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Reflection mode XAFS at the Ti K-edge of Lithium Intercalated TiO_2 Electrodes

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Abstract

Lithium intercalation and deintercalation in crystalline TiO_2-electrodes (rutile and anatase modifications) was investigated ex situ using grazing incidence reflection mode X-ray absorption spectroscopy in a specialized cell which permits the removal of the electrolyte and the subsequent measurement of grazing incidence X-ray absorption spectra under a protecting noble gas atmosphere. Small changes observed in near edge X-ray absorption spectra indicated that the Ti^{4+} ions are reduced by the electrochemical lithiation, depending on the TiO_2 modification, $Ti^{3.5+}$ states as well as Ti^{3+} states are observed for rutile and anatase, respectively. Angle dependent experiments reveal that the intercalation is not complete for rutile, while anatase seems to be fully intercalated. In addition, a certain amount of Li remains in the anatase electrode after a complete intercalation – deintercalation cycle. The results suggest that Li-ions are generally accumulated at the electrode/electrolyte interface during both intercalation and deintercalation.

1. Introduction

Rechargeable lithium ion batteries are attractive for their potential use as lightweight, compact energy storage device in applications ranging from portable electronics to vehicles. Therefore lithium ion insertion into metal oxides is one of the main objectives of recent battery research. In this contribution, we will report on ex-situ EXAFS studies of the electrochemical insertion of Li into smooth thin film TiO_2 rutile electrodes. The reversible storage of Li in TiO_2 finds its application in the use as anode material in non-aqueous rechargeable lithium batteries [1, 2]. Based on the change in color from transparent to dark blue when lithium is inserted, electrochromic devices can be realized using lithiated TiO_2 electrodes [3, 4]. In spite of the large number of studies, the origin of the electrochromic effect in Li- inserted TiO_2 remains unclear up to date. Compared to rutile, TiO_2 anatase can accommodate much more Li in its crystal lattice [5–8]. In fact, most of these studies report that hardly any Li inserts into bulk rutile at room temperature [5, 7, 8]. While the originally tetragonal anatase bulk phase undergoes an orthorhombic distortion upon Li insertion resulting in a lithium titanate structure characterised by the *Imma* space-group [9], the structure of Li-intercalated rutile has not yet been investigated in detail.

In this context, grazing incidence X-ray absorption spectroscopy is a well suited technique to obtain structural and electronic information about the electrode surfaces during the intercalation and deintercalation. Unfortunately, the parasitic absorption of the electrolyte is a significant drawback for real in situ studies at energies in the vicinity of the Ti K-edge (4966.4 eV) even if sophisticated detector equipment is employed at 3rd generation synchrotron sources. We therefore designed a new cell, which enables the electrochemical processing of samples which are sensitive towards oxidation by air or humidity. Additionally, it permits grazing incidence X-ray absorption experiments after the controlled emersion of the electrodes from the electrolyte; first results have been published recently [10, 11]. In this contribution, we will address the electrochemical intercalation of Li in two different TiO_2 modifications (rutile and anatase) and compare the observed structures.

2. Experimental

The X-ray absorption experiments were performed at the X-ray undulator beamline BW1 [12] at the DORIS III storage ring at HASYLAB (Hamburg, Germany) operating with 4.45 GeV positrons and injection currents of about 150 mA. The incident monochromatic X-ray beam from a Si(111) double-crystal monochromator with an energy resolution of about 0.9 eV was collimated to a vertical size of about 240 μm and 10 mm horizontally. Incident and reflected intensities were measured by means of argon filled ionization chambers. A second slit system in front of the second ionization chamber suppresses the intensity of non specularly reflected X-rays and shields this detector from the direct beam. All components of the reflectometer, i.e. the sample position, the angle of the detector arm and the slit system can be adjusted by stepper motors. The reflection mode XANES and EXAFS data were collected in the vicinity of the Ti K-edge (4966.4 eV) at ambient temperature. A Ti metal foil was measured in transmission between the second and a third ionization chamber in order to calibrate the energy scale of the monochromator simultaneously with each of the samples. Thin film TiO_2 working electrodes (thickness ≈25 nm, length 40 mm, width ≈25 mm) were prepared by RF sputter deposition on gold covered single crystal quartz substrates. Li intercalation was performed in an electrolyte consisting of 1 M $LiClO_4$ in propylene carbonate (PC). High purity copper wires served both as counter and reference electrodes in a three electrode compartment which is controlled by a potentiostat. Li intercalation and deintercalation was performed under potentiostatic conditions. After the electrochemical treatment, the electrolyte was removed from the samples surface and remaining electrolyte drops were removed by a jet of high purity He prior to the X-ray investigations. Rutile as well as anatase TiO_2, TiO, Ti_2O_3, $Li_4Ti_5O_{12}$ (Li-Ti-spinell) and $Li_{0.6}TiO_2$ samples – the latter with space group *Imma* (nr. 74, [9]) – were investigated in transmission geometry to obtain reference spectra. Further details are given elsewhere [10, 11].

3. Results and Discussion

In Figure 1(a), near edge XANES data determined from reflection mode spectra from a rutile electrode are presented for different

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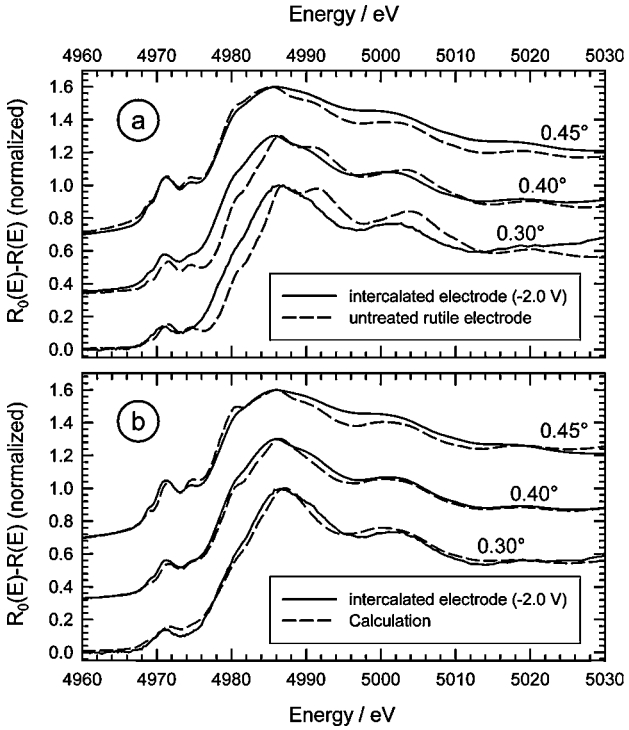

Fig. 1. (a) Comparison of absorption spectra determined as the normalized difference $|R_0(E) - R(E)|$ for the intercalated (-2.0 V for 1 h) and the untreated electrode for several glancing angles. (b) Comparison of the experimental XANES spectra of the intercalated electrode (full lines) to calculations for a multilayered structure (dashed lines) for different grazing angles as indicated. Assumed was a top layer of 5.7 nm $Li_{0.6}TiO_2$ on an underlying rutile TiO_2 layer with a thickness of 20 nm and a 12.5 nm thick gold backing electrode on the quartz substrate. (The spectra are shifted vertically by 0.3 for each angle for a better visualization.)

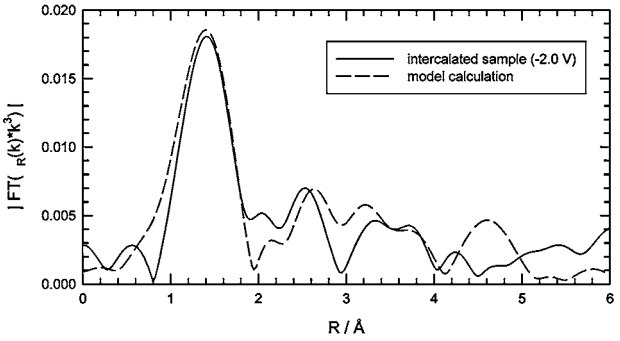

Fig. 2. Comparison of the magnitude of the Fourier- transform of the reflection mode fine structure spectrum of the intercalated rutile electrode ($\Theta = 0.30°$, full line) with that of a model calculation assuming a multilayered structure consisting of 5.7 nm $Li_{0.6}TiO_2$ on 20 nm rutile layer and 12.5 nm gold on the quartz substrate (dashed lines) (Data are not corrected for phase shifts. The k-range for the Fourier-transform is $2.2\,Å^{-1} \leq k \leq 10.2\,Å^{-1}$).

grazing angles. The spectra were calculated as the normalized difference between a linear pre-edge background $R_0(E)$ and the reflection mode XANES spectrum $R(E)$ in order to obtain a measure of the absorption (see ref. [10]). Spectra from the untreated electrode and intercalated rutile (-2.0 V vs. Cu) are shown.

Obviously, distinct differences between both data sets were observed, especially for $\Theta = 0.30°$ and $\Theta = 0.40°$. The most prominent is the shift of the absorption edge from about 4979.4 eV to about 4978.0 eV after the intercalation. The critical angle of total reflection is about 0.42°. Accordingly, the penetration depth of the X-rays amounts to ca. 3–4 nm at 0.30°, 5–10 nm at 0.40° to more than 50 nm at 0.45°. We can therefore conclude that the near surface region of the rutile is modified by the intercalation. The observed edge shift corresponds to a reduction of the rutile Ti^{4+} states to a Ti-valence of ca. 3.6 [10]. Thus a spinell type Li-Ti-O compound such as $Li_2Ti_2O_4$ [9] is very unlikely present due to its Ti^{2+} valence. Furthermore, significant changes can be observed above the edge, for example the double peaked structure in the spectrum of the untreated rutile electrode between ca. 4985 eV and 4992 eV was transformed to a single peak centered at about 4986 eV after the Li insertion. The comparison of the XANES spectra of the intercalated rutile electrode with those of other Li-Ti-oxide reference compounds and Ti-oxides shows that the near edge structures are very similar to those of $Li_{0.6}TiO_2$ [10].

We therefore conducted model calculations, results of which are presented in Fig. 1(b). For these calculations, the complex refractive index $n = 1 - \delta - i * \beta$ was extracted from transmission mode EXAFS spectra of the reference compounds by means of a Kramers-Kronig analysis, and the reflection mode spectra were calculated by applying the Fresnel theory for multilayered systems [13]. For the calculations shown in Fig. 1(b), a $Li_{0.6}TiO_2$ top layer with 5.7 nm thickness (t) on an underlying rutile TiO_2 layer ($t = 20$ nm) and a thin film gold backing electrode ($t = 12.5$) on the quartz substrate (dashed lines) was assumed. As can be seen, a good fit to the experimental data was achieved for all grazing angles. Therefore the structure of the Li intercalated rutile seems to be at least very similar to that of $Li_{0.6}TiO_2$. This is further supported by the results of reflection mode extended X-ray absorption spectra of the intercalated electrode. A typical result is presented in Fig. 2. Here, the Fourier-Transform of the reflectivity fine structure $\chi_R(E)$ extracted from the experimental data is compared to that of a model calculation. It has to be mentioned that similar calculations were performed using multilayered systems with different Li-Ti-O compounds and Ti-oxides such as $Li_2Ti_2O_4$, $Li_4Ti_5O_{12}$, TiO and Ti_2O_3. However, these calculations only fit poorly to the experimental data. Therefore it can be concluded that the structure of the lithiated rutile layer is very similar to that of $Li_{0.6}TiO_2$ (anatase type space group imma, [9]) in which Ti has a valence of 3.5 and Ti is surrounded by 6 nearest neighbour oxygen atoms in a strongly distorted octahedron with bond distances between 1.94 Å and 2.13 Å, and two different Ti-Ti coordination distances at 2.89 Å and 3.13 Å.

A completely different picture was observed for Li intercalation in anatase TiO_2. First of all, the electrochemical intercalation occurs for a significantly smaller negative potential, i.e. the intercalation requires a significantly smaller overpotential compared to Li intercalation in rutile. XANES spectra calculated from reflection mode EXAFS spectra measured after lithiation at -1.6 V (vs. Cu) for 1 h are presented in Fig. 3(a). In this figure, we also show XANES data of the untreated anatase electrode and data measured after a galvanostatic deintercalation (20 min with a current density of about $1\,\mu A/cm^2$).

The dramatic shift of the absorption edge towards smaller energies after the intercalation is evident. We obtained a value of 4976.2 eV compared to 4979.0 eV for the untreated electrode. This value corresponds well to the position of the Ti_2O_3 absorption edge at 4976.0 eV, i.e. the presence of a Ti^{3+} species is very likely after the intercalation. To our best knowledge, Li-Ti-oxide reference compounds with a Ti^{3+} valence have not been reported up to now. Therefore we simply compared the derivative spectrum of the intercalated anatase electrode with that of polycrystalline Ti_2O_3 measured in transmission in Fig. 3(b). The similarity of both derivative spectra is evident: Both derivative spectra show

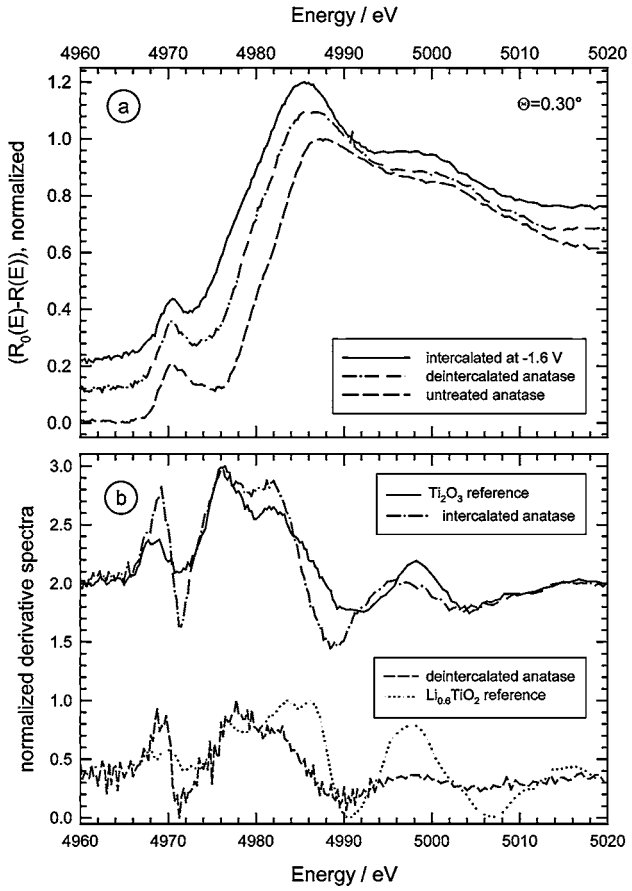

Fig. 3. (a): Normalized difference spectra $(R_0(E) - R(E))$ obtained ex situ from an anatase TiO_2 electrode in 1 M $LiClO_4$ in propylene carbonate for a glancing angle $\Theta = 0.30^\circ$ for untreated anatase, the intercalated and the deintercalated electrode. (b): Comparison of derivative spectra of the intercalated and deintercalated anatase sample with those of reference compounds measured in transmission.

minima and maxima at very similar energies. It should be noted at this point, that the effect of the anomalous dispersion influences the intensities of the peaks derived from the reflection data which might therefore be different [10]. Nevertheless, we can conclude from our measurements that the Ti atoms at the surface of the intercalated anatase electrode have a very similar electronic structure compared to Ti_2O_3 as was proved by preliminary model calculations using a layered structure with a Ti_2O_3 top layer of 4–5 nm thickness.

After deintercalation, an edge position of about 4978.2 eV was found. This energy corresponds well to that of the $Li_{0.6}TiO_2$ reference (4977.6 eV). Also the derivative spectrum of the deintercalated electrode is very similar to that of $Li_{0.6}TiO_2$. Thus the anatase electrode is not completely discharged but some of the intercalated Li remains within the sample. Angle dependent measurements show that the edge shifts to higher values for higher grazing angles, i.e. a larger X-ray penetration depth. Thus it can be concluded that the inserted Li is accumulated at the outer surface towards the electrolyte during deintercalation. The same observation was made for the intercalated material, i.e. the oxidation state seems to increase with increasing distance from the electrode/electrolyte interface. Therefore it can be deduced that only a surface layer of the lithiated material is in the Ti^{3+} state. More detailed model calculations are however necessary to clarify this point.

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