Detailed In Situ Investigation of the Electrochemical Processes in $\text{Li}_2\text{FeTiO}_4$ Cathodes

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The possible mechanism of lithium exchange from $\text{Li}_2\text{FeTiO}_4$ is discussed on the basis of three different in situ structural characterization methods. The in situ X-ray diffraction (XRD) showed that the mechanism of lithium exchange was through a solid solution formation whereby the change in volume during the oxidation was 1.4%. The reversibility in terms of charge recuperation was complete; however, after the first reduction, the change in volume was still 0.4%. In situ Mössbauer spectroscopy experiment showed complete Fe(II) oxidation to Fe(III), while the reduction was not reversible. After the complete first cycle, the number of local environments in the Mössbauer spectra needed for a successful fit increased by at least two. Several local environments can be explained on the basis of extended X-ray absorption fine structure results. In the as-prepared sample, Fe cations are coordinated to three oxygen atoms at 2.03 Å and another three at 2.13 Å. With the oxidation of Fe, the splitting of two oxygen atoms gradually increases to 0.18 Å, and the octahedra deformation gradually changes from 3 + 3 to 4 + 2. This deformation is not reversible and it can explain changes in the long-range order as observed from in situ XRD.

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Lithium-ion batteries are becoming the battery of choice in large-scale applications such as transportation, emergency power, and dispersed electric-power storage concepts.¹ For portable applications, a cobalt-based cathode material is mainly used and needs to be replaced for large-scale applications. The major reasons are the cobalt toxicity and the limited abundance, resulting in the high price of batteries. Large-scale batteries probably have to exploit the cheaper transition metal atoms such as iron or manganese. The discovery of electrochemical activity of LiFePO_4 seems to offer a perfect combination of relatively high capacity,² low cost, and environment-compatible cathode material; certainly, this compound has opened up another field of cathode materials. LiFePO_4 is considered as a polyanionic type of cathode material, where oxygen is covalently bonded in the PO_4 anion, which also makes LiFePO_4 more thermally stable than lithium transition metal oxides. Recently, a group of polyanionic cathode materials have been proposed with structural and electrochemical characterizations of Li_2MSiO_4 materials ($\text{M} = \text{Fe}, \text{Mn}, \text{and Co}$).³⁻⁶ The most attractive feature of silicates is at least a theoretical possibility to exploit more than one electron per transition metal, while other properties are similar as in phosphates. Research on silicates is still in progress, and presently, it is not completely clear if silicates would find application in commercial batteries. This is an additional motivation for a search of other combinations of cathode materials. Replacing the silicon atom with titanium atom leads to another attractive cathode material that is at least theoretically capable of high capacity.⁷ The presence of Ti^{4+} in the structure and its strong bond with O_2 enables the transition metals to be easily oxidized to a higher oxidation state. The cathode materials of the Li_2MTiO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{and Ni}$) family crystallize in a cubic rocksalt structure with considerable cation disorder so they should not be classified as a polyionic type of cathode material. To our knowledge, electrochemical results obtained on Li_2MTiO_4 cathode materials were published in 2004, showing the electrochemical activity of $\text{Li}_2\text{NiTiO}_4$.⁸ Recently, we demonstrated that $\text{Li}_2\text{FeTiO}_4$ and $\text{Li}_2\text{MnTiO}_4$ can deliver considerable capacity if they are prepared within the appropriate range of particle size and material morphology.⁹ In both cases, we observed a monotonous change in the potential implying the solid-solution mechanism of lithium ex-

change. Moreover, we observed the change in the voltage profile in the second and higher cycles compared to the first oxidation, but this voltage drop is not as high as in $\text{Li}_2\text{FeSiO}_4$.¹⁰

Structural changes during lithium exchange and the mechanism of lithium exchange can be easily monitored by in situ X-ray diffraction (XRD) by following the change in crystal cell parameters.¹¹ More information on the changes in the local environment can be obtained by in situ X-ray absorption spectroscopy (XAS)¹² and in situ Mössbauer spectroscopy.¹³ The advantage of in situ XAS measurements lies in monitoring detailed structural changes and electronic properties in the electrode material as the ion extraction/insertion proceeds.¹⁴ This, along with the electrochemical measurements, provides valuable information on the relationship between structure and electronic and electrochemical properties, which is not accessible in an ex situ measurement. In contrast to in situ XRD, which provides a good picture of the long-range structural changes in the active material, XAS provides detailed information on the electronic structure (oxidation state) as well as short-range order around the atoms of a selected type during lithium exchange, which may not be accessible in XRD.¹⁵

In this work, three different in situ characterization methods are used to elucidate the possible mechanism(s) during lithium extraction/insertion in $\text{Li}_2\text{FeTiO}_4$. The mechanism of lithium exchange and voltage profile change after the first oxidation are characterized by in situ XRD characterization that enables detection of long-range order. Changes in the local environment and in the oxidation state are probed by in situ Fe K-edge X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and Mössbauer spectroscopy. The combination of all three in situ methods gives insight into the electrochemical reaction mechanism during lithium exchange.

Experimental

The synthesis of $\text{Li}_2\text{FeTiO}_4/\text{C}$ cathode material is based on a patented citrate precursor method¹⁶ described in our recent publication.⁹ The structural properties of the as-prepared material were determined using PANalytical X'pert PRO MPD powder diffractometer in transmission mode with $\text{Cu K}\alpha_1$ radiation. The X-ray measurements were performed in a capillary (0.3 mm in diameter) to prevent oxidation of the sample. The surface morphology of the prepared composites was checked by a field-emission scanning electron microscope (Supra 35 VP, Carl Zeiss). The morphology of in-

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dividual nanoparticles were examined in a JEM-2010F 200 kV high resolution ($C_s = 0.5$ mm) transmission electron microscope (TEM).

For in situ XRD, the as-prepared $\text{Li}_2\text{FeTiO}_4/\text{C}$ cathode material was used. Powder diffraction patterns were collected in a home-made cell on a Siemens D-5000 diffractometer in reflection (Bragg–Brentano) mode using $\text{Cu K}\alpha$ radiation with an Autolab cycling/data recording system. Data were collected in the range from 35 to 47° and from 60 to 66° in steps of 0.04° and the integration time of 20 s per step. The cycling rate for $\text{Li}_2\text{FeTiO}_4$ was $C/50$. The experiment was limited either by an appropriate cutoff voltage (e.g., 3.9 and 1 V vs lithium reference) or by the time required for extraction/insertion of 1 mol of Li (time limit was 50 h). Each XRD scan corresponded to a compositional change of $\Delta x = 0.05$.

The electrodes for electrochemical characterization and for in situ XAS and in situ Mössbauer spectroscopy were prepared by ballmilling the active material with 10 wt % of ethylene propylene diene terpolymer in *n*-hexane. The obtained slurry was dried on 16 mm Al disks, and the typical active mass of material was 5 – 6 mg when the electrodes were prepared for electrochemical characterization and 30 – 35 mg for the XAS and Mössbauer experiments. The electrodes were left at 90°C in vacuum overnight before use. A typical electrochemical cell used either for electrochemical characterization or for in situ characterization consisted of two electrodes vacuum-sealed in triplex foil (coffee bag foil). The electrolyte was a 1 M solution of LiPF_6 (Aldrich) in ethylene carbonate:diethyl carbonate ($1:1$ ratio by volume) purchased from Aldrich. Solvents were used as received, and the salt was dried at 90°C in vacuum overnight before use. The working electrode and the counter electrode consisting of metallic lithium were separated with a Cellgard 2300 separator. The electrochemical characterization was performed on a VMP3 potentiostat/galvanostat at 60°C and at room temperature.

X-ray absorption spectra of the $\text{Li}_2\text{FeTiO}_4/\text{C}$ cathode material samples prepared in the form of half-batteries with the total absorption thickness (μd) of about 2 above the investigated Fe K-edge were measured at room temperature in transmission detection mode at the X-ray absorption fine structure (XAFS) beamline of the ELETTRA synchrotron radiation facility in Trieste, Italy. A Si(111) double-crystal monochromator was used with about 0.8 eV resolution at 7 keV. The intensity of the monochromatic X-ray beam was measured by three consecutive ionization detectors respectively filled with the following gas mixtures: 580 mbar N_2 and 1420 mbar He; 1000 mbar N_2 , 90 mbar Ar, and 910 mbar He; and 1900 mbar N_2 and 100 He (XAFS). In the XANES region, equidistant energy steps of 0.3 eV were used, while in the EXAFS region, equidistant energy steps of 2 eV were adopted with an integration time of 2 s/step. In all experiments, the exact energy calibration was established with a simultaneous absorption measurement on 5 μm thick Fe metal foil placed between the second and third ionization chambers. The absolute energy reproducibility of the measured spectra was ± 0.03 eV.

The half-battery was mounted on a sample holder between the first and second ionization detectors. The XAS spectra were measured initially on the as-prepared sample and were repeated continuously during the first cycle of charging and discharging the battery, with a current density corresponding to $C/10$ in a period of 638 min. The measuring time for each spectrum was 25 min so that 27 XANES and EXAFS spectra were collected. In addition, one spectrum was measured after a prolonged discharge for an additional 272 min, with a current density corresponding to $C/20$. Three ex situ XAS spectra were recorded during the second cycle of charging and discharging the battery: one before the start of oxidation, one at the end of the oxidation period of 240 min with $C/10$ current density, and one at the end of the reduction process after 3136 min with $C/70$ current density.

Absorption spectra of reference iron compounds with known Fe valence states and structures (LiFePO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, $\alpha\text{-FeOOH}$, Fe_2O_3 , and FePO_4) were recorded at beamline C of HASYLAB using a Si(111) double-crystal monochromator

with about 1 eV resolution at 7 keV. Higher order harmonics were effectively eliminated by detuning of the monochromator crystals to 60% of the rocking curve maximum using the beam-stabilization feedback control. The intensity of the X-ray beam was measured by three consecutive ionization detectors filled with 30 mbar Ar and 650 mbar N_2 , 380 mbar Ar, and 580 mbar Ar. The reference samples were prepared from micronized powders of the iron compounds homogeneously mixed with micronized boron nitride powder and pressed into homogeneous pellets with the total absorption thickness of about 1.5 above the Fe K-edge.

For in situ Mössbauer spectroscopy measurements, the $\text{Li}_2\text{FeTiO}_4/\text{C}$ sample was charged with a current density of $C/80$ (1.85 mA/g), where oxidation and reduction processes were limited with time (time limit was 80 h), and each measured spectrum represented an average of the composition interval $\Delta x = 0.1$ in the $\text{Li}_2\text{FeTiO}_4/\text{C}$ sample. ^{57}Fe Mössbauer experiments were performed in transmission geometry at room temperature using a constant acceleration spectrometer. The source was ^{57}Co in a Rh matrix. Velocity calibration and isomer shifts (ISs) are quoted relative to an absorber of metallic iron at room temperature. Parameters were fitted with a standard least-squares fitting routine with Lorentzian lines.

Results and Discussion

The $\text{Li}_2\text{FeTiO}_4$ sample used in this study was prepared by a citrate precursor synthesis method which, after carbonization, gives 15 wt % of carbon in the as-prepared sample. The powder XRD pattern of $\text{Li}_2\text{FeTiO}_4$ is shown in Fig. 1a. Rietveld refinement confirms that $\text{Li}_2\text{FeTiO}_4$ crystallizes in the cation disordered rocksalt structure with the space group $Fm\bar{3}m$. The obtained cell parameters are $a = 4.178(1)$ Å and $V = 72.93(1)$ Å³, with agreement factors $R_p = 3.24\%$ and $R_{wp} = 4.13\%$. Carbon is in the amorphous form because no other diffraction peaks were detected from the XRD pattern. Although we were not able to detect any impurities, the Mössbauer spectroscopy showed that 19.5 atom % of Fe was in the Fe(III) oxidation state (Fig. 1b). Based on the Mössbauer parameters (IS and quadrupole splitting), we can assign local environments of Fe(II) to octahedral and deformed octahedral coordination of Fe(II) with oxygen atoms.

The importance of particle size and composite morphology was discussed in our first publication.⁹ We showed that, in contrast to $\text{Li}_2\text{NiTiO}_4$,⁸ for good electrochemical behavior, $\text{Li}_2\text{FeTiO}_4$ particles have to be small and very well dispersed in the carbon matrix to enable ionic contact of electrolytes over the whole surface. According to our experimental results, we found that the microstructure of the $\text{Li}_2\text{FeTiO}_4$ sample had a strong influence on the electrochemical behavior, and the best capacities were obtained from samples with microstructures as shown in Fig. 2. Low (Fig. 2a) and high (Fig. 2b) magnification scanning electron microscopy (SEM) micrographs confirm sample porosity and homogeneity. A better insight into the sample morphology was obtained from high resolution transmission electron microscope (HRTEM) micrographs. The micrographs in Fig. 2c and d show that the $\text{Li}_2\text{FeTiO}_4$ particles are 15 nm larger on average and are embedded into an amorphous carbon matrix.

Although in our study, we used small particles embedded in a carbon matrix, most of the electrochemical tests were done at an elevated temperature of 60°C . Figure 3a shows the charging/discharging of $\text{Li}_2\text{FeTiO}_4$ during the first three cycles, with the current density corresponding to a cycling rate of $C/20$. During the first oxidation, the potential is changed monotonously from an open-circuit potential of approximately 2.4 V vs metallic lithium of up to 2.8 V followed by a rapid increase in voltage. The oxidation and reduction cutoff voltages have been determined experimentally in our previous work.⁹ The material shows a small drop of capacity only in the first cycle; at the higher cycles, the charging/discharging is fully reversible, with some increase in the reversible capacity. From all our experimental results on the $\text{Li}_2\text{FeTiO}_4/\text{C}$ samples, we observed a small change in the voltage profile in the oxidation curve when we compared the first charge curve with the charge curves

Figure 1. (Color online) (a) Refined XRD pattern of $\text{Li}_2\text{FeTiO}_4$ sample (blue line is a measured pattern and red line is a fitted pattern) and (b) corresponding fitted Mössbauer spectroscopy spectra (black squares are measured values and lines are calculated values).

Figure 2. [(a) and (b)] SEM images (low and high magnifications) of $\text{Li}_2\text{FeTiO}_4$ and [(c) and (d)] HRTEM images (low and high magnifications) of $\text{Li}_2\text{FeTiO}_4$.

obtained at higher cycles. In the electrochemical tests of the $\text{Li}_2\text{FeTiO}_4/\text{C}$ samples at room temperature, we obtained only about 40% of the capacity that was observed at 60°C (Fig. 3b). Upon increasing the charge/discharge rate, the polarization between the charge and discharge curves increases rapidly, which indicates a high transport/reaction resistance inside this material (Fig. 3c); this explains why the $\text{Li}_2\text{FeTiO}_4/\text{C}$ samples need to be of nanometric size and very well dispersed in the conductive matrix, thus enabling homogeneous insertion of lithium along very short diffusion paths. The $\text{Li}_2\text{FeTiO}_4/\text{C}$ samples can be cycled many times without any significant capacity fading, however, the obtained capacity at high current densities is very low (Fig. 3d). It is believed that the rate limitation of the present $\text{Li}_2\text{FeTiO}_4$ material can be overcome with further proper engineering of composite $\text{Li}_2\text{FeTiO}_4$ cathodes by im-

Figure 3. (Color online) Electrochemical characterization of $\text{Li}_2\text{FeTiO}_4$: (a) First three charge/discharge curves obtained at C/20. (b) Comparison of electrochemical behavior at 60°C and room temperature (inset shows cycling stability at two temperatures). (c) Charge/discharge curves obtained at different current densities. (d) Cycling performance at different current densities.

Figure 4. Voltage-limited in situ XRD experiment: (a) Charge/discharge curves in the first two cycles at C/50. (b) Insets of obtained XRD patterns during oxidation/reduction processes (left column shows the shift of [002] peak and right column shows the shift of [222]). (c) Selected XRD patterns showing [002] peak at the beginning and at the end of each cycle. (d) Change in lattice parameters during in situ experiment.

proved wiring of 10–15 nm large particles. Before doing so, it is important to thoroughly understand the mechanism of lithium extraction/insertion.

The technique that can give the most accurate answer as to what is happening with a structure is a combination of electrochemistry and XRD. Because those experiments were performed at room temperature, we decided to increase the potential window by setting the reduction cutoff voltage to 1.0 V vs metallic lithium reference. Using a low current density corresponding to a cycling rate of C/50 and an enlarged potential window, we were able to exchange 0.8 mol of lithium. In practice, this should mean that we were able to reversibly oxidize and reduce all Fe(II) in the structure (Fig. 4a). The shape of the electrochemical curves in the first two cycles remains similar to the one observed at 60°C (Fig. 3a). The monotonous change in the voltage during oxidation and reduction is connected with small changes in the Bragg positions of the peaks in the measured XRD patterns (Fig. 4b). The position of the [002] peak is shifted from $2\theta = 43.27$ to 43.47° during the first oxidation and back to 43.32° during the first reduction. At higher cycles, the change in lattice parameters during the oxidation/reduction process was just between the oxidized and reduced states. The same has also been observed for peak [222] at $2\theta = 63.86^\circ$. Such continuous change in the Bragg positions of the peaks with increasing exchanged amount of lithium is typical of solid-solution exchange mechanism. A more detailed comparison of the XRD patterns at the beginning and at the end of the oxidation/reduction cycle reveals that the positions of the peaks and their intensities change after reduction when compared to the XRD pattern of the as-prepared sample (Fig. 4c). This small difference in the position and in the intensity of the peaks after reduction when compared to the as-prepared sample implies that the small change in the potential is probably connected with small changes in the structure. All measured in situ XRD patterns were fitted according to our model obtained from Fig. 1a, and the change in the crystal lattice parameters (volume) is shown in Fig. 4d. During the first oxidation, the change in the lattice parameters is linear up to the point where the potential of the electrochemical curve is increasing monotonously. In the last part of the first oxidation process, the

change in the lattice parameters approaches slowly to about 1.4% in the crystal lattice parameters. This small change in the crystal lattice parameters during lithium removal from the structure suggests that $\text{Li}_2\text{FeTiO}_4$ should be considered as a stable cathode material from a structural point of view. Although we have obtained the full reversible capacity in the first cycle, the structural changes are not completely reversible. After the first reduction, the change in the crystal lattice parameters is still 0.4% when compared to the as-prepared material. The second cycle is reversible in the context of charge recuperation and structural changes. Here we point out that the structural changes are linear with the exchanged lithium in the main part of the electrochemical curve, but not at the end of the oxidation/reduction processes. Extending the lower cutoff voltage to a lower value enabled us to recover the whole capacity, but what would happen if the electrochemical measurement is not limited with pre-selected cutoff potentials but with a time limit which corresponds to an exchange of 1 mol of lithium? We have tackled this question with in situ XRD, and the results are shown in Fig. 5. The electrochemical curve shows that, in the first cycle, 1 mol of lithium can be reversibly exchanged from $\text{Li}_2\text{FeTiO}_4$. A part of the capacity (about 0.2 mol of lithium) is obtained at potentials above 3.9 V vs metallic lithium reference, which serves as the usual cutoff voltage in our electrochemical experiments. The refined XRD patterns (Fig. 5b) show that the change in the lattice parameters is the same as when cutoff voltages are used for the termination of the electrochemical process. The additional capacity induces no structural changes, as observed from Fig. 5b, where no change in the lattice parameters occurs above 0.7 mol of the exchanged lithium. During the reduction process, the structural reversibility is similar to the one shown in Fig. 4d. Both experiments show that, during the first oxidation/reduction process, there is a small structural change, and we presume that this is connected with the slight change in the electrochemical curve during the first oxidation.

More insights into the mechanism of lithium exchange are obtained by two in situ complementary techniques of XAS and Mössbauer spectroscopy, whereby the changes in the local environment of iron are monitored.

Figure 5. Time-limited in situ XRD experiment: (a) Charge/discharge curves in the first cycle at C/50 and (b) change in lattice parameters during in situ experiment.

Mössbauer spectroscopy.— Figure 6 shows a set of Mössbauer spectra during the first charge/discharge cycle. The cycling rate was C/80. Each Mössbauer spectrum is an average of the change in composition for $\Delta x = 0.1$ in Li₂FeTiO₄. The experiment was limited with the time that corresponds to the exchange of 1 mol of lithium per Li₂FeTiO₄ formula unit (Fig. 6b, left axis). The change in oxidation state determined by Mössbauer spectroscopy (Fig. 6b, right axis) follows the electrochemical experiment, and it shows a linear change of up to the usually used cutoff voltage (close to 3.9 V vs lithium reference). The calculated charge at this voltage also corresponds to the removal of 0.8 mol of lithium from the structure, so one expects a complete change from the oxidation state to the Fe(III) form. The measured spectra at the end of the oxidation process can be fitted assuming a small amount of Fe(II) originated from the measurement because the points in Fig. 6, presented as an average oxidation state, which were obtained inside the time interval of 8 h during the dynamic change in the oxidation state of iron. Although the last two spectra measured during the oxidation process indicate that all iron was oxidized to Fe(III), we were able to obtain

an additional capacity above the cutoff voltage of 3.9 V vs lithium reference. We showed with an in situ XRD experiment that this additional capacity was reversible. We presume this is connected with a reversible formation of the surface film on Li₂FeTiO₄.¹⁷ The change in the oxidation state of iron during the reduction process follows the linear dependence during the insertion of about 0.7 mol of lithium. After that, the average oxidation state of iron in the structure remains constant, although we were able to obtain an additional charge from the electrode at potentials close to 1 V vs lithium reference. It is believed that this additional charge is due to a reversible reduction of the surface film on Li₂FeTiO₄ that was formed at the other end of the electrochemical curve. Finally, we can compare the in situ XRD experiment with the in situ Mössbauer spectroscopy: both consistently demonstrate that the structural changes are not fully reversible due to the incomplete recovery of the oxidation state of iron in Li₂FeTiO₄. We presume that the originally present Fe(III) in the structure cannot be reduced to Fe(II), and

Figure 6. (Color online) (a) Oxidation/reduction curve during in situ Mössbauer spectroscopy experiment in the first cycle (left y-axis) and the relative amount of Fe(III) (in atom %) of Fe in Li₂FeTiO₄ obtained from in situ measured Mössbauer spectra (right y-axis). (b) Mössbauer spectra measured during oxidation (left column) and during reduction (right column). (c) and (d) show selected Mössbauer spectra at the end of oxidation and at the end of the first cycle.

Figure 7. (Color online) (a) Oxidation/reduction curve during in situ XAS experiment in the first cycle (left y-axis) and the relative amount of Fe(III) component in the $\text{Li}_2\text{FeTiO}_4$ cathode material during the first cycle of charge/discharge process, determined from Fe XANES spectra. (b) Fe K-edge XANES spectrum of the $\text{Li}_2\text{FeTiO}_4$ material after 245 min of charging of the battery, where 59.1% of Fe(III) was determined by a linear combination fit. The solid line is the experiment; the dashed line is the best-fit linear combination of XANES profiles of the starting (as-prepared) $\text{Li}_2\text{FeTiO}_4$ compound (50.8%), where 19.5% of Fe(III) was present, and 49.2% of the spectrum at the highest oxidation state [pure Fe(III)] obtained after 240 min of charging in the second cycle. Both components are shown below.

the additional capacity observed in electrochemical experiments should be connected with the reversible surface film formation.

The local environment of iron in the as-prepared $\text{Li}_2\text{FeTiO}_4$ can be described with at least three different contributions from Fe(II) and one contribution from Fe(III) . After complete oxidation, the Mössbauer spectra can be fitted with three different local environments of Fe(III) (Fig. 6c). The Mössbauer parameters for the two local environments of Fe(III) are typical of the octahedral coordination of Fe(III) , although different from the as-prepared sample. The Mössbauer parameters for the third local environment of Fe(III) and the Mössbauer parameters for the local environment of Fe(II) are relatively undefined, and they can be easily assigned to Fe(III) and Fe(II) with planar fourfold coordination. The reduction process introduces an even higher disorder in the structure because the Mössbauer spectra after reduction can be fitted with four local environments of Fe(II) and two different local environments of Fe(III) . The introduction of a higher disorder into the structure after the first cycle can be correlated with the slight change in the voltage profile during the second and higher oxidation cycles.

Another in situ technique that enables monitoring of the changes in the local environment of iron is XAS. The basic electrochemical curve of the oxidation and reduction of $\text{Li}_2\text{FeTiO}_4$ for this experiment is shown in Fig. 7a (left axis). During continuous charge/discharge, X-ray absorption spectra were recorded every 25 min, and all of them were used for analysis.

Fe K-edge XANES.— The Fe K-edge XANES analysis is used to determine the change in the Fe valence state during the charge/discharge process. The energy positions of the edge and pre-edge features are correlated with the valence state of the absorbing atom in the sample.¹⁸ If the sample contains the same cation in two or more sites with different local structures and valence states, the measured XANES spectrum is a linear combination of individual XANES spectra of the different cation sites. The relative amount of the cation at each site can be precisely determined by the linear combination fit.¹⁹ The procedure is applied to the Fe XANES spectra measured during the charge/discharge process. These spectra can be completely described by the linear combination of the XANES spectrum of the starting (as-prepared) $\text{Li}_2\text{FeTiO}_4$ compound, where 19.5% of Fe(III) was present, and the spectrum at the highest oxidation state [pure Fe(III)] obtained after complete charging in the second cycle. The fit result is illustrated in Fig. 7b. In this way, we were able to determine the relative amount of Fe(III) component in the cathode material with a precision of 0.2% (Fig. 7a, right axis). During battery oxidation in the first cycle, with the current density corresponding to C/10, the relative amount of Fe(III) is gradually increased from 19.5 to 82.2%. After reduction, the cathode material

does not return to its initial state. After 192 min of reduction, with a current density corresponding to the C/10 cycling rate, there is still 55.3% of Fe(III) present, and even after an additional 297 min of reduction, with the current density corresponding to C/20, the relative amount of Fe(III) is 42.2%. Consistent with the other two in situ techniques shown above, a higher reversibility is again observed in the electrochemical curve; as above, it can be ascribed again to surface film degradation because the oxidation state of iron does not suggest a complete reduction.

Fe K-edge EXAFS analysis.— Fe K-edge EXAFS analysis is used to directly probe the changes in the short-range order around the Fe cations in the $\text{Li}_2\text{FeTiO}_4/\text{C}$ cathode during oxidation and reduction. Fourier transforms (FTs) of the representative EXAFS spectra from the series obtained during the first and second charge/discharge cycles are shown in Fig. 8, revealing the contributions of individual shells of atoms around Fe. The series of FT spectra show significant changes in the local structure around the Fe cations during oxidation. The shape of the Fe EXAFS spectra measured during reduction indicates that the process is not completely reversible. The structure goes through the same intermediate states (we have selected spectra with similar oxidation states of iron recorded during oxidation and reduction), but even after prolonged reduction, it does not reach the same structure as in the as-prepared sample.

To obtain quantitative structural data from the series, we modeled the spectra with an ab initio FEFF model.²⁰ The basic model is built from the crystallographic data of $\text{Li}_2\text{FeTiO}_4$ with $Fm\bar{3}m$ space group ($a = 4.1784 \text{ \AA}$). In this structure, Fe atoms are located at the centers of oxygen octahedra with an Fe–O distance of 2.089 Å. The second coordination sphere at a distance of 2.955 Å is occupied by six Li, three Fe, and three Ti atoms. The third Fe coordination shell is composed of eight O atoms at 3.617 Å.

The quantitative analysis of Fe EXAFS spectra is performed with the IFEFFIT program package.²¹ Structural parameters are quantitatively resolved by comparing the measured signal with the model signal. The model includes all neighbor shells described above, comprising four single-scattering paths with lengths of up to 3.7 Å. The Debye–Waller parameters for each path are varied, with an overall expansion coefficient and a common shift of energy origin ΔE_0 . To describe the observed structural changes during the oxidation and reduction processes, a deviation from the basic rocksalt structure is introduced artificially into the FEFF model by replacing the single sixfold degenerate Fe–O scattering path with two paths having slightly different Fe–O distances and a relative number of oxygen atoms at each distance to describe the deformation of the octahedron. The stoichiometry, however, is not varied: the degeneracy of individual scattering paths is left as defined from the crys-

Figure 8. (Color online) FT of k^3 -weighted Fe EXAFS spectra of $\text{Li}_2\text{FeTiO}_4$ sample during the processes of charging and discharging, calculated in the k range of 3.5–14 $\text{\AA}^{-1}$: Experiment (solid line) and EXAFS model (dashed line).

tallographic data except for the amount of Li atoms, which is adjusted to the extent of lithium extraction or insertion. The EXAFS amplitude reduction factor S_0^0 is kept fixed at a value of 0.72 that agrees with previous Fe K-edge EXAFS analyses.^{18,19}

The model fits very well all the measured EXAFS spectra in the series in the R range of 1–3.5 $\text{\AA}$. The obtained structural parameters clearly show that all structural changes around the Fe atoms in the material during the charge/discharge process are limited to the nearest oxygen coordination shell. There are no significant changes in the local structure of more distant coordination spheres (Li, Ti, and Fe) compared to the basic rocksalt structure.

The fit of the spectrum obtained ex situ in the second cycle after prolonged charging of 240 min at C/10 cycling rate containing only Fe(III) cations shows the Jahn–Teller deformation (4 + 2) of the octahedron. The Fe–O distance to the four planar oxygen atoms is 1.95 $\text{\AA}$, i.e., 0.18 $\text{\AA}$ shorter than in the basic rocksalt structure containing Fe(II) cations. The two axial oxygen atoms remain at about the same distance (2.13 $\text{\AA}$) as in the undeformed structure. The fit of the spectrum of the as-prepared sample containing 19.5% Fe(III) shows that, on average, Fe cations are coordinated to three oxygen atoms at 2.03 and 2.13 $\text{\AA}$. All spectra measured in the intermediate states during charging and discharging show that the average octahedron deformation is directly correlated with a relative amount of Fe(III) in the structure, with the above described states as limiting cases (Fig. 8): the splitting of the two oxygen distances gradually increases from 0.10 $\text{\AA}$ in the as-prepared state to 0.18 $\text{\AA}$ in the final, fully charged state of the battery, and the octahedron deformation gradually changes from 3 + 3 to 4 + 2.

EXAFS results thus clearly indicate that the change in the Fe valence state from Fe(II) to Fe(III) on individual crystallographic sites is accompanied with the Jahn–Teller deformation of the oxygen

octahedron around the Fe cation. The process is reversible in the process of battery discharging: The Jahn–Teller octahedron deformation is gradually removed after reduction of Fe(III) back to Fe(II). In the final state after the first cycle after 483 min of discharging, where 42.2% of Fe(III) remains in the structure, the average octahedron deformation also does not return to the initial as-prepared state.

All three in situ techniques used in this study show some structural changes in $\text{Li}_2\text{FeTiO}_4$ during the first cycle in the long and short ranges. The observed changes are not deteriorative for long operation while the cycling stability of $\text{Li}_2\text{FeTiO}_4$ is excellent and the change in the lattice parameters in the second cycle and probably in higher cycles is fully reversible. We propose that these changes (shrinkage in volume of crystal cell and deformation of octahedra, which can be observed also from Mössbauer spectroscopy as an introduction of local environments) are responsible for a small change in the voltage profile in the oxidation curve after the first cycle.

Conclusion

A different cathode material for lithium-ion batteries has been the subject of three different in situ characterization methods. The aim of using in situ XRD, in situ Mössbauer spectroscopy, and in situ XAS was to elucidate the mechanism of lithium exchange and possible structural changes in the short- and long-range orders. The in situ XRD experiment reveals that lithium exchange from the rocksalt structure in which $\text{Li}_2\text{FeTiO}_4$ crystallizes is through solid-solution formation, and the structural changes as observed from in situ XRD experiment are not fully reversible. The shrinkage of cell volume during full oxidation is only 1.4%, which, in practice, ensures good structural stability. The process is not fully reversible, and after the first oxidation, the cell volume decreased to about 0.4%. In the second cycle, we have not detected any further shrinkage of the crystal cell volume. Probably connected with small structural changes in the first cycle, there is also a small drop in the voltage in the oxidation part of the electrochemical curve in the second and higher cycles. Use of in situ Mössbauer spectroscopy showed that all Fe(II) in the structure can be oxidized up to the potential of 3.9 V vs metallic lithium reference; however, the oxidation is not fully reversible and some of the additional Fe(III) was detected after oxidation. The local environment of additionally obtained Fe(III) is different from the one observed in the as-prepared sample. Comparison of the Mössbauer spectra of the as-prepared sample and after the first cycle shows that even a higher disorder was introduced into the structure if we compare the number of local environments of iron. The appearance of local environments of iron can be explained from in situ EXAFS measurements. In the as-prepared sample, Fe cations are coordinated to three oxygen atoms at 2.03 $\text{\AA}$ and another three at 2.13 $\text{\AA}$. With the oxidation of Fe during charging, the splitting of two oxygen subshells gradually increases to 0.18 $\text{\AA}$ and the octahedra deformation gradually changes from 3 + 3 to 4 + 2. This deformation is not fully reversible, and it can explain changes in the long-range order, as observed from in situ XRD. Finally, working with low current densities (C rates of C/50 and C/80), we have observed an additional capacity that can be stored if the battery was charged above 3.9 V and discharged below 2 V. With the in situ XRD experiment, we showed that this storage of additional capacity was not connected with any structural changes. While using in situ Mössbauer spectroscopy, we showed that no change in the oxidation state of iron was detected above 3.9 V during oxidation and close to 1 V during reduction. This phenomenon is connected with a reversible surface film formation on $\text{Li}_2\text{FeTiO}_4$ particles.

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References

1. M. Armand and J.-M. Tarascon, *Nature (London)*, **451**, 652 (2008).
2. A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.*, **144**, 1188 (1997).
3. A. Nyten, A. Abouimrane, M. Armand, T. Gustafsson, and J. O. Thomas, *Electrochem. Commun.*, **7**, 156 (2005).
4. R. Dominko, M. Bele, M. Gaberscek, A. Meden, M. Remskar, and J. Jamnik, *Electrochem. Commun.*, **8**, 217 (2006).
5. A. S. Prakash, P. Rozier, L. Dupont, H. Vezin, F. Sauvage, and J.-M. Tarascon, *Chem. Mater.*, **18**, 407 (2006).
6. C. Lyness, B. Delobel, A. R. Armstrong, and P. G. Bruce, *Chem. Commun. (Cambridge)*, **46**, 4890 (2007).
7. L. Sebastian and J. Gopalakrishnan, *J. Solid State Chem.*, **172**, 171 (2003).
8. S. R. S. Prabaharan, M. S. Michael, H. Ikuta, Y. Uchimoto, and M. Wakihara, *Solid State Ionics*, **172**, 39 (2004).
9. M. Kuzma, R. Dominko, A. Meden, D. Makovec, M. Bele, J. Jamnik, and M. Gaberscek, *J. Power Sources*, **189**, 81 (2009).
10. A. Nyten, S. Kamali, L. Hängström, T. Gustafsson, and J. O. Thomas, *J. Mater. Chem.*, **16**, 2266 (2006).
11. M. Morcrette, Y. Chabre, G. Vaughan, G. Amatucci, J.-B. Leriche, S. Patoux, C. Masquelier, and J.-M. Tarascon, *Electrochim. Acta*, **47**, 3137 (2002).
12. M. Balasubramanian, X. Sun, X. Q. Yang, and J. McBreen, *J. Electrochem. Soc.*, **147**, 2903 (2000).
13. A. S. Andersson, B. Kalska, L. Hängström, and J. O. Thomas, *Solid State Ionics*, **130**, 41 (2000).
14. A. Deb and E. J. Cairns, *Fluid Phase Equilib.*, **241**, 4 (2006).
15. O. Haas, A. Deb, E. J. Cairns, and A. Wokaun, *J. Electrochem. Soc.*, **152**, A191 (2005).
16. M. Kuzma, R. Dominko, M. Bele, M. Gaberscek, and J. Jamnik, Slovenia Pat. Appl. P-200800065 (2008).
17. D. Ensling, M. Stjern Dahl, A. Nyten, T. Gustafson, and J. O. Thomas, *J. Mater. Chem.*, **19**, 82 (2009).
18. I. Arčon, J. Kolar, A. Kodre, D. Hanžel, and M. Strlič, *X-Ray Spectrom.*, **36**, 199 (2007).
19. R. Dominko, I. Arčon, A. Kodre, D. Hanžel, and M. Gaberšček, *J. Power Sources*, **189**, 51 (2009).
20. J. J. Rehr, R. C. Albers, and S. I. Zabinsky, *Phys. Rev. Lett.*, **69**, 3397 (1992).
21. B. Ravel and M. Newville, *J. Synchrotron Radiat.*, **12**, 537 (2005).