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

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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 \textit{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 Li$_2$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 \textit{ab initio} based simulation.

\textbf{Keywords}

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

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

Thanks to being composed of abundant, low-cost, environmental benign, and non-toxic elements Li$_2$FeSiO$_4$ has received great interest as an alternative cathode material for LIB, since the discovery of its electrochemical activity more than a decade ago. Its stability is at least as high as commercialised LiFePO$_4$ (LFP) but features potentially increased energy and power density owing to the elevated intercalation potential and the faster charge transport. Its complex polymorphism has been intensively studied and is mostly under-
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.\textsuperscript{18} and experimentally claimed by Lv et al.\textsuperscript{13} was not supported by later studies.\textsuperscript{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.\textsuperscript{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 Li$_2$FeSiO$_4$.\textsuperscript{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,\textsuperscript{19} later studies suggest active participation of oxygen already at an earlier stage in the redox process.\textsuperscript{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.\textsuperscript{21}

Unfortunately, all of the previously published studies on the elucidation of charge compensation mechanism in Li$_2$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
such surface confined spectroscopic measurements greatly depend on the sample preparation method and conditions.

To overcome the experimental limitations of soft XAS and obtain a more reliable and exhaustive picture of the electronic structure than theoretical studies can provide, we present here a thorough bulk study of anionic O 2p and cathodic TM 3d electronic states of Li2FeSiO4 cathode material at different states during one complete electrochemical cycle using XRS spectroscopy.

2 Experimental

2.1 Sample and Electrode Preparation

Synthesis of electrode material has been described elsewhere. All samples were taken from the same electrode casting batch and have identical electrode loading and composition. The electrode thickness is about 30 µm the particle size is in the sub-micrometer range. The active material electrodes were mounted in electrochemical half-cells with lithium metal as counter and reference electrode. The cells were cycled in EC:DEC (1:1) with 1 M LiPF6 at C/6 rate, whereas 1 C corresponds to deinsertion/insertion of one lithium per formula unit in one hour, 165 mA g$^{-1}$. For the ex-situ cells used in this experiment the rested and cycled batteries were opened in an argon filled glovebox, electrodes were removed and washed thoroughly with anhydrous ethanol to remove electrolyte remnants and any SEI formed, primarily to minimise the oxygen spectral contribution from carbonate species. The washed electrodes were dried under vacuum and were then vacuum sealed under argon, in laminated pouch cells with aluminium windows (Al thickness 15 µm) in the centre of the pouch on both sides.

2.2 X-ray Raman Scattering

All X-ray Raman scattering (XRS) spectroscopy data were gathered at the beamline ID20 of the ESRF. The pink beam from four U26 undulators was monochromatized using a cryogeni-
cally cooled Si(111) monochromator and focused to a spot size of approximately 10 µm × 20 µm (V × H) at the sample position using a mirror system in Kirkpatrick-Baez geometry. The large solid angle spectrometer at ID20 was used to collect XRS data with 36 spherically bent Si(660) analyser crystals. The data were treated with the XRStools program package as described elsewhere. The ex situ electrodes, sealed in pouch cells, were placed at an incident beam angle of ≈ 10° into the beam. The beam position was verified by the presence of Li 1s peak at ≈ 55 eV, see spectra in S.I.. All measurements were collected at room temperature. Acquisition scans lasted around 10-14 h per sample. We collected several scans of the oxygen K-edge by scanning the incident beam energy to create energy losses in the vicinity of the oxygen K-edge. All scans were checked for consistency and signals from different analyser crystals were averaged over. The overall energy resolution was 1.0 eV, and the mean momentum transfer was 6.2 ± 0.4 Å⁻¹. All spectra have been normalised and a smoothing function has been applied to the spectra presented.

2.3 Simulation

To elucidate the electronic structure of the material, O K-edge ab initio simulation were performed using the Finite Difference Method Near Edge Structure (FDMNES) software package. The simulation have been performed by using the multiple scattering theory based on the muffin-tin approximation on the potential shape on the Green scheme. The muffin-tin radii were tuned to have a good overlap between the different spherical potentials. A non-relativistic calculation was performed and the Hedin-Lundqvist exchange potential was used. The approximation of non-excited absorbing atoms was used which, in this case, best reproduces the experimental data. The semi-empirical parameters screening and dilatorb were used to reproduce the electronic configuration of the material. In this respect, two matrices of different simulated spectra corresponding to different values of screening and dilatorb were calculated and a combination of both was matched to the experimental data set for obtaining best agreement. Furthermore, the total density of states (DOS) as well as
the individual projections of $p$ and $d$-DOS at Oxygen K-edge for the Li$_2$FeSiO$_4$ structure were calculated and are reported in S.I..

2.4 X-ray Absorption Spectroscopy

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

3 Results

3.1 X-ray Raman Scattering

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

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

The evolution of the oxygen K-edge upon charge and discharge is shown in Fig. 2. Two main features can be identified. Firstly, the pre-edge peak related to the transition from
Figure 1: (a) Scheme of electrochemical cycling curve of Li$_2$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.

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

Upon charging an increase of the normalised intensity of pre-edge feature is observed which is in good agreement with the recent study by Lu et al. applying surface confined soft XAS. According to Yoon et al. the pre-edge reveals important information about the hole state distribution and the effective charge on the oxygen atom since the density of empty bound state in molecular energy level is related to the hybridisation of the transition metal 3$d$- oxygen 2$p$. In this regard the observed increase in intensity, see inset Fig. 2 reflects the emptying of the d-orbitals, resulting from the oxidation of Fe$^{+2}$ to Fe$^{+3}$. On the contrary to our findings, Masese et al. found no change of the pre-edge intensity for the extraction of the first lithium from Li$_2$FeSiO$_4$ structure. However, the authors report a strong increase in
the pre-edge intensity for extraction of more than one lithium per formula unit, which is in line with our observation of sample E, held several hours at elevated potential of 4.8 V. The authors attributed this to the formation of O 2p ligand holes, reflecting primary contribution of oxygen to the charge compensation process. However, their results are based on ex situ fluorescence yield detection XAS with limited number of samples and probing depth which penalises the reliability and representativeness.

Upon discharge the trend of pre-edge intensity increase is partially reversed, as shown in Fig. 2. While the intensity of the pre-edge intensity is effectively reduced upon discharge, at the highest state of discharge (sample G) a more pronounced pre-edge feature than for the pristine sample (A) is maintained. The irreversible phase transition from monoclinic to orthorhombic structure upon first delithiation could be partially accountable for the 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 Li₂FeSiO₄ measured via X-ray Raman Scattering. The inset shows the evolution of normalised integrated pre-edge peak area within the hatched box.

To highlight the evolution of O 2p main edge spectra, a cumulative and constant stacking
of the spectra acquired during charge (sample A to E) and discharge (sample D to G) are presented in Fig. 3 (a) and (b), respectively. The position of the O\textsubscript{2}p main edge remains largely unchanged upon electrochemical cycling indicating that oxidation state of lattice oxygen is globally maintained. However, Fig. 3 shows clearly that upon lithium deinsertion a gradual change in intensity ratio of main edge twin peak occurs, which points towards an alteration of oxygen orbitals during Li deinsertion process. Upon lithium reinsertion these changes of the O\textsubscript{2}p band structure are partially reversed. Nevertheless, the trend is incomplete which could be connected to the fact that the discharge reaction was incomplete 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.

### 3.2 Soft edge simulation

In order to gain a more fundamental understanding of the electronic structural changes the FDMNES code was used to simulate the spectra in an \textit{ab initio} approach. Within this approach, the two semi empirical parameters \texttt{dilatorb} and \texttt{screening} were systematically adjusted to
reproduce the electronic configuration of the investigated material. The dilatorb parameter modifies the valence orbitals by dilating or contracting them, hence allowing one to alter the degree of covalency. This can be very useful for ionic materials to address the ionic species, for instance the oxygen the formal charge of $\text{O}^{2-}$ where the atomic bases are calculated for neutral atoms. By changing the screening parameter the electronic charge in the non-full valence orbital of the absorber can be modified, by placing an additional electron on the first non-occupied state while the absorbing atom remains (almost) neutral.\textsuperscript{40} Two matrices of different simulated spectra corresponding to gradually increasing values of screening and dilatorb were calculated and are presented in Fig. 4 (a) and (b), respectively. In Fig. 4(a) we show that an increase in dilatorb parameter leads primarily to a reduction of the pre-edge feature intensity accompanied by a shift to lower energy. The effect of the screening value, pictured in Fig. 4(b), is more complex as it leads to a change in intensity ratio of the pre-edge and main edge feature, but also strongly influences the shape of the latter. In this regard, the change of the intensity ratio of the twin-peak is particularly apparent.

![Figure 4](image_url)

Figure 4: Influence of empirical parameters (a) dilatorb which alters covalency and (b) screening which changes electron confinement on the simulated spectra of $\text{Li}_2\text{FeSiO}_4$ using FDMNES code.

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

The changes of the shape of the O 2p main edge during charge and discharge, which are shown in Fig. 3, reflect the rearrangement of oxygen orbitals and the redistribution of charge during electrochemical lithium extraction and insertion. The fact that the intensity ratio of the twin-peak can be partially reproduced using the screening parameter, shown in Fig. 4(b), connotes that the observed changes are linked to a change in electron confinement and a 3d electron correlation effect upon charge. A lowering of electron confinement at the oxygen upon charge implies an increased sharing of the charge with the transition metal. In this sense the observed changes in electronic structure suggests that oxygen provides charge for the Fe^{2+} / Fe^{3+} redox couple throughout the electrochemical reaction which could sustain the reversible extraction of more than one lithium per formula unit. Regrettably, the resolution of the experimental data not allow us to interpret the O 2p spectra in more detail.
For the sample at lowest state of discharge (sample G), best agreement of simulation and experimental data was achieved applying the same value of screening as for the pristine sample (A). This implies that changes of electron confinement are largely reversible. Nevertheless, a slightly elevated dilatorb value was found, indicating a change in covalency of the bond.

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

3.3 Fe L-edge

Similarly to the O K-edge, XRS was used to probe the Fe L₃-edges. L-edges are arguably the most direct probe of TM redox activity. Besides formal valence the 3d L-edges fingerprint the spin-state as well as chemical bond configuration via the 2p to 3d electron excitation. The evolution of Fe L₃-edge spectra upon charge and discharge of Li₂FeSiO₄ are illustrated in Fig. 6 (a) and (b), respectively. The spectra of the Fe L₃-edge which derives from the 2p₃/₂ → 3d transition is composed of two main features centred at 708.2 and 709.8 eV. Upon charge a change of peak intensity ratio from ≈ 708 to 710 eV is observed. This is in good agreement with evolution of pre-edge features of Fe K-edge upon charge shown in the inset of Fig. 6a.

Please refer to the S.I. for complete XANES spectra and enlarged version pre-edge evolution graph. The good agreement between complementary iron K-edge XAS results and L-edge XRS underline that XRS is an effective and reliable method to probe electron transition
of redox active $d$-orbitals via direct $2p \rightarrow 3d$ transition of the L-edge, with the benefit of significantly higher intensity than indirect dipole forbidden $1s \rightarrow 3d$ K-edge pre-edge features via XAS. The observed peak intensity shift is well in line with the values reported in the literature for a Fe$^{2+} \rightarrow$ Fe$^{3+}$ transformation.\textsuperscript{2,27,41,42} The continuous increase of Fe$^{3+}$ peak for the sample held at elevated potential (E) indicates that the oxidation from the ferrous to the ferric state was incomplete at sample D stage, which can be attributed to kinetic hindrance due to sluggish charge transfer.\textsuperscript{43} Although the experimental resolution does not allow us to exclude the oxidation beyond Fe(III) with certainty, the formation of Fe(IV) has been rebutted by a complementary \textit{operando} XANES analysis, see S.I., as well as in multiple other studies.\textsuperscript{15,19–21} It should be noted that the pristine sample contained a slight share of Fe$^{3+}$ originating from phase impurities.

Upon discharge the changes of the Fe L$_3$-edge are only partially reversed and the initial 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 Li$_2$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.  

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

4 Discussion

The above presented results highlight the effectiveness and usefulness of X-ray Raman scattering spectroscopy for accessing bulk electronic structure information to elucidate the complex electrochemical charge transfer process in electrode materials. Additionally we demonstrate that the observed electronic structural changes can be reproduced for intermediate states of charge by the FDMNES code which could have been hardly achieved applying DFT calculations. In detail, our results show that the electrochemical activity of Li$_2$FeSiO$_4$ is primarily based on Fe$^{2+}$/3+ redox centre. XRS reveals a reversible shift in Fe L$_3$ edge corresponding to the oxidation of Fe$^{2+}$ to Fe$^{3+}$, which are supported by complementary XAS results. Furthermore, XRS allowed us to monitor the change in occupancy of the hybridised oxygen orbitals which result in a change of intensity of the oxygen K-edge pre-edge fea-
ture. Moreover, our findings show that the charge distribution of oxygen changes during the lithium extraction process, notably an increased delocalisation of oxygen electron at EOD. Whether the alteration of the main edge is also linked the enhanced metal-oxygen hybridisation or indicates an additional charge compensation by lending electrons to the Fe$^{2+/3+}$ redox couple, can not be answered with certainty based on these results. Although the role of oxygen can not be determined beyond doubt within this study, it is certain that it plays an important role for preserving electronic and structural stability of the host material by preventing the formation of unstable Fe$^{4+}$. The oxygen contribution suggested by our XRS spectroscopy analysis is therefore much more subtle and uncertain than previously claimed in calculation-based predictions$^{15,21,28}$ or surface confined soft XAS$^{19,27}$ studies which somewhat frivolously attribute changes of oxygen pre-edge feature directly to anodic charge contribution instead of metal-oxygen hybridisation. We like to highlight that our findings represent bulk electrode information and reflect therefore the electronic structure of lattice elements of the full electrode. Nevertheless, a major anodic charge compensation that would explain most of the additional reversible capacity observed was not confirmed by our study. Therefore, previously suggested phenomena such as rich surface chemistry are to be considered to explain the observed additional capacity.$^{14,44}$

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

Improving energy resolution of XRS spectroscopy remains a challenge for complex samples such as electrode materials due to strong parasitic scattering. Tailored sample holders
which effectively shield non-desired scattering contribution could lead to much increased
signal-to-noise ratio which will enhance reliability as well as reduce acquisition time.

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

5 Conclusion

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

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

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