states (vide supra) made it virtually impossible to detect reliably any changes in the in situ XANES for the device in the nominally fully charged and fully discharged states. As will be described, far more success was achieved by monitoring the temporal dependence of the intensity of transmitted photons through the

supercapacitor at fixed incident X-ray energies within the Ru K-edge XANES region, while the device was being charged and discharged. This same tactic was employed previously in our laboratory for following, in real time, carbon monoxide electrooxidation adsorbed on Pt dispersed on high-area carbon [6].

Experimental

The $\text{RuO}_x|\text{Nafion}|\text{IrO}_x$ supercapacitor used for in situ transmission Ru K-edge XAS measurements, shown schematically in Fig. 1, comprised a Nafion membrane covered with a layer of high-area RuO_x (5 mg/cm², ICET) on one side, and a layer of high-area IrO_x (ca. 5 mg/cm², ICET) on the other. Although IrO_x is not a practical material for technical supercapacitor applications owing to its high cost, it avoids in this case spectral interferences at the Ru K-edge, derived from a second RuO_x electrode in the beam. Very thin Pt foils, placed away from the central 5 cm² circular area to avoid blocking the incident X-ray beam, were used as current collectors. This assembly was mounted on a Lucite holder designed for Mössbauer effect spectroscopy measurements on an operating fuel cell described elsewhere [7], and then compressed with two additional Lucite plates (not shown in the figure). The total cross-sectional area of the supercapacitor was 11 cm². A PAR-173 potentiostat/galvanostat was used to cycle the device galvanostatically (20 mA/cm² for charging and 10 mA/cm² for discharging), while monitoring the cell potential, defined as $E = E(\text{RuO}_x) - E(\text{IrO}_x)$. No attempt was made to insert a reference electrode into the supercapacitor for measurements of individual electrode potentials. The sign of the current was reversed when the potential reached values in the range $1.0 < E < 1.2$ V during charge, and ca. $-0.1 < E < -0.2$ V during discharge. The X-ray energy was calibrated using the edge inflection point of a Ru foil at 22,117 eV as a reference. Both the supercapacitor voltage during charge/discharge cycles and the intensity of the transmitted X-ray were acquired

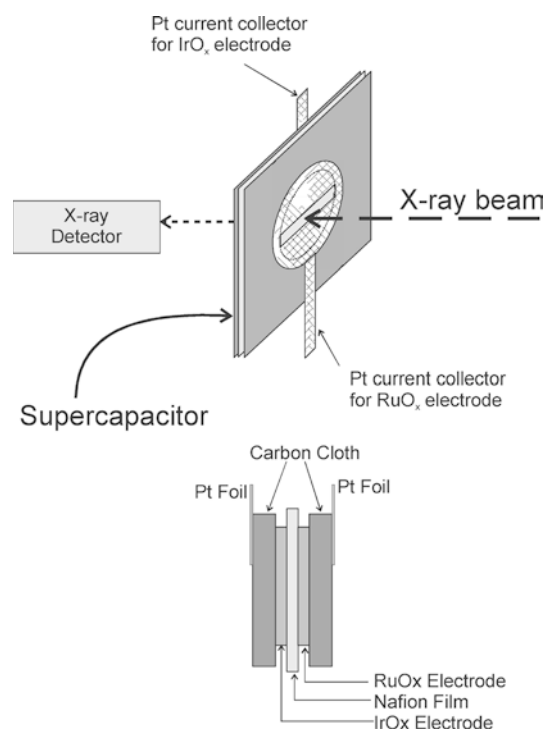


Fig. 1 Schematic diagram of the $\text{RuO}_x|\text{Nafion}|\text{IrO}_x$ supercapacitor for in situ XAS measurements (see text for details)

simultaneously using a home-made data acquisition system controlled by a computer. All XAS measurements 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(220) crystals were used to monochromatize the beam, which measured 1×6 mm² at the sample (see Fig. 1).

Results and discussion

Although the in situ Ru K-edge transmission XANES obtained with the supercapacitor was very well defined (see Fig. 2), no clear differences in the overall edge could be discerned for the device in the nominally fully charged and fully discharged states, suggesting that under these specific experimental conditions the energy shifts may be too small to be reliably measured in independent scans. In particular, careful inspection of numerous spectra recorded in sequence revealed slight and random shifts in the energy of the inflection point, even for measurements performed at a constant state of charge, for which the electrode composition could be regarded as invariant. This behavior was traced to a lack of reproducibility in the absolute position of the stepper motor driven crystals in the monochromator, and thus in the energy of X-ray incident on the specimen. In order to enhance the sensitivity to variations in the intensity of the absorbed beam induced by corresponding changes in the composition of the RuO_x electrode, such as those derived from changes in the oxidation state of Ru sites, the X-ray energy was fixed (by setting the position of the monochromator crystals at a fixed, albeit not accurately known, value), while monitoring the intensity of the transmitted radiation as the supercapacitor was being continuously charged and discharged. Under such conditions the fluctuations in the energy of the incident beam would reflect drifts in the position of the positron trajectory in the storage ring (which would change the angle of incidence of the beam on the monochromator), and therefore may be expected to be quite small.

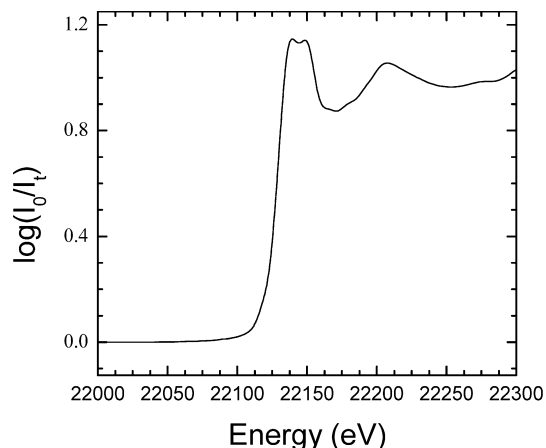


Fig. 2 In situ Ru K-edge transmission XANES obtained with the supercapacitor shown in Fig. 1. No reliable changes in this signal were observed for measurements performed at various states of changes at steady state (see text)

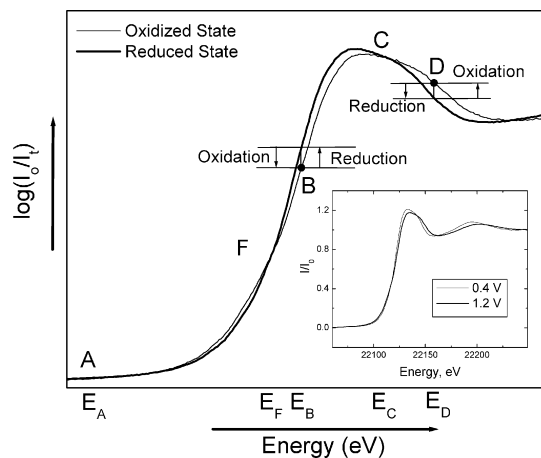


Fig. 3 Schematic diagram of the Ru K-edge XANES spectra obtained in situ for RuO₂ electrodeposited on a Au substrate in the reduced (*thick line*) and oxidized states (*thin line*). Shown in the *insert* are the actual Ru K-edge XANES

The results of such an experiment may be better visualized by considering, without loss of generality, the diagram shown in Fig. 3, which displays in an expanded form the in situ Ru K-edge XANES of a RuO_x film electrodeposited on a Au electrode reported in an earlier work (see insert) [2, 3], where the thick and thin lines correspond to spectra obtained in the fully oxidized and fully reduced states. Differences between the in situ Ru K-edge XANES of RuO₂ (electrode in the fully oxidized) in such films and that of RuO₂ in the supercapacitor electrode may be attributed to corresponding differences in the crystallinity and extent of hydration of the two forms of the material, as illustrated by the work of McKeown et al. [8]. Based on the schematic diagram in Fig. 3, if the X-ray energy E is fixed at points A (E_A), C (E_C), or F (E_F), no changes in the observed signal would be observed as the material is charged (oxidized) or discharged (reduced). Very different results would be expected, however, by setting the monochromator at E_B or E_D . In particular, when the energy is fixed at E_B , the intensity of the transmitted signal I_t would increase during oxidation and then decrease during subsequent reduction, whereas precisely the opposite would be observed at fixed E_D . It becomes evident from these arguments that the highest resolution in I_t to changes in oxidation state would be achieved for energy values at which the differences between the spectra of the two species are most pronounced, e.g. B and D in Fig. 3.

The experimental results obtained with the RuO_x|Nafion|IrO_x supercapacitor were found to be in remarkably good agreement with this model. Shown in Fig. 4 are plots of $\log(I_o/I_t)$ vs. time (see scattered points, right ordinate), where I_o and I_t are the intensities of the beam incident (as measured with a gas ionization detector placed in front) and transmitted through the supercapacitor, respectively, recorded while the device was charged (20 mA/cm²) and discharged (10 mA/cm²) at two values of E_i , i.e. 22,129.7 eV (panel A) and

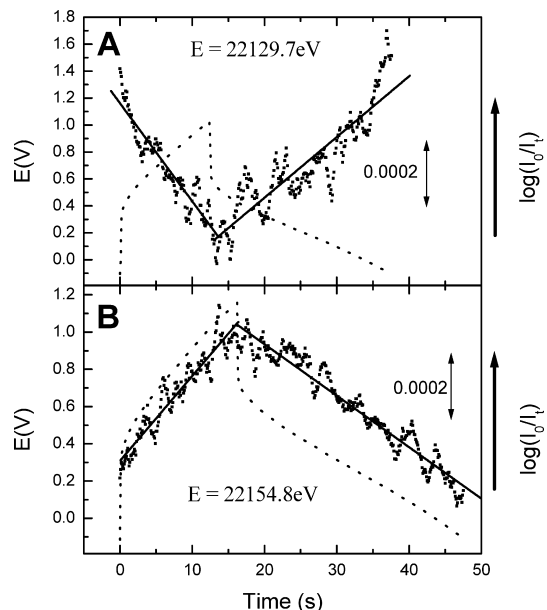


Fig. 4 Cell potential vs. time (*left ordinate, dotted lines*) and Ru K-edge $\log(I_o/I_t)$ versus time profiles recorded simultaneously during one of many charge and discharge cycles of the supercapacitor with the beam energy fixed at (A) $E=22,129.7$ eV (B in Fig. 3) and (B) $E=22,154.8$ eV, i.e. the inflection point of the trailing edge of the main peaks (see text for details)

22,154.8 eV (panel B) and thus very close to the points identified as B and D in Fig. 3. Also given in these figures is the temporal dependence of the measured potential across the capacitor (*left ordinate*). The times involved in the charge and discharge were controlled so as not to exceed the compliance of the electrodes in the device, i.e. the potential across the supercapacitor was never allowed to fall outside the range -0.2 to 1.15 V. It may be noted that polarization of Ru metal in acid media at high enough potentials generates RuO₄, a liquid species at room temperature [9].

In direct accordance with the diagram in Fig. 3, for point B, $\log(I_o/I_t)$ decreases during charge (oxidation) and then increases during discharge (reduction), whereas for point D, precisely the opposite is observed. If the XANES of the material in the fully reduced and oxidized forms are known with certainty and the properties of the electroactive material are assumed to remain unaltered following operation, it would be possible to extract from transient data of the type shown in Fig. 4 quantitative, real-time information regarding film composition. However, problems were encountered while attempting to perform such a more refined analysis. In particular, the total change observed in $\log(I_o/I_t)$ between the charged and discharged states of the capacitor amounts to about 4×10^{-4} and thus much smaller than that expected based on Fig. 3, within the energy range in which the supercapacitor measurements were performed, which are on the order of 0.1. Several factors must be considered in order to explain these gross differences. As was mentioned briefly above, the spectral properties of

RuO_x in the supercapacitor, which was prepared by more conventional means, are somewhat different than those of electrodeposited RuO_x shown in Fig. 3; hence, it is not possible to use with sufficient confidence information derived from such supported films to analyze data obtained with the supercapacitor. In addition, the potential drop observed upon current reversal, i.e. 0.5 V, is directly related to the internal resistance of the device R , i.e. for a change in current of 330 mA ($30 \text{ mA/cm}^2 \times 11.1 \text{ cm}^2$), $R \approx \text{ca. } 1.5 \Omega$. Based on measurements performed on film electrodes, the potential required for nominal full charge of the electrode is about 0.8–0.9 V with respect to its fully discharged counterpart. Because of the iR , the actual voltage applied to the RuO_x electrode may only be half that measured across the entire device, and hence, since the pseudocapacity peak is symmetric about the peak potential, the actual state of charge would also be about half. Also not known with certainty is the extent to which the RuO_x material in the supercapacitor electrode is actually utilized. However, reasonable estimates for two latter factors combined would account for perhaps one order of magnitude, but still insufficient to explain the much large discrepancies observed.

A more likely explanation of these results may be found in problems associated with non-uniform current distribution derived primarily from the need to use a rather thin Lucite plate on the area of the electrode exposed to the beam to decrease attenuation of the X-rays. The fragile nature of this material makes it impossible to exert the required pressure to achieve good contact with the electrolyte along the entire electrode without compromising the mechanical integrity of the device. Some support for this model is afforded by the shape of the

potential versus time scale, which do display RC -type behavior upon current reversal.

Despite these quantitative shortcomings, the results presented in this work illustrate quite conclusively that changes in the state of charge of RuO_x electrodes in a Nafion supercapacitor environment can be monitored using in situ XAS, yielding results in qualitative agreement with those expected based on the behavior found for electrodeposited RuO_x films under more conventional electrochemical conditions. Most importantly, a series of limitations were identified in the performance of the supercapacitor employed, pointing to means for improving its overall design.

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