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ARTICLE

Identifying Different States of Lithiation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Spinel by Energy-Dispersive Inelastic X-Ray Scattering (EDIXS) SpectroscopyJosé Ignacio Robledo^{a,b}, Juan José Leani^{*a,c}, Susana Chauque^d, Osvaldo Cámara^{a,e}, Fabiana Yolanda Oliva^{a,e} and Héctor Jorge Sánchez^{a,c}Received 00th January 20xx,
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The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) compound has been investigated as an alternative negative electrode material for lithium ion batteries (LIBs), which are being used as energy storage devices in stationary systems as well as for electric vehicles due to their many interesting features. LTO compound has shown a remarkable Li-ion intercalation/de-intercalation reversibility, demonstrating also zero-strain volume change during the cycling process, with the addition of a notable safety performance. Furthermore, LTO has a high voltage plateau in comparison with other negative material candidates, helping to avoid the deposition of metallic lithium in dendrites form. Due to its performance and potential applications in LIBs, a deep knowledge regarding the behavior of this LTO compound is of high interest. In this work, Energy-Dispersive Resonant Inelastic X-ray Scattering (EDIXS) is used to fulfill this need. In addition, XANES measurements were carried out as complementary methodology. The results show that EDIXS can differentiate LTO chemical compounds (lithiated and de-lithiated) with high sensitivity and that it is a reliable tool to perform chemical speciation analysis on this kind of samples. In addition, the results confirm theoretical predictions regarding the composition of the different oxidation states of titanium associated to different states of charge/lithiation of the LTO-spinel as well. The proposed methodology can be easily applied to other lithium-based materials and beyond them, such as those based on sodium and novel technologies based on polyvalent cations as magnesium and aluminium.

Introduction

Since the several oil crises occurred in the past decades, and the widespread concern on climate change, the use of renewable energy resources (as well as efficient energy storage systems) has a relevant place in the agenda of governments and international organizations. Clearly, a more sustainable energy matrix is urgently required by modern society considering the global warming effects, the fluctuating price of oil and its predicted exhaustion, and the air contamination produced by the fossil-fuel combustion. Because of the intermittency in the development and exploitation of renewable energy resources, such as wind and solar power, the scientific and technological community has focused on the search for improved electrochemical storage systems that can safely and efficiently store the energy coming from these sustainable sources. An adequate storage system is needed, not only for stationary purposes, but also for transportation and residential use.

The technology of lithium-ion batteries (LIB) have had a remarkable attention due to its application in portable electronic devices [1–5], particularly from the introduction by Sony in 1991 of a commercial battery consisting of a Li^+ ion intercalation anode made of graphite microparticles and a layer oxide cathode made of transition metal oxide such as cobalt, nickel and/or manganese dioxide [6,7]. The energy storage capacity of the LIB system is five times higher than that of lead-acid batteries, and has an average voltage of 3.8 V per cell in comparison with 2.0 - 2.2 V of the lead-acid batteries [8]. LIBs also have the advantage of lower weight, higher energy, power density, and faster charge and discharge rates, compared to other similar technologies [9,10]. However, it is important to address several issues regarding their safety, and to improve further the energy storage capacity and cycle life in order to be used in electric vehicles, which are predicted to replace those with internal combustion engines in the near future. Since graphite has a fragile structure and incorporates lithium at a similar potential to that of lithium metal deposition, with the risk of metallic dendrites formation, the use of better and safer negative electrode is necessary [11,12]. Particularly, the compound $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (also known as LTO) has been investigated as an alternative negative electrode material for LIBs because of its remarkable properties [13,14]. The negative electrode materials for use in LIBs applications, as graphite or LTO, are synthesized in a chemical state that is not able to deliver spontaneously electric charge to an external circuit, when they are connected to an adequate positive electrode. This means

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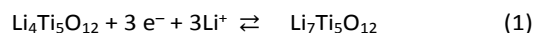
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that the electrode materials are initially prepared in a discharged state, after that they are assembled in the cell and then charged by an external voltage source. For the LTO compound, the charging process requires the electrochemical reduction of three Ti^{4+} centers (until 1.0 V vs. Li^+/Li^0) of the five present per formula unit^[15]. This electrochemical process of charge storage, occurring through the reduction reaction $\text{Ti}^{4+} + e \rightarrow \text{Ti}^{3+}$, must be accompanied by a Li^+ ion insertion process in the crystalline network in order to maintain the electroneutrality in charge along the whole structure, as can be seen in the following Equation 1^[16]:



This is why the charging process of the LTO electrodes is commonly referred as a "lithiation" of the negative electrode material.

Nowadays, several spectrometric techniques based on the use of synchrotron radiation are commonly used for determining the oxidation state of elements on materials. The applicability of each methodology depends on the type of sample, measurement conditions and experimental setups, among others. Energy-Dispersive Resonant Inelastic X-ray Scattering (EDIXS) presents particular features that makes it especially useful to analyze doped materials.

In the last few years, EDIXS has become a powerful technique for the discrimination and characterization of chemical environments in a variety of samples of interest^[17]. This technique makes use of core-level Resonant Inelastic X-ray Scattering (RIXS) since the analysis of the RIXS peak enables to establish a correspondence between the peak's fine structure and the chemical state of the atom under study. In addition, EDIXS exploits the benefits of an Energy Dispersive detection System (EDS) and multivariate methods for the data analysis. As a result, this novel methodology shows a fast acquisition, energy-scanning free experiments, low self-absorption effects and an objective interpretation of the results. As it has been widely probed, by applying EDIXS the local chemical environment of an element of interest can be studied in a variety of irradiation geometries and experimental setups commonly used by conventional techniques, such as total reflection^[18], grazing incidence^[19] and confocal setups^[20].

In this work, the EDIXS technique is applied for the study and characterization of different states of charge of LTO electrodes. The measurements were carried out in the IAEA end-station of the XRF beamline at Elettra Sincrotrone Trieste (Italy) using a monochromatic beam. After a minimum processing of the raw RIXS data, a multivariate analysis was performed by means of Principal Component Analysis (PCA). Similar measurements were performed applying X-ray Absorption Near Edge Structure (XANES) technique as to cross check the results and comparing the performance of both techniques in this kind of samples as well.

An outcome of the present study is that the results confirm the theoretical predictions regarding the composition of the different oxidation states of titanium (Ti^{4+} and Ti^{3+}) associated to different states of lithiation of the LTO spinel during the

charge/discharge process. In addition, the results show that the fine structure of the RIXS peaks are clearly correlated with the different LTO chemical compounds ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$). The EDIXS spectroscopy showed to be a reliable tool to perform chemical speciation analysis of samples presenting slight changes in their local chemical environments.

Experimental

Sample preparation

For the present work three-electrodes T-cells (Swagelok type) were assembled to introduce different amount of lithium ions into the structure of the LTO spinel, that is to say: fully lithiated, partially lithiated and completely de-lithiated samples, which correlates with high, intermediate and null amounts of Ti^{3+} in the LTO material.

For this purpose, LTO-working electrodes using a mixture of the active material (LTO, synthesized following previous works procedure^[21,22]), a binder (polyvinylidene fluoride) and a conductive carbon black (Timcal Super P) in a weight ratio of 80:10:10, respectively, were prepared. The mixture was dispersed in an adequate solvent (*N*-methyl-2-pyrrolidone) and maintained under stirring for 12 hours to obtain a homogeneous slurry. Afterwards, the slurry was coated on a current collector (copper foil) and dried in a vacuum oven at 80 °C for 12 hours. Finally, the coated foil was punched into an 8 mm diameter disks to obtain the working electrode. Metallic lithium disks were used as reference and counter electrodes, separated with fiberglass disks. As electrolyte, a solution of 1 mol L⁻¹ of LiPF_6 as lithium salt in a solvent mixture composed by ethylene carbonate (EC) and dimethylcarbonate (DMC), 1:1 by mass, was employed. The cells were assembled in a glovebox chamber (MBraun MB10 compact) in Ar atmosphere with concentrations of O_2 and H_2O lowers than 0.5 ppm.

For the preparation of each sample, with different amount of lithium ions into the LTO structure, 10 galvanostatic charge/discharge (GCD) cycles to stabilize the cells was previously performed, applying a current of 0.5 C (allowing for the charge or discharge of the cell in just 2 hours) in a potential range of 3.0-1.0 V (vs. Li^+/Li^0). After the stabilization of each cell, the same previous current to fully lithiate the LTO-electrode was applied, stopping the galvanostatic charging experiment at a cut-off potential of 1.0 V vs. Li^+/Li . Afterwards, the potential was kept at 1.0 V for 2 hours. In those conditions the fully lithiated samples, named *Li-100%* samples, were obtained. In another cell, after the previous described stabilization of 10 cycles, the same lithiation current with a time cut-off of 3600 seconds was applied. This time corresponds to the half time of the complete lithiation process, *i.e.* half of the time required to prepare the *Li-100%* samples. At this point, the electrode potential was around 1.55 V vs. Li^+/Li^0 . Afterwards, the potential was kept at 1.55 V vs. Li^+/Li for 2 hours. The resulting sample was named *Li-50%*. Finally, to prepare the completely de-lithiated LTO-electrode, the cells performing the 10 GCD cycles were stabilized and the higher potential cut-off (3.0 V vs. Li^+/Li) applied to assure a completely oxidized state of the LTO

compound and no lithium ion was inserted in the structure. This completely discharged sample was named *Li-0%*. **Figure 1** illustrates the galvanostatic charge/discharge curves of the LTO compounds showing each potential cut-off applied to obtain the samples with different amount of lithium ions insertion.

These different states of charge for our lithium titanate material are highly reproducible and easy to achieve. The procedure is also commonly applied in the battery research field. About this subject, M. Verde et al. [23] have characterized these charge states with XPS and AFM techniques. The authors also have determined where each LTO phase exists at each state of charge along the voltage-specific capacity curve. On the other hand, H. Schneider et al. [24] have followed the lithium content and its lateral distribution in spinel-type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ based electrodes at different states of charge by means of Raman microspectrometry and colorimetry. These experimental results support our trust on the methodology employed to assign the expressed lithiation percentages.

For all samples (fully, partially lithiated and de-lithiated electrodes), the three-electrodes cells were carefully disassembled in the glovebox chamber to avoid the spontaneous Ti^{3+} oxidation that occurs in the presence of air atmosphere. Each electrode was packed in a Kapton envelope. A total of five samples were prepared with different amounts of lithium ions and measured by both techniques at ultra-high vacuum (UHV) conditions.

Measurements

The measurements were carried out at Elettra Sincrotrone Trieste (EST, Italy) in the XRF beamline using the IAEA end-station facility (IAEAXSpe) [25]. The core of this end-station is an ultra-high vacuum chamber (UHVC) with a seven-axis motorized manipulator, for samples and detectors positioning. The detector used in this work was an ultrathin window Silicon Drift Detector (SDD) mounted in a fixed position of 90° with respect to the excitation beam (energy resolution of ~ 131 eV for the Mn-K α line). The flux of the primary X-ray beam was monitored by a diamond membrane detector and a LabVIEW Graphical User Interface (GUI) was utilized for data acquisition [26]. This XRF beamline is equipped with a double crystal channel-cut monochromator, using a Si(111) crystal (with a resolving power of 1.4×10^{-4}).

In order to apply the EDIXS methodology, RIXS spectra were acquired at a fixed energy of 4900 eV, i.e., beneath the K absorption edge of titanium, with the aim of studying changes in its chemical environment. The measuring time was of 450 s per spectrum/sample.

XANES spectra across the Ti-K edge were also acquired in the energy range 4930-5080 eV, considering 3 seconds per step in the range 4930-5008 eV (with 0.5 eV step) and 1 second per step in the range 5009-5080 eV (with 1 eV step).

All the measurements were performed at 45° - 45° under UHV conditions.

In order to discriminate changes on the titanium chemical state of the LTO molecule, Principal Component Analysis (PCA) [27]

was applied on both the RIXS and XANES spectra, as described below.

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By the end, a brief clarification regarding the acquired RIXS spectrum, for applying the EDIXS technique, and the peak fine structure responsible for the sample discrimination. It was observed that, under the current resonant conditions, a RIXS spectrum recreates a mirror image of a lifetime-broadening-suppressed (LBS) K-edge XAFS profile [28-30], in this case convoluted with the resolution of the used detection system (EDS). Due to the modest energy resolution of the utilized EDS (~ 131 eV for the Mn-K α line), the XANES contribution to the mentioned profile can be neglected, being the oscillation pattern present in an typical EXAFS profile the main responsible for the measured RIXS peak fine structure. Due to this fact, the main aim of measuring XANES spectra in this work is for having a complementary technique; i.e., for validation purposes and comparison of the characterization powers by applying both methods, due to the vast application of XANES in chemical speciation.

Data Analysis

For a better understanding of the fine structure behavior in the RIXS peaks, a deconvolution process was applied with the aim of highlighting the internal oscillation pattern (see for example Ref [31]).

In brief, a Lorentzian decay curve was fitted in the low energy side (this is, from the channel of maximum amplitude to lower energies) of each RIXS peak, as it can be seen in **Figure 2** for a particular sample (fully lithiated sample, Li-100%(1)). The region of interest (ROI) for the analysis is also highlighted. It should be mentioned that the fitting procedure presented a remarkable accuracy ($r^2 > 0.9999$) in all of the analyzed spectra [32]. This level of precision assures that residuals between theoretical model and the experimental data are not mere statistical artifacts.

After the fitting, a standard denoising method was employed based on the frequency decomposition of the signal [33]. An FFT smoothing procedure was applied to the mentioned residuals considering a Gaussian instrumental function with an σ of 49 eV. The smoothing is accomplished by removing Fourier components with frequencies larger than $(1/nt)$, where n is the number of data points considered at a time and t the time spacing between two adjacent data points. By suppressing the high-frequency components, the noise associated with them can be excluded. **Figure 3** shows the fitting residuals before and after the FFT procedure for a particular sample (fully lithiated sample, Li-100%(1)).

The final resulting oscillation patterns can be observed for each sample in the inset of **Figure 4**. Even when some correlations between samples are evidenced by simple observation of the FFT results, a statistical procedure should be applied for an objective evaluation and for quantification purposes.

As it was mentioned, it may be difficult from simple observation establishing any kind of correlation between energy channels that may aid to the identification of the sample's chemical environment from the obtained RIXS oscillation patterns. An

interesting approach to study the variability present in the data set is to perform an exploratory multivariate statistical analysis, such as Principal Component Analysis [27]. By doing so, the variability in the data set may be partitioned into independent components, allowing to study the components which consider the variability present in the energy channels that enable for discrimination. This is one of the bases of EDIXS [17].

In the case of the RIXS oscillation patterns, a Region of Analysis (ROA) ranging from 4152.0 eV to 4388.0 eV was used. It consisted in a total of 25 energy channels. These are the channels from the low energy tail of the Ti-RIXS peak, where the chemical state information is present. In the case of the XANES spectra, a ROA ranging from 4959.5 eV to 4989.0 eV was considered, consisting in a total of 60 energy channels. In this case, the whole XANES spectrum was considered for the PCA to give the analysis a larger total variability, and therefore more information.

Both EDIXS and XANES datasets were standardized prior to the application of the PCA procedure. A first pre-processing was performed to RIXS data by normalizing to the energy channel with the maximum intensity. In the case of XANES data, the normalization was performed to the maximum of the white peak. Afterwards, standardization was carried out by subtracting the mean of each energy channel and dividing by the standard deviation.

PCA analysis was achieved by using the Infostat software [34].

Table 1 and **Table 2** show the resulting eigenvector values of the first principal component responsible for the discrimination in both PCA procedures for EDIXS and XANES, respectively.

It should be noted that the values in tables 1 and 2 are related with the principal component (PC) projections by:

$$PC_i = \vec{E} \cdot \vec{e}_i \quad (2)$$

where \vec{E} is the vector containing the counts of the different energy channels considered for the PCA and \vec{e}_i is the i -th eigenvector of the correlation matrix.

Results and discussion

Figure 4 shows the Ti RIXS peaks for the studied samples with different state of charge. In the inset, it is possible to appreciate the fine structure of each peak after a deconvolution procedure involving data fitting and a Fast Fourier Transform (FFT) process, as described above.

Clearly, a mathematical procedure for an objective evaluation and quantitative interpretation of the previous data was required, as it was mentioned in the data analysis section.

Figure 5 shows the EDIXS results in speciation for the different charged LTO samples analyzed by PCA. The projections of the samples in the second and third principal components resulting from the PCA procedure are plotted.

Table 3 shows the percentage of each titanium oxidation state expected for the samples according to the applied electrochemical treatment and the lithium titanate compounds present after the different lithiation stages.

Figure 6 and **Figure 7** shows XANES spectra for the different LTO samples with different state of charge, and the corresponding PCA results, respectively. As can be seen, all the XANES spectra present a similar structure and practically there are no differences among them. In agreement with other authors the only small difference is observed in the region around 4977 eV [35,36]. The analysis of scores of the PCA confirms this observation, showing that the channels around this energy exhibit the highest values of variability.

The results of the PCA depicted in **Figure 7** demonstrate that the state of charge of the LTO can be qualitatively discriminated by XANES. Nevertheless, the sensitivity is not high enough to correlate the amount of charge with the oxidation state of titanium as precisely as EDIXS does.

It is interesting to notice that the energy regions presenting higher variability, and then being the main responsible for the sample discriminations, are located around 4200 eV and 4270 eV in the EDIXS dataset (table 1). It is possible to see that these two regions are located more than 150 eV above the Ti-K absorption edge, if we consider again that a RIXS spectrum is recreating the mirror image of a XAFS profile. This fact demonstrates that the energy regions more responsive to changes in the chemical environment of Ti are not contemplated by a XANES measurement, since they would be included in the EXAFS region of the mentioned Ti-K XAFS profile. From the previous results, it follows that EDIXS seems to be a very sensitive tool for this kind of studies, since the mere inspection of the principal component 2 (PC2) is enough for a proper discrimination of the different categories of samples. Moreover, a simple first quantification procedure can be attempted, assuming a linear dependency between the state of charge of the sample and its value in the PC2 axis (similar first quantification can be found elsewhere [37]). For this, the PC2 value of the sample with 0% of Ti^{3+} , i.e. *Li-0%*, (PC2=3.68) and the average value of the fully lithiated samples (60% of Ti^{3+}), i.e. *Li-100%(i)*, (PC2=-1.79) are considered as reference. Assuming the mentioned linear dependency, it is then:

$$Ti^{3+} [\%] = -10.97 \cdot (PC2) + 40.37 \quad (3)$$

If the partially lithiated sample, i.e. *Li-50%*, (PC2=1.69), is considered as unknown (or validation sample), by the use of Equation 3 a state of charge corresponding to a 78% of Ti^{4+} + 22% of Ti^{3+} should be present. As it can be seen from **Table 3**, these values are in good agreement with the theoretical predictions.

The fact that PC2 is the discriminating component may be understood by observing the inset in **Figure 4**. The residuals are relatively noisy, and this noise, that mainly has to do with a statistical contribution, is the dominant variability in the dataset. Since principal components are ranked by their proportion of the total variability contribution, it is expected then that the variability due to differences in the chemical states of Ti will be present in the second principal component. In this analysis, PC1 contemplates 59.6% of the total variability, while PC2 a 26.0%. For a normal PCA, this percentage is relatively high, meaning that a large percentage of the

variability present in the dataset is due to chemical environment changes.

Conclusions

The results clearly demonstrate that EDIXS is a very sensitive tool, allowing the detection of slight changes in the chemical state of the LTO compound due to the different states of charge. The application of the EDIXS technique to the research field in electrode materials for lithium-ion batteries provides a novel and adequate way to determine the state of charge/discharge of an electroactive compound at different times during the galvanostatic cycling. For the case of the LTO compound, the information obtained by EDIXS complements that given by the electrochemical analysis, allowing to correlate the presence of the Ti³⁺/Ti⁴⁺ oxidation states in the LTO, equivalent to the Li⁺ ions inserted/de-inserted in the material, with the amount of electric charge supplied/recovered in the cell. These kinds of coupled experimental studies can provide new insights into the behaviour and performance of several others active electrode materials based on lithium, such as LiFePO₄, LiMnPO₄ and LiMnOF, in addition to the LTO discussed here and currently used as a negative electrode in LIBs. By the end, chemical state characterizations by EDIXS can be also extended beyond lithium-based materials, such as those based on sodium (Na) and novel technologies based on polyvalent cations as magnesium (Mg) and aluminium (Al).

In conclusion, chemical studies similar to those performed with absorption techniques (XANES, EXAFS) can be also accomplished with this novel EDIXS technique, showing a high sensitivity and with clear advantages of fast acquisition, user-friendly arrangement and overcoming the need of applying any energy scan during the survey.

Conflicts of interest

There are no conflicts to declare.

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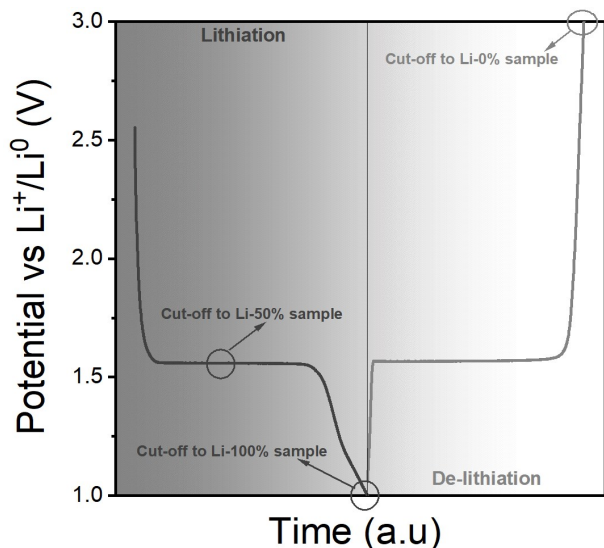


Figure 1. Galvanostatic charge/discharge curves of LTO-negative electrode between 3.0 and 1.0 V vs. Li^+/Li^0 in a 1 mol L^{-1} LiPF_6 EC: DMC. The indications with an arrow correspond to the cut-off applied to prepare the samples with different states of lithiation.

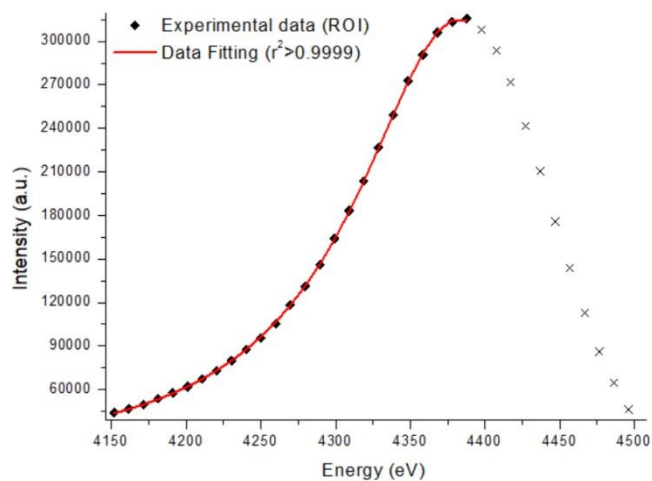


Figure 2. Example of a Ti-RIXS peak for a LTO sample (fully lithiated sample, Li-100%(1)). Incident energy of 4900 eV. Solid line represents data fitting. ROI for the analysis also indicated.

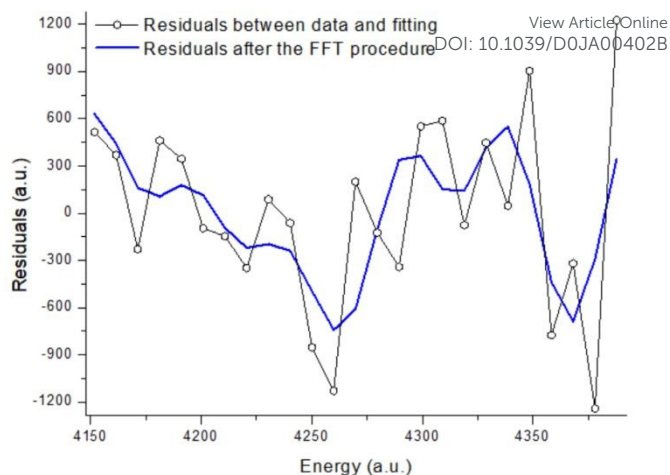


Figure 3. Example of residuals between the experimental RIXS spectrum and the data fitting (fully lithiated sample, Li-100%(1)) before and after the FFT smoothing procedure ($\sigma = 49$ eV).

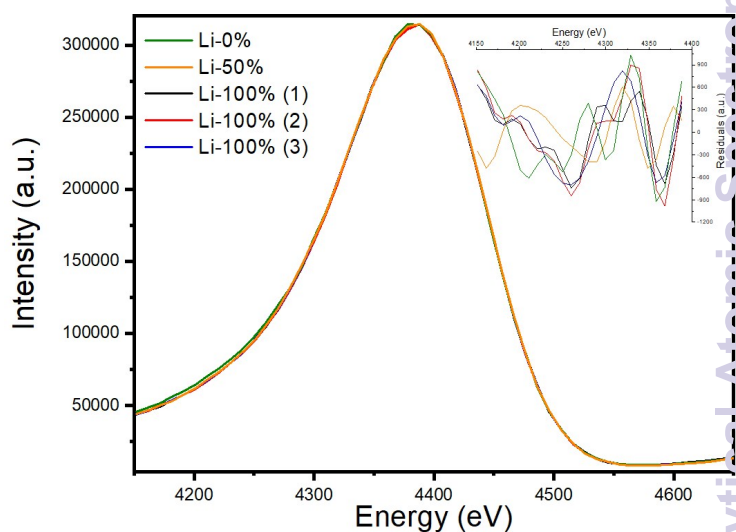


Figure 4. Ti-RIXS peaks for the different charged LTO samples. Inset showing the oscillation pattern of the fine structure after deconvolution procedure.

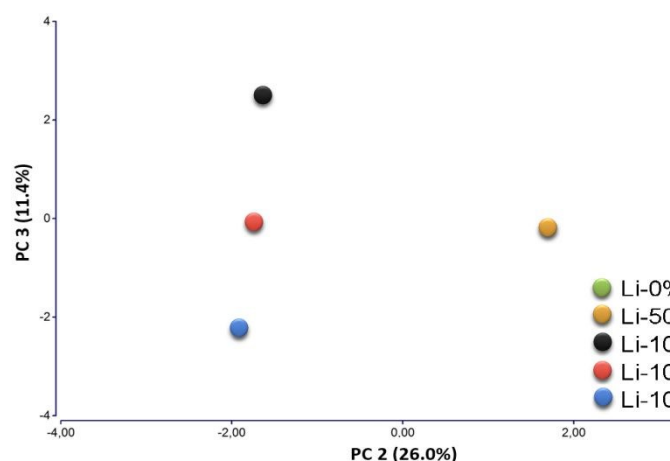


Figure 5. EDIXS speciation of Ti for the different charged LTO samples analysed by PCA.

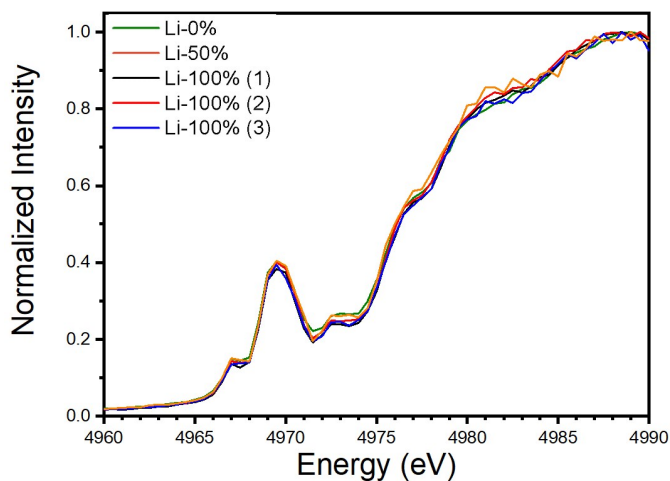


Figure 6. XANES spectra for the different LTO samples with different state of charge.

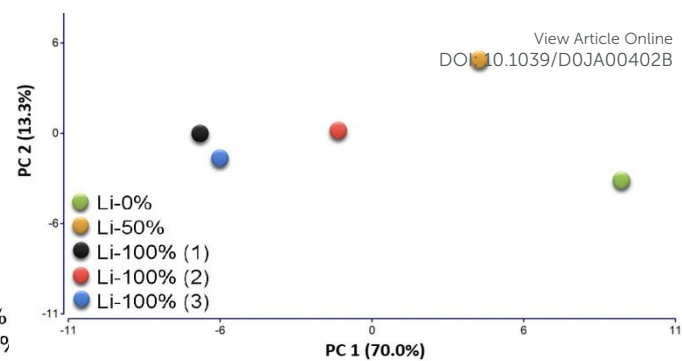


Figure 7. XANES speciation of Ti for the different charged LTO samples analysed by PCA.

Table 1. e_2 eigenvector values of principal component 2 (PC2) for EDIXS database.

Energy [eV]	e_2
4152	-0.1
4161	-0.1
4171	-0.01
4181	0.11
4191	-0.24
4201	-0.24
4211	-0.17
4221	-0.02
4230	0.12
4240	0.11
4250	0.19
4260	0.35
4270	0.38
4280	0.24
4289	-0.17
4299	-0.38
4309	-0.24
4319	0.05
4329	0.13
4339	-0.05
4348	-0.23
4358	-0.12
4368	0.14
4378	0.29
4388	0.12

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Table 2. e_1 eigenvector values of principal component 1 (PC1) for XANES database.

Energy (eV)	e_1
4959.5	0.15
4960	0.13
4960.5	0.14
4961	0.15
4961.5	0.15
4962	0.15
4962.5	0.15
4963	0.15
4963.5	0.14
4964	0.15
4964.5	0.13
4965	0.15
4965.5	0.14
4966	0.14
4966.5	0.15
4967	0.15
4967.5	0.14
4968	0.13
4968.5	0.14
4969	0.14
4969.5	0.15
4970	0.14
4970.5	0.15
4971	0.14
4971.5	0.12
4972	0.15
4972.5	0.15
4973	0.15
4973.5	0.15

4974	0.14
4974.5	0.14
4975	0.15
4975.5	0.15
4976	0.15
4976.5	0.15
4977	0.15
4977.5	0.15
4978	0.15
4978.5	0.15
4979	0.14
4979.5	0.12
4980	0.12
4980.5	0.12
4981	0.08
4981.5	0.1
4982	0.14
4982.5	0.08
4983	0.13
4983.5	-0.01
4984	0.1
4984.5	0
4985	-0.04
4985.5	0.01
4986	-0.01
4986.5	-0.03
4987	-0.03
4987.5	-0.13
4988	0.01
4988.5	-0.12
4989	0.12

Table 3. Description of the different samples prepared, the expected oxidation state and the corresponding unit formula

Sample	Expected Oxidation State	Unit Formula
<i>Li-0% (De-lithiated)</i>	100% of Ti^{4+}	$Li_4Ti_5O_{12}$
<i>Li-50% (Partially Lithiated)</i>	70% of Ti^{4+} + 30% of Ti^{3+}	$Li_4Ti_5O_{12}/Li_7Ti_5O_{12}$
<i>Li-100% (Fully Lithiated)</i>	40% of Ti^{4+} + 60% of Ti^{3+}	$Li_7Ti_5O_{12}$

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