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Fehse, Marcus and Sahle, Christoph J. and Hogan, Matteo P. and Cavallari, Chiara and Kelder, Erik M. and Alfredsson, Maria and Longo, Alessandro (2019) Bulk-Sensitive Soft X-ray Edge Probing for Elucidation of Charge Compensation in Battery Electrodes. *The Journal of Physical Chemistry C*, 123 (40). pp. 24396-24403. ISSN 1932-7447.

DOI

<https://doi.org/10.1021/acs.jpcc.9b06552>

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Bulk Sensitive Soft X-Ray Edge Probing for Elucidation of Charge Compensation in Battery Electrodes

Marcus Fehse,^{*,†,‡,¶} Christoph J. Sahle,[§] Matteo P. Hogan,^{||} Chiara Cavallari,[§]
Erik M. Kelder,^{†,¶} Maria Alfredsson,^{||,¶} and Alessandro Longo^{*,†,⊥}

[†]*Faculty of Applied Sciences, Delft University of Technology, Delft, Netherlands.*

[‡]*Dutch-Belgian (DUBBLE), ESRF-The European Synchrotron, Grenoble, France.*

[¶]*Alistore European Research Institute, CNRS, Amiens, France.*

[§]*ESRF-The European Synchrotron, Grenoble, France.*

^{||}*School of Physical Sciences, University of Kent, UK.*

[⊥]*Istituto per lo Studio dei Materiali Nanostrutturati (ISMN)-CNR, UOS Palermo,
Palermo, Italy*

E-mail: marcus.fehse@umontpellier.fr; alessandro.longo@esrf.fr

Abstract

To this day, elucidating the charge transfer process in electrode material upon electrochemical cycling remains a challenge, primarily due to the complexity of chemical reactions at the electrode surfaces. Here we present an elegant and reliable method to probe bulk sensitive soft edges for elucidating anodic and cathodic charge compensation contribution via x-ray Raman scattering spectroscopy. By using a hard x-ray incident beam this technique circumvents surface limitations and is practically free of self-absorption due to its non-resonant nature. In addition, it does not require complex

sample preparation or experimental setups, making it an ideal tool for potential *in situ* analysis of the electronic structure of electrode materials. In this study we monitored for the first time bulk soft edges of both oxygen and transition metal (iron) of the cathode material $\text{Li}_2\text{FeSiO}_4$ during one complete electrochemical cycle concurrently. Our results reveal that the redox mechanism relies primarily on the iron (cathodic) contribution. Nevertheless, a change in electron confinement of the oxygen suggests its active involvement in the charge compensation process (anodic). Moreover, we were able to support the experimentally observed changes of the electronic structure with *ab initio* based simulation.

Keywords

X-ray Raman Scattering; Soft x-ray edges; Li-ion batteries; high voltage cathode materials; anodic charge compensation; $\text{Li}_2\text{FeSiO}_4$

1 Introduction

Numerous experimental and theoretical studies have been dedicated to elucidate the complexity of electrochemical redox reactions in battery materials. However, the distinction between surface confined and bulk electrode phenomena remains a subject of controversy and debate. Therefore, there is a strong urge to overcome the limitation of conventional experimental methods and go beyond the theoretical predictions. In this study, we present a reliable and elegant solution to address this challenge.

X-ray absorption spectroscopy (XAS) offers plentiful insights into battery materials and is a standard tool for investigation of diverse electrode materials.¹ Regrettably, absorption K-edges of low Z elements and transition metal (TM) L-edges are cumbersome to access or completely inaccessible with conventional XAS. This is unfortunate as many promising electrode materials comprise these low Z elements (N, O, Si, S, Li, Na, Ca, Al, etc.) and

13 the majority of cathode electrode materials are based on TM redox centres.² X-ray Raman
14 Scattering (XRS) spectroscopy is a unique element specific technique that can circumvent
15 these limitations. It allows direct observation of soft x-ray edges of bulk samples without
16 sophisticated sample preparation thanks to the use of a hard x-ray incident beam (≈ 10 keV),
17 which is inelastically scattered by the sample.³ In this way XRS combines the advantages of
18 hard x-ray techniques, i.e. bulk sensitivity, with the sensitivity of soft XAS (sXAS). Unlike
19 XAS, XRS is not limited to dipolar excitations, therefore non-dipole excitations can pro-
20 vide additional information for obtaining full density of projected states. Furthermore, XRS
21 allows the accommodation of complex sample environments and circumvents cumbersome
22 experimental setups under vacuum or inert atmosphere as well as avoids the self-absorption
23 problematic due to the non-resonant nature of this technique, which make sXAS experiments
24 very challenging. The superiority of XRS over the sXAS technique in terms of probing depth
25 and data quality was impressively demonstrated by *Braun et al.* by investigating electronic
26 structure of transition metal cathode material for lithium ion batteries (LIB). In their study
27 the authors highlight that spectroscopic results of bulk XRS and surface confined sXAS
28 greatly differ, underlining the importance of bulk analysis for obtaining an extensive and
29 representative picture of the bulk physicochemical process in electrode materials.⁴ Due to its
30 strong photon scattering yield and its prominence, graphite has been the most intensively
31 studied LIB electrode material using XRS.⁵⁻⁷ Moreover, the capability of XRS to probe
32 Fe L-edge and oxygen K-edge in complex sample environments has been recently demon-
33 strated.⁸⁻¹⁰

34 Thanks to being composed of abundant, low-cost, environmental benign, and non-toxic
35 elements $\text{Li}_2\text{FeSiO}_4$ has received great interest as an alternative cathode material for LIB,
36 since the discovery of its electrochemical activity more than a decade ago.¹¹ Its stability
37 is at least as high as commercialised LiFePO_4 (LFP) but features potentially increased en-
38 ergy and power density owing to the elevated intercalation potential and the faster charge
39 transport.¹²⁻¹⁵ Its complex polymorphism has been intensively studied and is mostly under-

stood.^{16,17} However, recently the capability of reversibly extracting more than one lithium per formula unit has led to a vivid scientific debate and numerous publications. The initial hypothesis of more than one electron extraction on the basis of Fe(III) to Fe(IV) transformation proposed by *Islam et al.*¹⁸ and experimentally claimed by *Lv et al.*¹³ was not supported by later studies.^{14,15,19–21} While the formation of Fe(IV) as the origin of additional capacity at elevated voltage has been rebutted, the role of oxygen as active anionic redox agent has shifted into focus of research. Numerous studies have emerged since the first observation of such anionic redox contribution in layered transition metal oxides about five years ago.^{22–26} The discovery of an anodic charge contribution was met with enthusiasm by the battery research community, since it holds the promise to boost capacity and energy density of traditional cathode materials. In this regard, an important role of oxygen in the charge compensation at elevated potential has been also proposed for the reversible extraction of more than one lithium from polyanionic $\text{Li}_2\text{FeSiO}_4$.^{15,19–21,27,28} While *Masese et al.* claim that oxygen charge compensation occurs exclusively during extraction of a second lithium per formula unit,¹⁹ later studies suggest active participation of oxygen already at an earlier stage in the redox process.^{27,28} In their recent Density Functional Theory (DFT) calculation based study *Zheng et al.* point out the importance of $3d$ electronic configuration for the involvement of oxygen $2p$ in the charge compensation along with the necessity of oxygen polaron formation.²¹

Unfortunately, all of the previously published studies on the elucidation of charge compensation mechanism in $\text{Li}_2\text{FeSiO}_4$ bear inherent drawbacks. On the one hand, the theoretical studies are unable to deliver information on intermediate states of electrochemical process due to intrinsic limitations of functionals. On the other hand, spectroscopic techniques are limited by low penetration depth, unrealistic sample environment, or ambiguity of spectral results. In this regard the surface limitation of soft x-ray absorption spectroscopy is particularly troubling since electrode-electrolyte interfaces are very complex systems, often covered with surface layers (e.g. solid-electrolyte interphase, SEI). Therefore, the outcome of

67 such surface confined spectroscopic measurements greatly depend on the sample preparation
68 method and conditions.

69 To overcome the experimental limitations of soft XAS and obtain a more reliable and
70 exhaustive picture of the electronic structure than theoretical studies can provide, we present
71 here a thorough bulk study of anionic O $2p$ and cathodic TM $3d$ electronic states of $\text{Li}_2\text{FeSiO}_4$
72 cathode material at different states during one complete electrochemical cycle using XRS
73 spectroscopy.

74 **2 Experimental**

75 **2.1 Sample and Electrode Preparation**

76 Synthesis of electrode material has been described elsewhere.¹⁴ All samples were taken from
77 the same electrode casting batch and have identical electrode loading and composition. The
78 electrode thickness is about $30\ \mu\text{m}$ the particle size is in the sub-micrometer range. The active
79 material electrodes were mounted in electrochemical half-cells with lithium metal as counter
80 and reference electrode. The cells were cycled in EC:DEC (1:1) with 1 M LiPF_6 at C/6 rate,
81 whereas 1 C corresponds to deinsertion/insertion of one lithium per formula unit in one hour,
82 $165\ \text{mA g}^{-1}$. For the *ex-situ* cells used in this experiment the rested and cycled batteries
83 were opened in an argon filled glovebox, electrodes were removed and washed thoroughly
84 with anhydrous ethanol to remove electrolyte remnants and any SEI formed, primarily to
85 minimise the oxygen spectral contribution from carbonate species. The washed electrodes
86 were dried under vacuum and were then vacuum sealed under argon, in laminated pouch
87 cells with aluminium windows (Al thickness $15\ \mu\text{m}$) in the centre of the pouch on both sides.

88 **2.2 X-ray Raman Scattering**

89 All X-ray Raman scattering (XRS) spectroscopy data were gathered at the beamline ID20 of
90 the ESRF. The pink beam from four U26 undulators was monochromatized using a cryogeni-

91 cally cooled Si(111) monochromator and focused to a spot size of approximately $10\ \mu\text{m} \times$
92 $20\ \mu\text{m}$ (V \times H) at the sample position using a mirror system in Kirkpatrick-Baez geometry.
93 The large solid angle spectrometer at ID20 was used to collect XRS data with 36 spheri-
94 cally bent Si(660) analyser crystals.²⁹ The data were treated with the XRStools program
95 package as described elsewhere.³⁰ The *ex situ* electrodes, sealed in pouch cells, were placed
96 at an incident beam angle of $\approx 10^\circ$ into the beam. The beam position was verified by the
97 presence of Li $1s$ peak at $\approx 55\ \text{eV}$, see spectra in S.I.. All measurements were collected at
98 room temperature. Acquisition scans lasted around 10-14 h per sample. We collected several
99 scans of the oxygen K-edge by scanning the incident beam energy to create energy losses in
100 the vicinity of the oxygen K-edge. All scans were checked for consistency and signals from
101 different analyser crystals were averaged over. The overall energy resolution was 1.0 eV, and
102 the mean momentum transfer was $6.2 \pm 0.4\ \text{\AA}^{-1}$. All spectra have been normalised and a
103 smoothing function has been applied to the spectra presented.

104 2.3 Simulation

105 To elucidate the electronic structure of the material, O K-edge *ab initio* simulation were
106 performed using the Finite Difference Method Near Edge Structure (FDMNES) software pack-
107 age.^{31,32} The simulation have been performed by using the multiple scattering theory based
108 on the muffin-tin approximation on the potential shape on the Green scheme.³³ The muffin-
109 tin radii were tuned to have a good overlap between the different spherical potentials. A non-
110 relativistic calculation was performed and the Hedin-Lundqvist exchange potential was used.
111 The approximation of non-excited absorbing atoms was used which, in this case, best re-
112 produces the experimental data.³⁴ The semi-empirical parameters `screening` and `dilatorb`
113 were used to reproduce the electronic configuration of the material. In this respect, two
114 matrices of different simulated spectra corresponding to different values of `screening` and
115 `dilatorb` were calculated and a combination of both was matched to the experimental data
116 set for obtaining best agreement. Furthermore, the total density of states (DOS) as well as

117 the individual projections of p and d -DOS at Oxygen K-edge for the $\text{Li}_2\text{FeSiO}_4$ structure¹⁹
118 were calculated³⁵ and are reported in S.I..

119 **2.4 X-ray Absorption Spectroscopy**

120 The sample preparation and experimental details for the complementary *operando* Fe K-edge
121 XAS study have been previously reported elsewhere.¹⁴

122 **3 Results**

123 **3.1 X-ray Raman Scattering**

124 A scheme of a typical electrochemical cycling curve of $\text{Li}_2\text{FeSiO}_4$ is depicted in Fig. 1,
125 along with seven red markers indicating the state of charge/ discharge of the prepared *post*
126 *mortem* samples. The charge (delithiation) comprises samples A to E, whereas A corresponds
127 to pristine material, D at the end of charge (EOC) at 4.7V, and E to EOC held for several
128 hours at 4.8V to ensure that the oxidation reaction reached equilibrium conditions. The
129 discharge (lithiation) comprises samples D to G, whereas G is the relithiated material after
130 one cycle. Although the discharge was incomplete at this point we will refer to this sample
131 as “end of discharge” (EOD) in the following. Due to experimental issues we were not able
132 to acquire spectra of a sample at a higher degree of discharge.

133 From the electrochemical cycling curve it is salient that more than the theoretical capacity
134 based on the transition metal redox couple $\text{Fe}^{2+} / \text{Fe}^{3+}$ is reversibly obtained when cycling
135 beyond 4.2V vs. Li^+/Li . Typically, not the complete extracted capacity during charge is
136 reversed upon discharge which can be mostly attributed to irreversible lithium extraction
137 and parasitic side reactions of the electrolyte. The latter is particularly strong when cycling
138 at elevated potential, as previously pointed out.¹⁴

139 The evolution of the oxygen K-edge upon charge and discharge is shown in Fig. 2. Two
140 main features can be identified. Firstly, the pre-edge peak related to the transition from

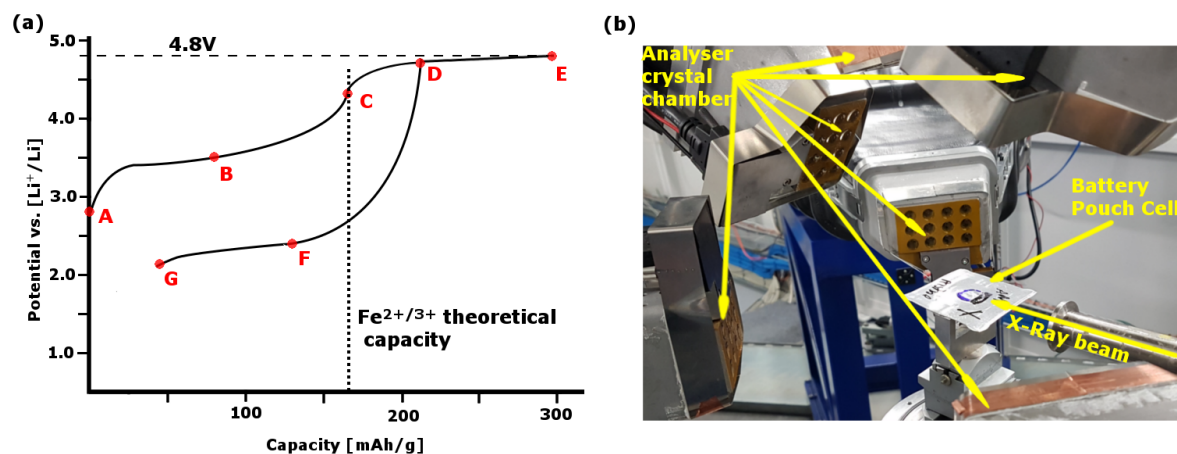


Figure 1: (a) Scheme of electrochemical cycling curve of $\text{Li}_2\text{FeSiO}_4$ vs. lithium. Red markers indicate the state of charge /discharge of the seven *post mortem* samples.(b) Experimental setup of pouch cell in grazing XRS.

141 $\text{O } 1s$ to the empty $\text{Fe } 3d$ mixed with $\text{O } 2p$ orbital at $\approx 531 \text{ eV}$. The position is well in line
 142 values reported in the literature³⁶ as well as with our *d*-DOS projection which illustrate
 143 that the pre-edge peak originates primarily from $\text{Fe } 3d$ states, see S.I.. The evolution of
 144 normalised pre-peak area shown in the inset was obtained by single peak fitting of the area
 145 marked by the hatched box. Secondly, the broad main peak associated to the excitation of
 146 oxygen $1s$ electrons above the Fermi level into the $\text{Fe } 4sp$ band hybridised with $\text{O } 2p$ states,
 147 centred around $\approx 539 \text{ eV}$. The absence of carbonate species in the oxygen spectra confirms
 148 the effective removal of SEI by ethanol washing procedure.³⁷

149 Upon charging an increase of the normalised intensity of pre-edge feature is observed
 150 which is in good agreement with the recent study by *Lu et al.* applying surface confined soft
 151 XAS.²⁷ According to *Yoon et al.* the pre-edge reveals important information about the hole
 152 state distribution and the effective charge on the oxygen atom since the density of empty
 153 bound state in molecular energy level is related to the hybridisation of the transition metal
 154 $3d$ - oxygen $2p$.³⁸ In this regard the observed increase in intensity, see inset Fig. 2 reflects the
 155 emptying of the *d*-orbitals, resulting from the oxidation of Fe^{+2} to Fe^{+3} . On the contrary to
 156 our findings, *Masese et al.* found no change of the pre-edge intensity for the extraction of
 157 the first lithium from $\text{Li}_2\text{FeSiO}_4$ structure. However, the authors report a strong increase in

158 the pre-edge intensity for extraction of more than one lithium per formula unit, which is in
 159 line with our observation of sample E, held several hours at elevated potential of 4.8 V. The
 160 authors attributed this to the formation of O 2*p* ligand holes, reflecting primary contribution
 161 of oxygen to the charge compensation process.¹⁹ However, their results are based on *ex situ*
 162 fluorescence yield detection XAS with limited number of samples and probing depth which
 163 penalises the reliability and representativeness.

164 Upon discharge the trend of pre-edge intensity increase is partially reversed, as shown in
 165 Fig. 2. While the intensity of the pre-edge intensity is effectively reduced upon discharge,
 166 at the highest state of discharge (sample G) a more pronounced pre-edge feature than for
 167 the pristine sample (A) is maintained. The irreversible phase transition from monoclinic
 168 to orthorhombic structure upon first delithiation^{17,39} could be partially accountable for the
 169 observed discrepancy between the charge and the discharge process.

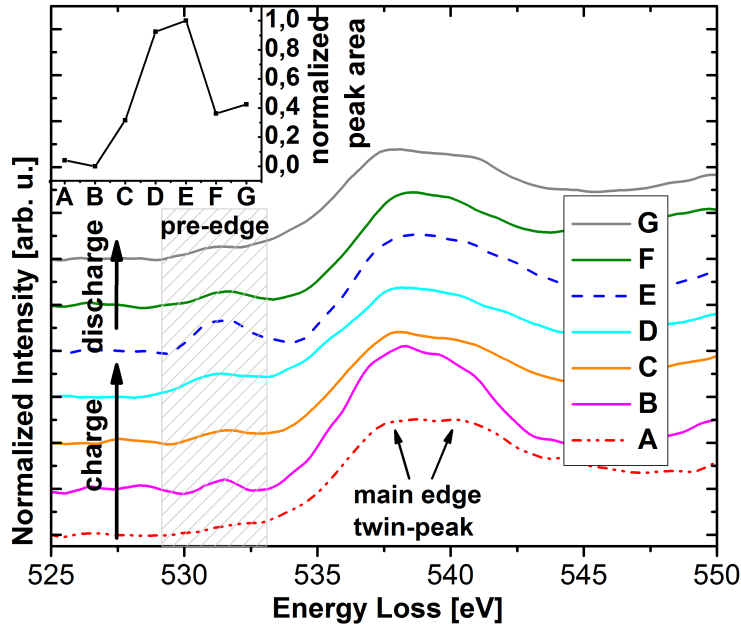


Figure 2: Evolution of oxygen K pre-edge (hatched box) and main edge during charge and discharge of bulk $\text{Li}_2\text{FeSiO}_4$ measured via X-ray Raman Scattering. The inset shows the evolution of normalised integrated pre-edge peak area within the hatched box.

170 To highlight the evolution of O 2*p* main edge spectra, a cumulative and constant stacking

171 of the spectra acquired during charge (sample A to E) and discharge (sample D to G) are
 172 presented in Fig. 3 (a) and (b), respectively. The position of the O 2p main edge remains
 173 largely unchanged upon electrochemical cycling indicating that oxidation state of lattice
 174 oxygen is globally maintained. However, Fig. 3 shows clearly that upon lithium deinsertion
 175 a gradual change in intensity ratio of main edge twin peak occurs, which points towards
 176 an alteration of oxygen orbitals during Li deinsertion process. Upon lithium reinsertion
 177 these changes of the O 2p band structure are partially reversed. Nevertheless, the trend is
 178 incomplete which could be connected to the fact that the discharge reaction was incomplete
 179 at sample G state as well as to the irreversible phase transformation upon first charge.

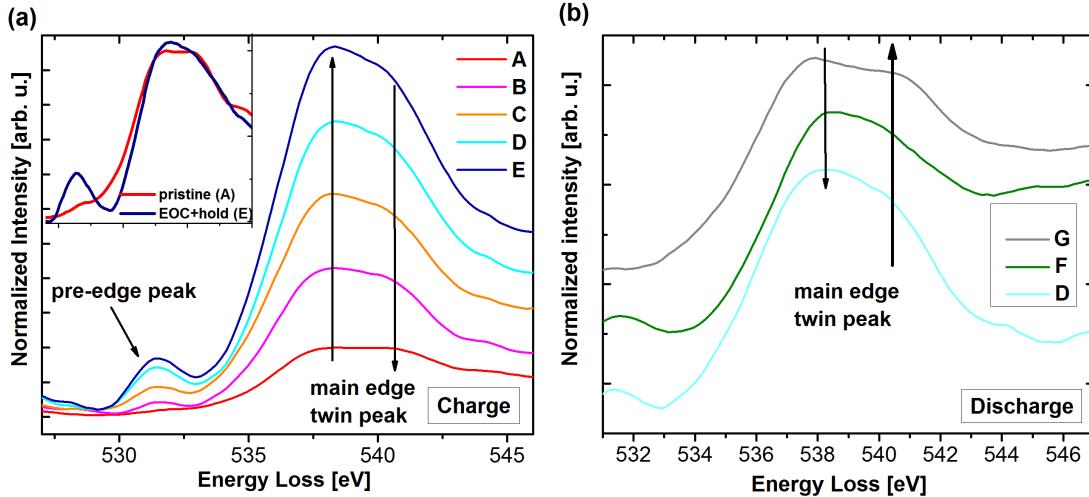


Figure 3: (a) Cumulative stacking of main oxygen K-edge spectra upon charge and inset without stacking. (b) Constant stacking of main oxygen K-edge spectra upon discharge. Arrows indicate the twin-peak intensity ratio changes.

180 3.2 Soft edge simulation

181 In order to gain a more fundamental understanding of the electronic structural changes the
 182 FDMNES code was used to simulate the spectra in an *ab initio* approach. Within this approach,
 183 the two semi empirical parameters `dilatorb` and `screening` were systematically adjusted to

184 reproduce the electronic configuration of the investigated material. The `dilatorb` parameter
 185 modifies the valence orbitals by dilating or contracting them, hence allowing one to alter the
 186 degree of covalency. This can be very useful for ionic materials to address the ionic species,
 187 for instance the oxygen the formal charge of O^{2-} where the atomic bases are calculated for
 188 neutral atoms. By changing the `screening` parameter the electronic charge in the non-full
 189 valence orbital of the absorber can be modified, by placing an additional electron on the first
 190 non-occupied state while the absorbing atom remains (almost) neutral.⁴⁰ Two matrices of
 191 different simulated spectra corresponding to gradually increasing values of `screening` and
 192 `dilatorb` were calculated and are presented in Fig. 4 (a) and (b), respectively. In Fig. 4(a)
 193 we show that an increase in `dilatorb` parameter leads primarily to a reduction of the pre-
 194 edge feature intensity accompanied by a shift to lower energy. The effect of the `screening`
 195 value, pictured in Fig. 4(b), is more complex as it leads to a change in intensity ratio of the
 196 pre-edge and main edge feature, but also strongly influences the shape of the latter. In this
 197 regard, the change of the intensity ratio of the twin-peak is particularly apparent.

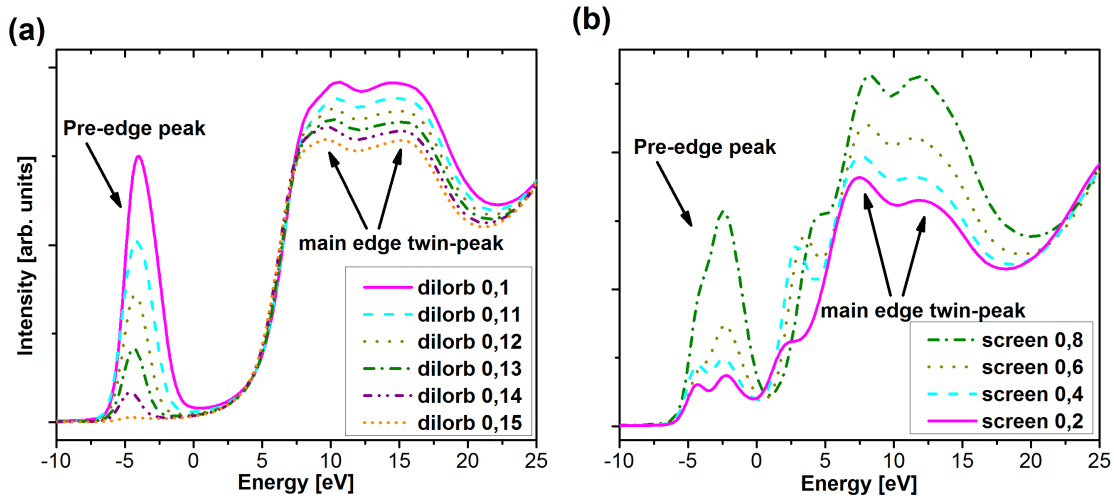


Figure 4: Influence of empirical parameters (a) `dilatorb` which alters covalency and (b) `screening` which changes electron confinement on the simulated spectra of Li_2FeSiO_4 using FDMNES code.

198 Subsequently, for a defined value of `dilatorb` another matrix with different values of

199 **screening** was simulated in order to achieve best agreement with the three experimental
200 spectra of samples pristine (A), end of charge plus hold (F), and end of discharge (G), see
201 Fig. 5. Within the examined energy range all main features of the electronic band structure
202 around the oxygen K-edge were reasonably well reproduced by applying **dilatorb** value of
203 0.09, and **screening** values of 0.7, and 0.8 for sample A, and E, respectively. By default
204 the **screening** value is one. The fact that the core hole charge is not completely screened
205 (partial electron charge missing) points to a correlation effect, caused by presence of the ex-
206 cited $3d$ electron, hindering the screening process.⁴⁰ The observed change of the **screening**
207 value indicates the modification of the local environment of oxygen upon delithiation. More
208 specifically, the 0.1 increase in **screening** value upon charge reflects a less filled state of the
209 d -orbital, which results in the rise of the pre-edge feature. This reduction in **screening** po-
210 tential is also accompanied by a reduction in electron confinement of the O $2p$ band resulting
211 in upwards shift of the Fermi level, which is in good agreement with recently published DFT
212 calculations.²¹ The observed reduction in electron confinement is furthermore in line with
213 previously reported shortening of Fe–O bond length, arising from an increase in covalency
214 and increased electron delocalisation upon delithiation.¹⁷

215 The changes of the shape of the O $2p$ main edge during charge and discharge, which are
216 shown in Fig. 3, reflect the rearrangement of oxygen orbitals and the redistribution of charge
217 during electrochemical lithium extraction and insertion. The fact that the intensity ratio of
218 the twin-peak can be partially reproduced using the **screening** parameter, shown in Fig.
219 4(b), connotes that the observed changes are linked to a change in electron confinement and a
220 $3d$ electron correlation effect upon charge. A lowering of electron confinement at the oxygen
221 upon charge implies an increased sharing of the charge with the transition metal. In this
222 sense the observed changes in electronic structure suggests that oxygen provides charge for
223 the $\text{Fe}^{2+} / \text{Fe}^{3+}$ redox couple throughout the electrochemical reaction which could sustain the
224 reversible extraction of more than one lithium per formula unit. Regrettably, the resolution
225 of the experimental data not allow us to interpret the O $2p$ spectra in more detail.

226 For the sample at lowest state of discharge (sample G), best agreement of simulation and
227 experimental data was achieved applying the same value of `screening` as for the pristine
228 sample (A). This implies that changes of electron confinement are largely reversible. Nev-
229 ertheless, a slightly elevated `dilatorb` value was found, indicating a change in covalency of
230 the bond.

231 The disagreement of the simulated spectra compared to experimental data for the energy
232 range beyond the main edge features stems from the complex data extraction process. In
233 the here presented results the emphasis of data extraction procedure lay on elucidating the
234 energy range of pre-edge feature. By adequately adjusting the extraction parameters a better
235 agreement for the spectra beyond first O $2p$ feature can be achieved. However, this comes
236 as a trade-off for the agreement in the pre-edge feature range. In this regard, it should
237 be also noted that the electrode samples in pouch cell assembly used for this spectroscopic
238 investigation were optimised for their electrochemical performance and not for scattering
239 yield.

240 **3.3 Fe L-edge**

241 Similarly to the O K-edge, XRS was used to probe the Fe L_3 -edges. L-edges are arguably the
242 most direct probe of TM redox activity. Besides formal valence the $3d$ L-edges fingerprint the
243 spin-state as well as chemical bond configuration via the $2p$ to $3d$ electron excitation. The
244 evolution of Fe L_3 -edge spectra upon charge and discharge of $\text{Li}_2\text{FeSiO}_4$ are illustrated in Fig.
245 6 (a) and (b), respectively. The spectra of the Fe L_3 -edge which derives from the $2p_{3/2} \rightarrow 3d$
246 transition is composed of two main features centred at 708.2 and 709.8 eV. Upon charge a
247 change of peak intensity ratio from ≈ 708 to 710 eV is observed. This is in good agreement
248 with evolution of pre-edge features of Fe K-edge upon charge shown in the inset of Fig. 6a.
249 Please refer to the S.I. for complete XANES spectra and enlarged version pre-edge evolution
250 graph. The good agreement between complementary iron K-edge XAS results and L-edge
251 XRS underline that XRS is an effective and reliable method to probe electron transition

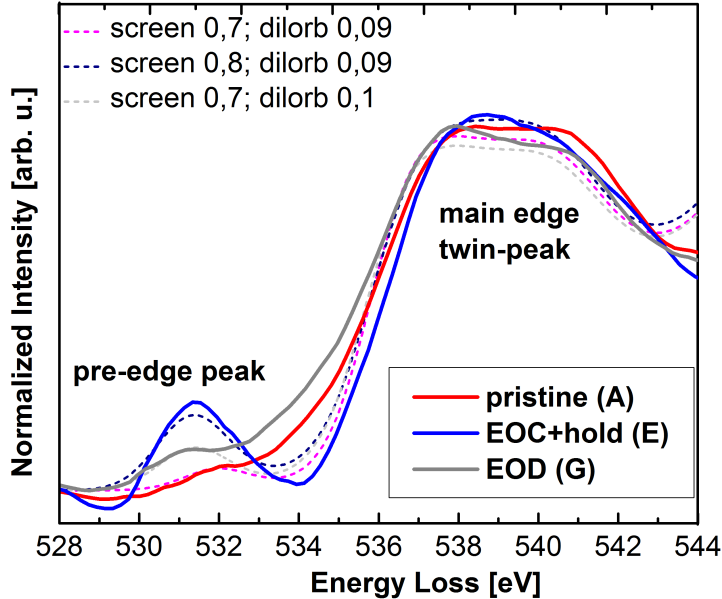


Figure 5: Experimental spectra (solid lines) and FDMNES simulated spectra (dotted lines) of the oxygen K-edge of $\text{Li}_2\text{FeSiO}_4$ of pristine (sample A), end of charge + holding at 4.8 V (EOC+hold, sample E) and end of discharge (EOD, sample G).

252 of redox active d -orbitals via direct $2p \rightarrow 3d$ transition of the L-edge, with the benefit of
 253 significantly higher intensity than indirect dipole forbidden $1s \rightarrow 3d$ K-edge pre-edge features
 254 via XAS. The observed peak intensity shift is well in line with the values reported in the
 255 literature for a $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ transformation.^{2,27,41,42} The continuous increase of Fe^{3+} peak
 256 for the sample held at elevated potential (E) indicates that the oxidation from the ferrous
 257 to the ferric state was incomplete at sample D stage, which can be attributed to kinetic
 258 hindrance due to sluggish charge transfer.⁴³ Although the experimental resolution does not
 259 allow us to exclude the oxidation beyond Fe(III) with certainty, the formation of Fe(IV) has
 260 been rebutted by a complementary *operando* XANES analysis, see S.I., as well as in multiple
 261 other studies.^{15,19–21} It should be noted that the pristine sample contained a slight share of
 262 Fe^{3+} originating from phase impurities.

263 Upon discharge the changes of the Fe L_3 -edge are only partially reversed and the initial
 264 state of pristine is not recovered, analogously to our observation for the O K-edge, see Fig.

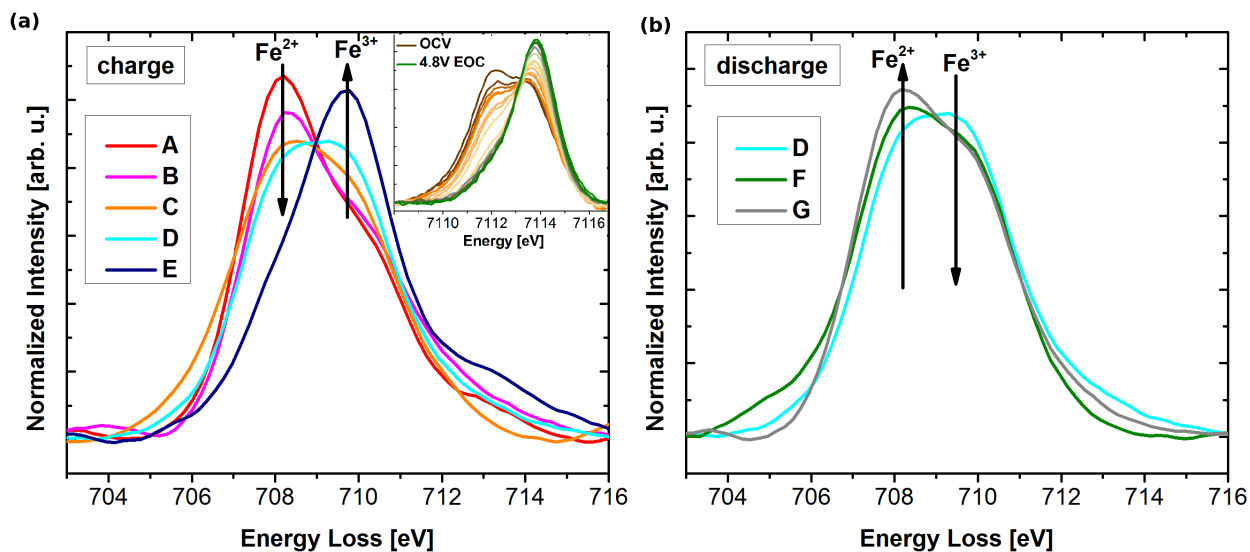


Figure 6: Iron L_3 -edge evolution during (a) charge and (b) discharge of $\text{Li}_2\text{FeSiO}_4$ measured via X-ray Raman Scattering. The inset depicts evolution of Fe K-edge pre-edge features obtained via XAS, see S.I. for enlarged version.

265 6(b), inset of Fig. 2, and Fig. 3(b), respectively. This irreversibility is attributed to the
 266 incomplete state of discharge of sample G, as well as irreversible structural transformation
 267 during initial charge, *vide supra*. Fig. 6(b), inset of Fig 2, and Fig. 3(b), respectively

268 4 Discussion

269 The above presented results highlight the effectiveness and usefulness of X-ray Raman scat-
 270 tering spectroscopy for accessing bulk electronic structure information to elucidate the com-
 271 plex electrochemical charge transfer process in electrode materials. Additionally we demon-
 272 strate that the observed electronic structural changes can be reproduced for intermediate
 273 states of charge by the FDMNES code which could have been hardly achieved applying DFT
 274 calculations. In detail, our results show that the electrochemical activity of $\text{Li}_2\text{FeSiO}_4$ is
 275 primarily based on $\text{Fe}^{2+/3+}$ redox centre. XRS reveals a reversible shift in Fe L_3 edge cor-
 276 responding to the oxidation of Fe^{2+} to Fe^{3+} , which are supported by complementary XAS
 277 results. Furthermore, XRS allowed us to monitor the change in occupancy of the hybridised
 278 oxygen orbitals which result in a change of intensity of the oxygen K-edge pre-edge fea-

279 ture. Moreover, our findings show that the charge distribution of oxygen changes during the
280 lithium extraction process, notably an increased delocalisation of oxygen electron at EOD.
281 Whether the alteration of the main edge is also linked the enhanced metal-oxygen hybridi-
282 sation or indicates an additional charge compensation by lending electrons to the $\text{Fe}^{2+/3+}$
283 redox couple, can not be answered with certainty based on these results. Although the role
284 of oxygen can not be determined beyond doubt within this study, it is certain that it plays
285 an important role for preserving electronic and structural stability of the host material by
286 preventing the formation of unstable Fe^{4+} . The oxygen contribution suggested by our XRS
287 spectroscopy analysis is therefore much more subtle and uncertain than previously claimed in
288 calculation-based predictions^{15,21,28} or surface confined soft XAS^{19,27} studies which somewhat
289 frivolously attribute changes of oxygen pre-edge feature directly to anodic charge contribu-
290 tion instead of metal-oxygen hybridisation. We like to highlight that our findings represent
291 bulk electrode information and reflect therefore the electronic structure of lattice elements
292 of the full electrode. Nevertheless, a major anodic charge compensation that would explain
293 most of the additional reversible capacity observed was not confirmed by our study. There-
294 fore, previously suggested phenomena such as rich surface chemistry are to be considered to
295 explain the observed additional capacity.^{14,44}

296 By using a pouch cell assembly we demonstrated that the XRS technique offers the possi-
297 bility to work under sample relevant conditions with the potential of carrying out experiments
298 *in situ* configuration. Nevertheless, the challenge of overlapping spectral contribution from
299 other oxygen containing battery components (electrolyte, SEI, etc.) needs to be addressed.
300 Also, the reduction of background scattering and increase of signal-to-noise ratio is a crucial
301 requirement for reduced acquisition time that would permit *operando* measurements. The
302 recently published *in situ* XRS study on Li intercalation in graphite using a confocal-like
303 setup is an encouraging step in this direction.⁴⁵

304 Improving energy resolution of XRS spectroscopy remains a challenge for complex sam-
305 ples such as electrode materials due to strong parasitic scattering. Tailored sample holders

306 which effectively shield non-desired scattering contribution could lead to much increased
307 signal-to-noise ratio which will enhance reliability as well as reduce acquisition time.

308 Interestingly, XRS also allows the combination of depth profiling as well as 2D mapping
309 which could be coupled to perform a 3D screening of an electrode, unveiling exciting insights
310 on propagation of electrochemical reaction front propagation.^{46,47}

311 5 Conclusion

312 We have demonstrated that X-ray Raman scattering spectroscopy can be conveniently ap-
313 plied to probe bulk soft x-ray edges of both anionic and cathodic redox pairs to elucidate
314 the charge transfer process upon electrochemical cycling in battery materials. For the first
315 time we applied XRS to closely follow the change in electronic structure of polyanionic cath-
316 ode material $\text{Li}_2\text{FeSiO}_4$, monitoring the evolution of O $2p$ and Fe $3d$ orbitals concurrently
317 at distinct points during one complete electrochemical cycle, without cumbersome sample
318 preparation or the need for sophisticated sample environment. Furthermore, we show that
319 the FDMNES code is a suitable tool to reproduce soft edge spectra of intermediate states of the
320 redox reaction, allowing deeper insights into the electronic structural changes. Our findings
321 reveal a gradual emptying and filling of $3d$ orbitals upon charge and discharge, respectively,
322 reflecting the primary redox activity of the transition metal. Besides the evident enhanced
323 metal-oxygen hybridisation reflected by the oxygen pre-edge rise, the changes of charge dis-
324 tribution of O $2p$ could not be attributed with certainty. To the best of our knowledge the
325 XRS spectroscopy presented in this study is currently the only available technique that al-
326 lows studying soft edge electronic structures of bulk materials. Thus, providing the scientific
327 battery community with a tool to elucidate the ambiguity between surface vs. bulk as well
328 as unveiling anionic charge compensation contribution of low Z elements on the bulk level
329 of electrode materials.

330 Acknowledgements

331 Alistore-European Research Institute is gratefully acknowledged for financial support through
332 the postdoc grant to M. Fehse. ESRF and NWO are acknowledged for providing synchrotron
333 radiation beamtime at beamline ID20 and BM26A, respectively. The authors furthermore
334 like to thank Y. Joly for valuable comments and suggestion concerning the FDMNES simula-
335 tion.

336 Supporting Information

337 XRS spectra of quasi-elastic scattering and inelastic Li $1s$ peaks. Projection of individual
338 and total density of states for O K-edge of $\text{Li}_2\text{FeSiO}_4$. *Operando* Fe K-edge XANES during
339 first charge of $\text{Li}_2\text{FeSiO}_4$.

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