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Journal

Nature Energy, 4(11)

ISSN

2058-7546

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Publication Date

2019-11-01

DOI

10.1038/s41560-019-0493-0

Peer reviewed

Exploring the Bottlenecks of Anionic Redox in Li-rich Layered Sulfides

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Abstract

To satisfy the long-awaited need of new lithium-ion battery cathode materials with higher energy density, anionic redox chemistry has emerged as a new paradigm that is responsible for the high capacity in Li-rich layered oxides, for example, in $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ (Li-rich NMC). However, their market-implementation has been plagued by certain bottlenecks originating intriguingly from the anionic redox activity itself. To fundamentally understand these bottlenecks (voltage fade, hysteresis and sluggish kinetics), we decided to target the ligand by switching to isostructural Li-rich layered sulfides. Herein, we designed new $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ cathodes that enlist sustained reversible capacities of $\sim 245 \text{ mAh}\cdot\text{g}^{-1}$ due to cumulated cationic ($\text{Fe}^{2+/3+}$) and anionic ($\text{S}^{2-} / \text{S}^{n-}$, $n < 2$) redox processes. In-depth electrochemical analysis revealed nearly zero irreversible capacity during the initial cycle, very small voltage fade upon long cycling, with low voltage hysteresis and fast kinetics, which contrasts positively with respect to their Li-rich NMC oxide analogues. Our study, further complemented with DFT calculations, demonstrates that moving from oxygen to sulfur as the ligand is an adequate strategy to partially mitigate the practical bottlenecks affecting anionic redox, although with an expected penalty in cell voltage. Altogether the present findings provide chemical clues on improving the holistic performance of anionic redox electrodes via ligand tuning, and hence strengthen the feasibility to ultimately capitalize on the energy benefits of oxygen redox.

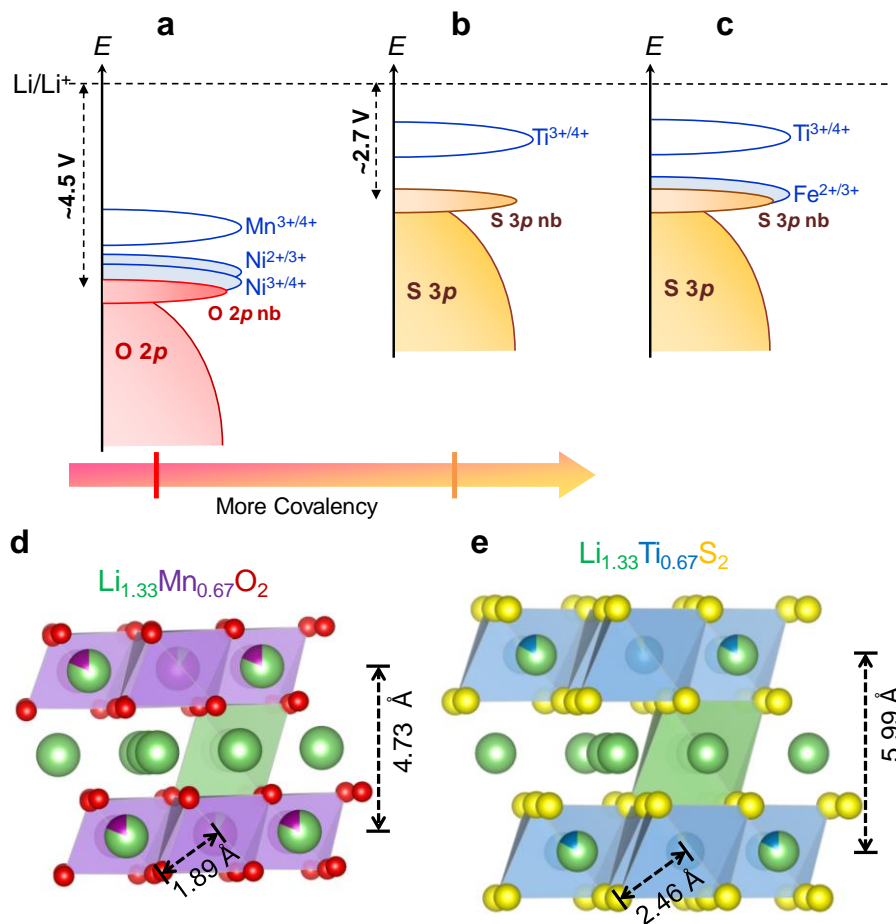
37 Introduction

38 Over the past three decades, Li-ion batteries (LIB) have revolutionized the portable electronics
39 industry, while more recently reorienting the automotive industry by enabling electric vehicles.^{1,2} To comply
40 with the ever-growing demands of energy for such applications, increasing the energy density of LIBs has
41 become a formidable challenge. For many years, the cathode materials in LIBs relied solely on the transition
42 metal (cationic) redox, until the recently discovered anionic redox, i.e., electrochemical participation of the
43 oxygen ligands, became a new approach for designing higher energy cathode materials. Li-rich Mn-based
44 layered oxides, for example, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ (Li-rich NMC) hold the highest
45 promises in this regard, as these cathodes can deliver a specific energy approaching $\sim 1000 \text{ Wh}\cdot\text{kg}^{-1}$ at the
46 material-level. These materials can potentially replace the currently used NMCs (e.g. $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$,
47 $\sim 700 \text{ Wh}\cdot\text{kg}^{-1}$). Thanks to a decade of intense research, it is now well established that the anomalous extra
48 capacity of Li-rich cathodes arises from the redox of O^{2-} anions, more specifically the ‘non-bonding’ O $2p$
49 orbitals that point towards excess-Li in the metal layers.³⁻⁸ Invigorated by this fundamental understanding,
50 solid-state chemists have extended the concept of oxygen redox to cation-disordered $\text{Li}_{1+y}\text{M}_{1-y}\text{O}_2$ (M = Nb,
51 Mn, Ti, Fe, V ...) as well as Na-based layered oxides.⁹⁻¹¹ Despite this rich materials design-space, certain
52 practical issues, such as voltage fade, poor kinetics, voltage hysteresis, and irreversible O_2 loss, have delayed
53 the commercialization of Li-rich NMCs.¹² Although the crucial role of oxygen redox towards these issues
54 was clearly highlighted by detailed investigations on a ‘practical’ Li-rich NMC and also on a ‘model’
55 $\text{Li}_{1.33}\text{Ru}_{0.5}\text{Sn}_{0.17}\text{O}_2$ electrode, much remains to be understood for further fundamental insights that will
56 ultimately lead to implementable solutions.¹²⁻¹⁴ Therefore, time has come to reinject the Li-rich systems
57 with a fresh perspective towards the above-mentioned practical roadblocks observed in oxides. So far, only
58 two materials-composition parameters were explored in Li-rich layered oxides, i.e. (i) going down from $3d$
59 Mn to $4d$ Ru and $5d$ Ir for stabilizing oxygen redox and (ii) increasing the Li-rich character to access higher
60 capacity (e.g. Li_3IrO_4).¹⁵⁻¹⁷ More recently, a third approach with mild success has emerged, that is to tune
61 the ligand by increasing electronegativity of the anionic sublattice via substituting fluorine for oxygen, but
62 so far limited only to disordered rocksalt structures.^{18,19} Herein, we decided to explore a fourth direction by
63 replacing the ligand oxygen with sulfur to design new Li-rich layered sulfides. Because sulfur is larger,
64 softer and less electronegative compared to oxygen, anionic redox in sulfides can be expected to behave
65 differently and possibly provide clues towards better performances.

66 Early sulfide electrodes, although long forgotten after the emergence of layered oxide cathodes,
67 played a crucial historical role. To recall, the path towards modern Li-ion technology was paved by attempts
68 of commercialization of Li-free layered transition-metal chalcogenides, such as TiS_2 , MoS_2 etc., way back
69 in the 1970s, which was rapidly terminated because of safety issues due to Li-metal dendrite formation.^{20,21}
70 Interestingly, unlike oxides, stable ligand-hole chemistry was well-known in sulfides, e.g., TiS_3 (believed
71 to exist as $\text{Ti}^{4+}\text{S}^{2-}(\text{S}_2)^{2-}$), $\text{Fe}^{2+}(\text{S}_2)^{2-}$, etc., since the pioneering works by Rouxel *et al.*^{22,23} In such materials,
72 S exists fully or partially as dimerized $\text{S}^-\text{—S}^-$ pairs and undergoes breaking of S—S bonds to regain the
73 standard S^{2-} state upon electrochemical insertion of Li.²⁴⁻²⁹ However, Li (de)intercalation is only partly
74 reversible in such materials besides rapid capacity fading.³⁰⁻³² Further studying the poly-sulfides such as
75 TiS_4 and VS_4 , mainly for their conversion-type mechanism leading to large capacities at low potential,
76 researchers have noted that such compounds were also enlisting sulfur redox activity.³³⁻³⁷ Similarly, by
77 reinvestigating the crystalline LiMS_2 (M = Ti, V, Cr, Fe) layered sulfides directly prepared from solid-state
78 reactions, scientists also found that in some of these phases, both Li removal and insertion are possible, but
79 it remains unclear whether the process involves anionic besides cationic redox activity.³⁸⁻⁴⁰ Thus,

80 deciphering the sulfur redox process in such compounds could be of paramount importance to further
81 understand the oxygen redox in Li-rich layered oxides.

82 Li-rich NMCs are derived from the layered $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ (commonly written as Li_2MnO_3) with
83 their anionic redox activity being a function of the competition between U (d - d coulomb interaction) and Δ
84 (charge transfer) terms.⁴¹ Preparing a similar Li-rich Mn-based layered sulfide is not possible, simply
85 because the S $3p$ band is situated much closer to the Li/Li⁺ reference than the O $2p$ band, leaving the Mn^{3+/4+}
86 redox band too low-lying, see Figure 1a,b. Hence to design an analogous layered sulfide $\text{Li}_{1.33}\text{M}_{0.67}\text{S}_2$, an
87 appropriate transition metal M needs to be chosen first. Amongst $3d$ metals, M = Ti⁴⁺ presents the best
88 choice for sulfides, because the Ti^{3+/4+} redox band is located above the S $3p$ band. However, since Ti⁴⁺ has
89 $3d^0$ electronic configuration, $\text{Li}_{1.33}\text{Ti}_{0.66}\text{S}_2$ is apparently electrochemically inactive, as shown recently, even
90 though it has a high theoretical capacity of 339 mAh·g⁻¹ (considering removal of all Li's).⁴² This situation
91 reminds that of the $\text{Li}_{1.33}\text{Mn}_{0.67}\text{O}_2$ phase (poor electrochemical performance without nano-sizing) that
92 required partial substitution with Ni²⁺ to instigate electrochemical activity (Figure 1a).⁴³⁻⁴⁵ A first hint to
93 address this problem in sulfides consists, as discussed by Li *et al.*, in using Co²⁺ as a substituent (owing to
94 its large U and small Δ) to initiate reversible anionic redox.⁴² Pursuing their idea, the authors succeeded in
95 preparing $\text{Li}_{1.2}\text{Ti}_{0.6}\text{Co}_{0.2}\text{S}_2$ showing anionic redox activity.⁴² Other successful strategies to adjust proper band
96 positioning have consisted in either preparing Ti³⁺-doped $\text{Li}_{1.33-y/3}\text{Ti}_{0.67-2y/3}\text{Ti}_{y/3}^{3+}\text{S}_2$, or triggering antisite
97 occupation as shown for $\text{NaCr}^{3+}\text{S}_2$, or preparing $\text{Li}_{1.33}\text{Ti}_{0.67}^{4+}\text{S}_2$ and $\text{Li}_{1.5}\text{Nb}^{5+}_{0.5}\text{S}_2$ having disordered rock-
98 salt structures.⁴⁶⁻⁴⁹ We herein demonstrate the feasibility to activate the anionic redox activity in Li-rich
99 layered $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_{y/3}^{2+}\text{S}_2$ via the use of Fe substitution. This situation is favourable for reversible
100 sulfur redox, since the Fe^{2+/3+} redox couple with available electrons ($3d^6$) is expected to be pinned at the top
101 of the S $3p$ band (Figure 1c).³⁸ We isolate the $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ compound showing, based on cumulated
102 cationic and anionic redox activity, a sustained reversible capacity of ~245 mAh·g⁻¹ at an average voltage
103 of ~2.5 V, hence leading to a specific energy of ~600 Wh·kg⁻¹ that compares favorably with LiCoO_2 .
104 Moreover, we demonstrate the advantages of choosing a softer ligand in partially mitigating both voltage
105 fade and hysteresis without any compromise in kinetics, hence providing confidence about the feasibility of
106 better capitalizing on the benefits of the anionic redox.

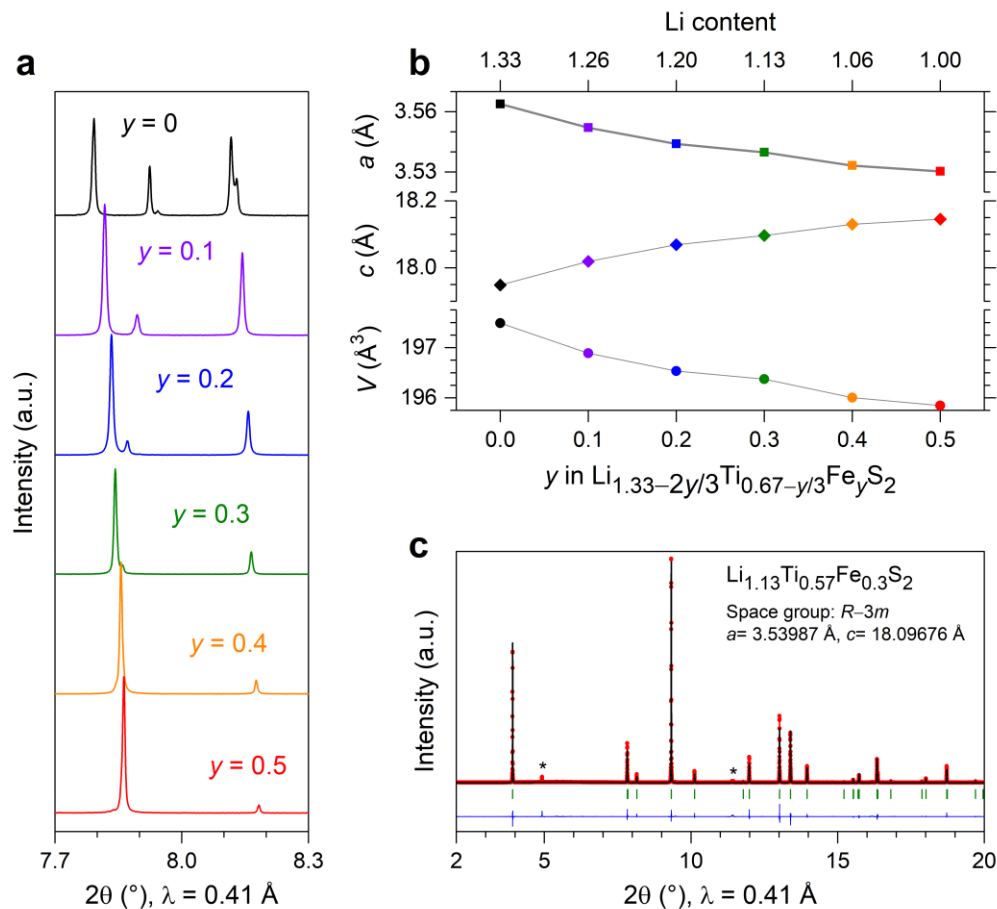


107
 108 **Figure 1. Moving from Li-rich layered oxides to sulfides.** Schematic band structure of Ni²⁺ substituted Li_{1.33}Mn_{0.67}O₂
 109 (a) and Li_{1.33}Ti_{0.67}S₂ (b) and its Fe²⁺ substituted derivative (c). The relative band positions are estimated based on Ref
 110 ^{3,38}. The label *nb* stands for non-bonding. The crystal structures of Li_{1.33}Mn_{0.67}O₂ (d, adapted from the Ref ⁵⁰) and
 111 Li_{1.33}Ti_{0.67}S₂ (e, this work), indicating the layer gap and the average metal-ligand bond distance.

112
 113 **Results**

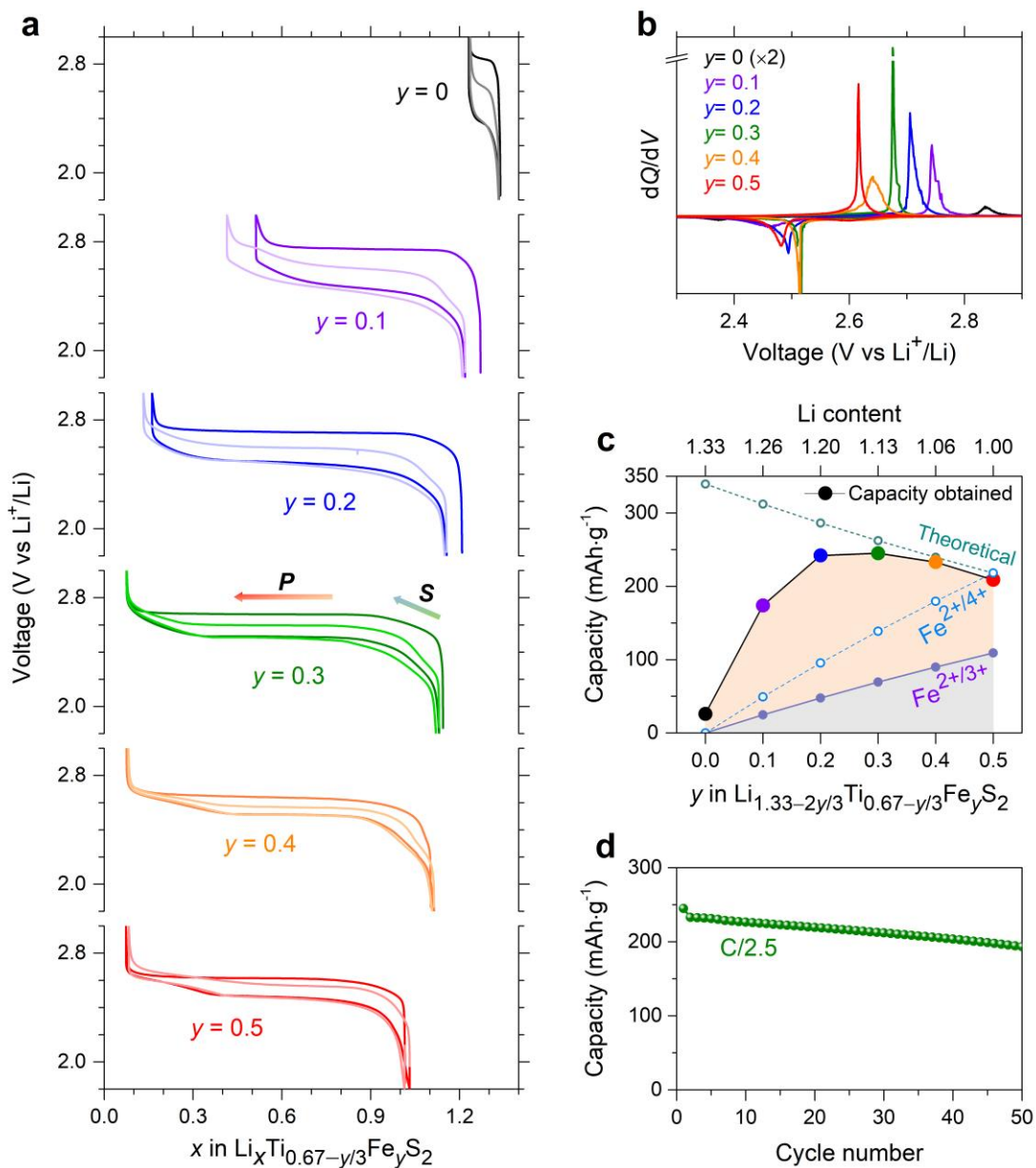
114 Nominal compositions of Li_{1.33-2y/3}Ti_{0.67-y/3}Fe_yS₂, with $y = 0 - 0.5$, were prepared by reacting Li₂S,
 115 TiS₂ and FeS in stoichiometric amounts in vacuum-sealed quartz tubes at 750 °C (see the Experimental
 116 Section for details). The X-ray diffraction (XRD) patterns are gathered in Figure S1a for all the
 117 compositions. The XRD pattern of the unsubstituted Li_{1.33}Ti_{0.67}S₂ (without Fe, $y = 0$) phase could be refined
 118 in the in *C2/m* space group alike for Li_{1.33}Mn_{0.67}O₂. The Rietveld refinement of its synchrotron XRD (SXR
 119 pattern is shown in Figure S1b with the obtained parameters summarized in Table S1. This crystal structure
 120 is similar to honeycomb-ordered Li-rich layered oxides, however with an expectedly larger unit cell to
 121 accommodate the bulkier S atoms, see Figure 1d,e. Upon increasing the Fe content y , there is a progressive
 122 shift of the Bragg peaks (Figure 2a) indicating the existence of a solid solution. Moreover, Fe-containing
 123 compositions ($y = 0.1 - 0.5$) do not show the superstructure peaks (Figure S1a), most likely because Fe²⁺
 124 disrupts the honeycomb Li⁺/Ti⁴⁺ ordering. Therefore, the Fe-containing phases could be fitted in a hexagonal

125 $R\bar{3}m$ description analogous to the well-known Li-rich layered $\text{Li}_{1+y}\text{M}_{1-y}\text{O}_2$ phases, with the obtained lattice
 126 parameters shown in Figure 2b. With increasing Fe content, we observe a monotonic increase in the c
 127 parameter that is accompanied by a decrease in the a parameter, such that the overall effect is a monotonic
 128 decrease in unit cell volume (V). Since among the $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ series, the compound with $y = 0.3$
 129 will be the center of interest in this study, we also performed the Rietveld refinement of its SXR
 130 D pattern (Figure 2c), which confirms that Fe, Ti and Li occupy same site in the metal layer (see the structural model
 131 in Table S2). This structure was further confirmed by Rietveld refinement of its neutron powder diffraction
 132 (NPD) pattern (see Figure S5a).



133
 134 **Figure 2. Structural behavior of the $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ series.** (a) SXR D patterns and (b) variation of lattice
 135 parameters (obtained from the Rietveld refinement of the SXR D patterns). In (b), for the $y = 0$ composition, the lattice
 136 parameters have been converted to the $R\bar{3}m$ description. (c) Rietveld refinement of the SXR D pattern of the
 137 $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ sample. The red circles, black continuous line, blue line, and green tick bars represent the observed,
 138 calculated and difference patterns, and Bragg positions, respectively. Note that minor Li_2TiO_3 impurity (indicated with
 139 *) was detected in the SXR D pattern, probably due to minor air-leakage during the preparation of the sample-capillary
 140 prior to the acquisition of SXR D patterns.

141 The electrochemical performances of the $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ samples were tested in Li-half cells
142 between 1.8 V and 3 V at a rate of C/20 and the voltage profiles are summarized in Figure 3a and S2a. The
143 unsubstituted $\text{Li}_{1.33}\text{Ti}_{0.67}\text{S}_2$ ($y = 0$) shows very poor electrochemical activity since only 0.1 Li could be
144 extracted reversibly. Attempts to enhance the activity by either ball milling the samples or by adding larger
145 amounts of carbon additive were unsuccessful, hence leading us to conclude that such a non-activity is
146 intrinsic to the phase and most likely nested in the fact that the $\text{Ti}^{3+/4+}$ redox band is empty and is situated
147 far above the S $3p$ band, hence unable to stabilize oxidized sulfur (Figure 1b). This contrasts with the Fe^{2+-}
148 containing phases (Figure 1c) that are electrochemically active, which show a specificity that is nested in
149 the second cycle's charge trace which mismatches the first one because it occurs at a lower potential (Figure
150 3a). Note also the appearance of a short sloped voltage (marked by 'S' in Figure 3a) at the early stage of
151 charge, and most likely related to Fe redox activity. This contrasts with a long plateau-like (marked by 'P')
152 activity on further oxidation. Lastly, the corresponding dQ/dV profiles are shown in Figure 3b and S2c,
153 which clearly highlights that the respective oxidation potentials shift to lower voltage with a systematic
154 decrease in hysteresis (Figure S2e) upon increasing the Fe content. After the first cycle, note that the
155 subsequent charge and discharge profiles are very similar (see Figure S2b for $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$) with the
156 polarization gradually reducing to ~ 100 mV for the $y = 0.3$ composition, instead of ~ 220 mV during the first
157 cycle. This indicates that the first cycle acts as an 'activation' cycle alike the Li-rich NMC oxides. The
158 variation of capacity as a function of the Fe-content shows a bell-shape type behaviour which peaks at 245
159 $\text{mAh}\cdot\text{g}^{-1}$ for the composition $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ ($y = 0.3$). Even by assuming full utilization of the multi-
160 electron oxidation of Fe^{2+} to Fe^{4+} , which is quite unlikely to occur in sulfide frameworks, we cannot account
161 for all the measured capacity, hence implying the activity of the anionic network, see Figure 3c. The capacity
162 decrease beyond $y > 0.3$ is simply due to the lower amount of available Li in the $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$
163 samples when the Fe content (y) increases. In contrast the raise noted until $y = 0.3$ is most likely nested in
164 the gradual amelioration of the band positioning with introduction of Fe content that triggers reversible
165 anionic redox activity. Among the various Fe compositions studied, the $y = 0.3$ sample not only shows the
166 largest capacity, but also a respectable capacity retention (Figure 3d and S2d) with also barely noticeable
167 irreversible capacity in the first discharge. Thus, we chose this composition for further investigation, starting
168 by exploring whether the activation process over the first cycle is related to structural aspects.



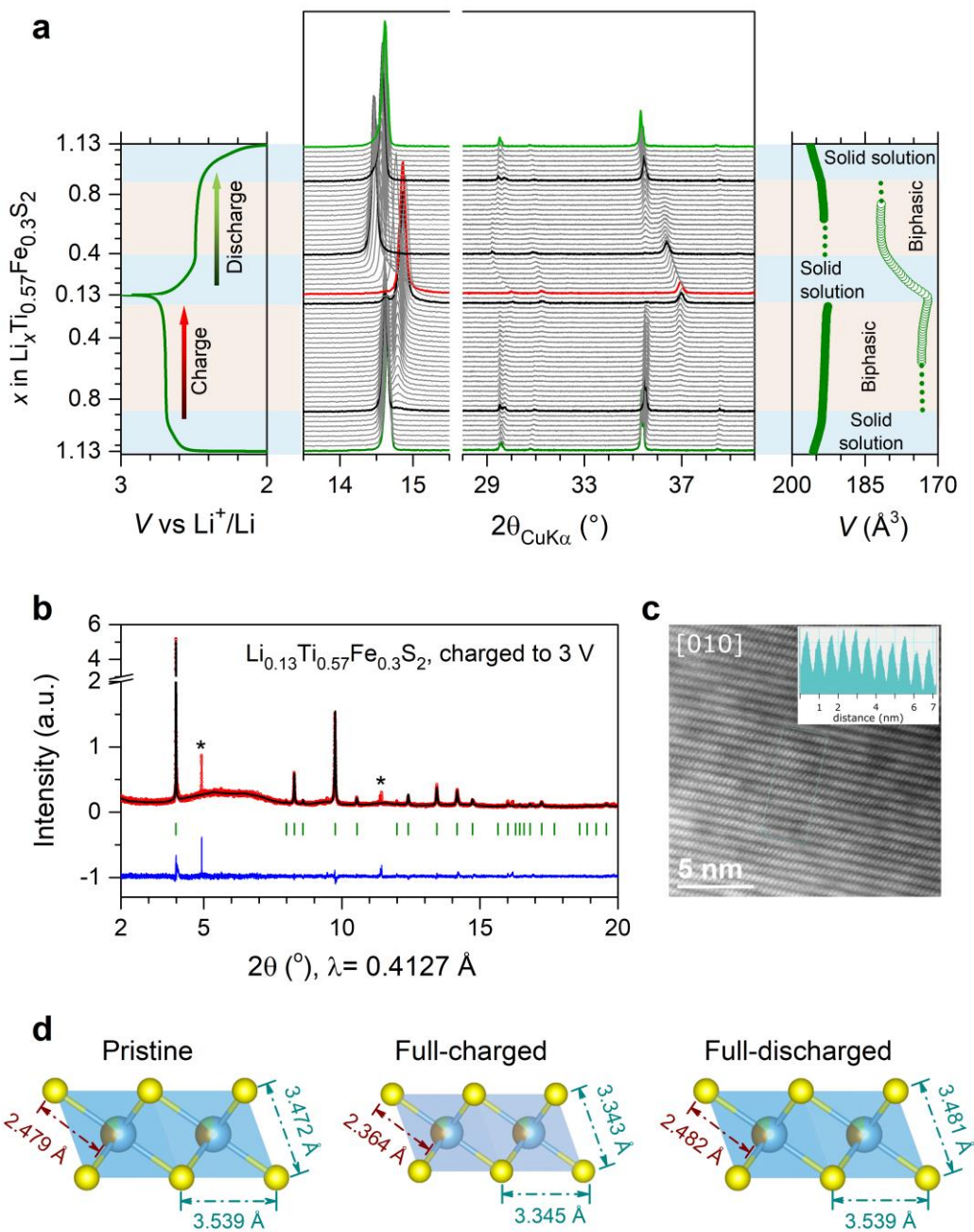
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170 **Figure 3. Electrochemical behavior of $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$.** (a) Voltage profiles of the compositions obtained over
 171 cycling vs Li at C/20 for the first two cycles. The curves in lighter colors denote the second cycles. The arrows marked
 172 by 'S' and 'P' denote the slope and the plateau, respectively. (b) dQ/dV curves obtained in the first cycle for the
 173 various compositions. (c) Theoretical capacity (considering total Li-removal) and the actual discharge capacity
 174 obtained for the compounds over cycling at C/20. The capacity expected from cationic $\text{Fe}^{2+/3+}$ and hypothetical $\text{Fe}^{2+/4+}$
 175 redox is also shown. (d) Cycling performance of a $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2/\text{Li}$ half-cell at a rate of C/2.5 (except the first
 176 formation cycle at C/20). The material was cycled as powder (mixed with 20 wt% C, see Figure S2d inset) in a Swagelok
 177 type cell, without any further optimization.

178 To better understand the structural evolution pertaining to the $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ phase during the Li
179 uptake-removal process, operando XRD measurements were conducted and XRD patterns were collected
180 for every change in lithium stoichiometry of ~ 0.1 (Fig. 4). Upon charge, we observed a slight initial shift of
181 the main peaks, indicating solid-solution behaviour. Over this regime, the unit cell volume decreases as a
182 consequence of an anisotropic variation of the a and c lattice parameters (see also, Figure S3a). Then, as the
183 voltage reaches the first plateau, there is a gradual change in the intensity of the peaks with some peaks
184 disappearing at the expense of new ones, which sharpen to give a well-defined XRD powder pattern at the
185 end of the full charge, hence suggesting a two-phase de-intercalation process. This new phase with
186 approximate composition $\text{Li}_{0.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$, whose structure remains as layered one as described in detail in
187 the next paragraph, has a lower unit cell volume (by $\sim 12.2\%$) than the pristine one. On discharge, the
188 compound undergoes first a solid-solution process for which both the a and c lattice parameters strongly
189 increase (Figure S3a). Then, a biphasic process is observed with the growth of a phase with increased
190 volume, followed again by solid-solution behaviour. We therefore have, for the first cycle, charge and
191 discharge processes that proceed through different structural paths, even though the pattern returns close to
192 the one for the pristine phase (see Figure S3b). This path-difference can be clearly observed from the
193 evolution of the unit cell volume (Figure 4a) and of the a and c lattice parameters (see Figure S3a). On the
194 other hand, over the 2nd cycle, the XRD patterns indicate more symmetric, although not perfect, pathways
195 on charge and discharge (Figure S4). Overall, throughout cycling the phase remains crystalline with well-
196 preserved long-range layered crystal structure.

197 Next, an in-depth exploration of the crystal structures at different states of charge (pristine, fully-
198 charged and fully-discharged after first cycle) was undertaken using SXRD. In agreement with the lab XRD
199 data, the patterns can be indexed in the $R\bar{3}m$ space group. The pristine $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ ($V = 196.384(2) \text{ \AA}^3$)
200 presents an average Ti–S bond-length of $2.4792(3) \text{ \AA}$, with average S–S distances of $\sim 3.505 \text{ \AA}$ (see the
201 structural model in Table S2). The Rietveld refinement of the SXRD pattern of the fully-charged
202 $\text{Li}_{0.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ phase (Figure 4b) indicates a much smaller unit cell ($V = 172.338(6) \text{ \AA}^3$) (see Table S3 for
203 the structural model). Moreover the average Ti–S bond length was found to shrink to $2.3635(1) \text{ \AA}$, leading
204 to decreased average S–S distances of $\sim 3.344 \text{ \AA}$.

205 In parallel, we collected the selected-area electron diffraction (SAED) of the fully-charged phase
206 which could again be successfully indexed with an $R\bar{3}m$ unit cell (Figure S5b). The corresponding high
207 angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image shows only
208 the (Ti/Fe) S_2 layers. The HAADF intensity profile (inset, Figure 4c) clearly demonstrates no scattering
209 density between the (Ti/Fe) S_2 layers and thus discards the possibility of transition-metal migration to the
210 interlayer sites (Figure 4c). The Rietveld refinement of SXRD pattern (Figure S5c, Table S4) of the fully-
211 discharged sample is very similar to the pristine phase ($V = 196.896(2) \text{ \AA}^3$) with an average Ti–S bond length
212 of $2.4825(3) \text{ \AA}$ and average S–S distance of $3.51(2) \text{ \AA}$. Worth mentioning is that such S–S distances are
213 quite larger than the (S–S) $^{2-}$ bond lengths reported early on for TiS_3 (2.04 \AA) (Figure 4d) suggesting either
214 an absence of complete dimerization in $\text{Li}_{0.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ or a possible error in the reported TiS_3 structure.⁵¹
215 Further investigations focusing specifically on the local structure of such sulfide compounds are hence
216 planned.

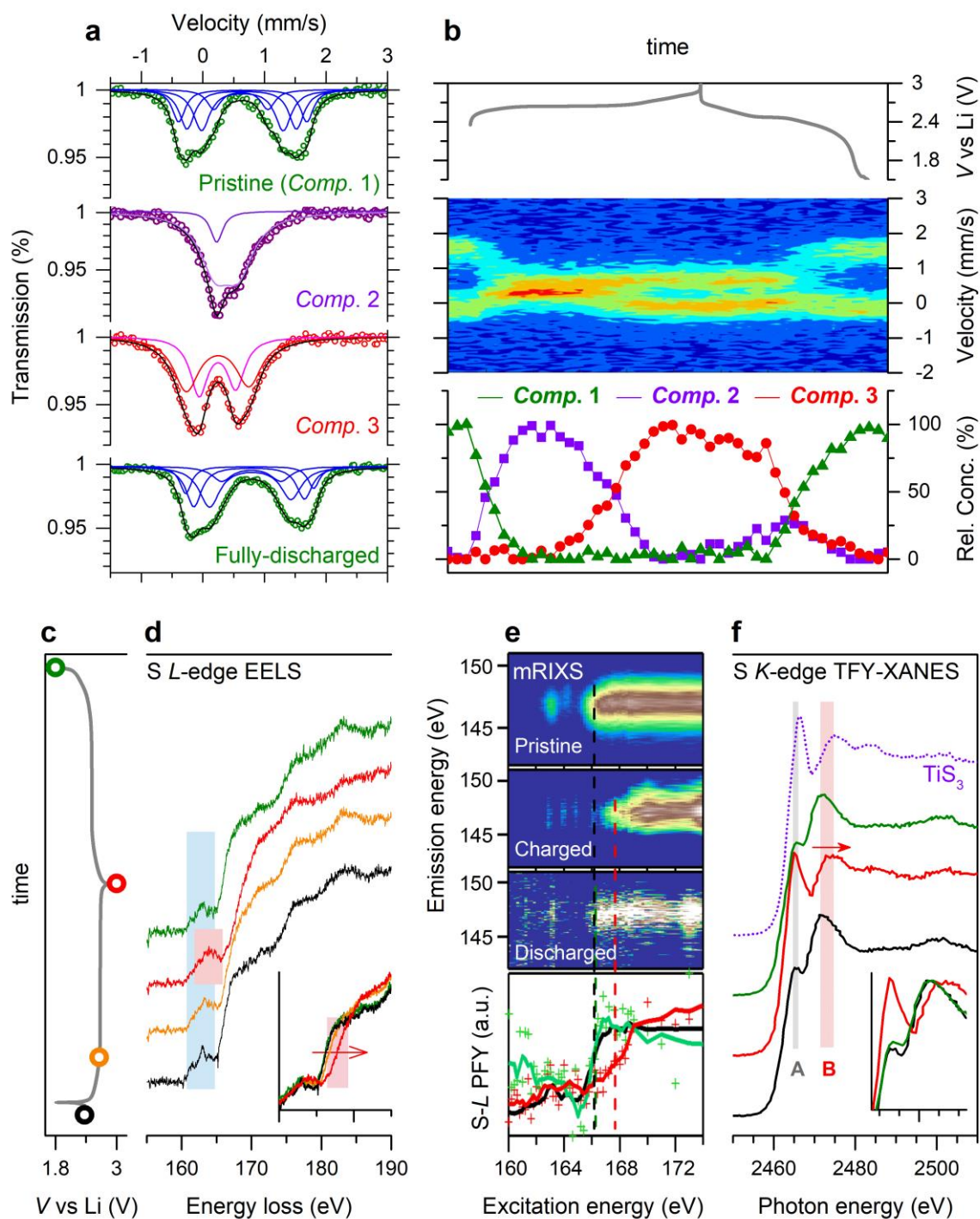


217

218 **Figure 4. Structural evolution upon Li (de)intercalation.** (a) Evolution of the *in situ* XRD patterns in the first cycle of a
 219 $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2/\text{Li}$ half-cell at a rate of C/20. The left panel shows the corresponding voltage profile and the right panel shows
 220 the evolution of the unit cell volume (V), as obtained from the Rietveld refinements of the XRD patterns. Note that the dotted
 221 lines represent extrapolations, where the XRD patterns could not be refined because of poor intensity of the peaks. (b-c) Rietveld
 222 refinement of the SXR patterns (b) and the HAADF-STEM image (c) of the full-charged phase. The peaks denoted by * in (b) show
 223 minor Li_2TiO_3 impurity. The inset in (c) shows the HAADF intensity profile. (d) The bond-lengths observed in the pristine, full-
 224 charged and full-discharged phase (as obtained from the Rietveld refinement of the corresponding SXR patterns).

225 To grasp some insights on the charge compensation mechanism, the cationic $\text{Fe}^{2+/3+}$ redox process
226 was probed by *operando* Mössbauer spectroscopy using an electrochemical cell designed in-house.⁵²
227 Spectra were collected while charging and discharging a $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2/\text{Li}$ cell at a rate of C/70 (Figure
228 5). The Mössbauer spectra for pristine $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$, that can neatly be fitted with four doublets (see
229 Table S5), highlights the presence of a distribution of high-spin (HS) Fe^{2+} , as already encountered for FeS
230 and various other iron (II)-based sulfides.^{53,54} The necessity of four doublets is simply due to different local
231 arrangements of intermixed Ti/Li/Fe cations around a given Fe site. The evolution of the spectra obtained
232 during *in situ* cycling is shown as a contour plot in Figure 5b, with the spectra analyzed using principal
233 component analysis (PCA), as described in Supplementary Note S1. All measured spectra could be
234 adequately fitted as linear-combinations of three reconstructed spectral components. As expected, the first
235 component (*Comp. 1*) is identical to the pristine material's spectrum. The *Comp. 2* can be fitted using at
236 least two doublets, see Figure 4a and Table S5. The major one (90%) has an isomer shift of 0.48 mm/s
237 which stands between what is expected for HS Fe^{2+} and HS Fe^{3+} , alike what has been seen in Fe_3S_4 and
238 FeV_2S_4 .⁵³ The second doublet with a 10 % contribution to the overall spectrum is indicative of the HS- Fe^{3+}
239 signature, as seen in NaFeS_2 .⁵³ Overall, the average oxidation state of *Comp. 2* is higher than Fe^{2+} but not
240 fully reaching Fe^{3+} . Note that *Comp. 2* reaches its maximum around $x_{\text{Li}} = \sim 0.93$, just before the voltage
241 plateau. During the plateau, the *Comp. 2* converts progressively to the *Comp. 3* (fully-charged, 3 V), as
242 shown in Figure 4c, in which can be fitted as low-spin Fe^{3+} state in agreement with previous reports (Figure
243 4a and Table S5).⁴⁰ On discharge, the evolution of the components is reversed, except for a much lower
244 contribution from the *Comp. 2* (Figure 4a). This is fully consistent with the path dependence observed above
245 with XRD. Overall, these data indicate the progressive oxidation of Fe^{2+} to Fe^{3+} on charge and its full
246 reduction back to Fe^{2+} on discharge.

247 Furthermore, Fe $L_{2,3}$ -edge X-ray absorption near edge structure (XANES) spectra were taken to
248 confirm the participation of Fe and are shown in Figure S6b. The spectra for the pristine material is similar
249 to that of FeS confirming the presence of Fe^{2+} .^{55,56} It enlists two main peaks corresponding to $2p_{3/2} \rightarrow 3d$
250 (L_3) and $2p_{1/2} \rightarrow 3d$ (L_2) transitions. These peaks shift to higher energy upon charge indicating gradual
251 conversion to Fe^{3+} . After discharge, the Fe $L_{2,3}$ edge is restored completely. The position and shifts of the
252 Fe $L_{2,3}$ -edge observed upon oxidation are consistent with observations of S-containing species with Fe^{2+} and
253 Fe^{3+} in literature,⁵⁷ indicating consistency with conclusions from Mössbauer spectroscopy. The Ti $L_{2,3}$ -edge
254 XANES spectra were also recorded for the aforementioned samples (Figure S6c). As expected, the spectrum
255 for pristine $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ is identical to that of Ti^{4+}S_2 , confirming the formal oxidation state of Ti as 4+.⁵⁸
256 Moreover, no changes in the position of L_2 and L_3 peaks could be observed, irrespective of the sample state
257 of charge, hence indicating the invariance of Ti^{4+} throughout the charge/discharge cycle.⁵⁸



258

259 **Figure 5. Spectroscopic characterizations to identify the redox processes.** (a) Typical Mössbauer spectra and their deconvolution
 260 for the pristine (*comp. 1*), *comp. 2*, *comp. 3* (fully charged) and the fully-discharged product. (b) Contour plot of evolution of the
 261 Mössbauer spectra collected during *in situ* cycling of a $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2/\text{Li}$ half-cell at a rate of $C/70$. For reference the voltage
 262 profile is shown in the top panel. The lowest panel shows the evolution of the reconstructed components during the cycling. (c-f)
 263 The EELS spectra of the S L-edge (d), mRIXS of the S L-edge with integrated PFY spectra on the bottom (e) and S K-edge XANES
 264 spectra (f) collected *ex situ* on the pristine (black curves), partially-charged (2.66 V, only EELS, orange curve), fully-charged (3 V,
 265 red curves) and fully-discharged phase (green curve) as shown in the voltage profile in (c).

266 To check the electrochemical activity of S within the $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ phase during the Li uptake
267 and removal process, *ex situ* electron energy loss spectroscopy (EELS) spectra at the S $L_{2,3}$ edge were
268 collected (Figure 5d) for pristine, partially-charged (2.66 V, after removing ~ 0.16 Li), fully-charged (3 V)
269 and fully-discharged (1.8 V) samples. The spectra consist of a weak pre-edge and an intense broad edge
270 feature that correspond to a series of transitions from the S $2p$ core levels to unoccupied states.⁵⁹ The S $L_{2,3}$
271 edge for the pristine material is similar to that of FeS indicating the predominance of S^{2-} state (Figure 5d
272 and S7a).⁵⁹ It remains nearly alike for the partially charged sample (at 2.66 V) with the exception of minor
273 alterations that could be ascribed to a probable decrease of the Ti/Fe–S bond covalency. In contrast, for the
274 fully-charged sample (at 3 V), the S $L_{2,3}$ rising-edge shifts by ~ 1.6 eV towards higher energies and this is
275 indicative of a partial oxidation of S^{2-} .⁵⁵ However the S $L_{2,3}$ pre-edge does not show the typical peak splitting
276 seen in pyrite-FeS₂ or elemental S⁰ (Figure S7b).⁵⁶ Lastly, it is worth mentioning that the initial shape as
277 well as the energy of the rising-edge of the S $L_{2,3}$ edge are fully recovered towards the end of the discharge,
278 further indicative of the reversibility of the sulfur redox process.

279
280 To complement the EELS data that were collected locally on individual electrode particles (see
281 Methods), we further probed the S L -edge by soft X-ray absorption spectroscopy (sXAS) performed in
282 fluorescence mode which provides bulk-sensitive information about sulfur redox activity. However, direct
283 measurements of the electrodes on the S L -edge through conventional sXAS turned out to be challenging,
284 because of interfering background signals from the carbon present in the electrodes which contributes an
285 overwhelming background through 2nd order harmonic around 140 eV, right below the S- L signals around
286 160 eV (Figure S7c,d). We could successfully distinguish the S signals from the strong C background, by
287 employing high-efficiency mapping of resonant inelastic X-ray scattering (mRIXS), see Methods and Figure
288 S7e for details. This advanced technique, which has emerged as a seminal technique for detecting oxygen
289 redox, further resolves the emitted photon energy, called emission energy, after each sXAS excitation
290 process.⁶⁰ Figure 5e displays these S- L mRIXS signals collected from the pristine, fully-charged, and fully-
291 discharged electrodes. The integration of all the signals within the emission energy range (142 - 151 eV)
292 provides the partial fluorescence yield (PFY) signals of the clean S- L sXAS, as summarized in the bottom
293 panel. The pristine $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ without carbon additive displays the strongest S- L features. The
294 relatively sharp features in mRIXS at 163 and 164.1 eV excitation energies correspond well with the pre-
295 edge peaks observed in EELS. The sharp features suggest these are dominated by the localized TM $3d$
296 character that is hybridized with S orbitals.⁵⁹ At higher excitation energy, the continuous band-like feature
297 corresponds to the intrinsic sulfur states hybridized with TM $4s/4p$ orbitals. It is clear that the leading edge
298 of these sulfur band-like feature shifts towards high energy for over 1.2 eV in the full charged phase, in
299 complete agreement with EELS and indicating the oxidation of sulfur states. Furthermore, the leading edge
300 position completely recovers after discharge, suggesting a reversible redox reaction of the sulfur.

301
302 S K -edge XANES spectra were equally collected for the aforementioned samples (except partially
303 charged) and they are reported in Figure 5e. The spectrum presents two main regions. The pre-edge feature,
304 below 2471 eV, arises generally from unoccupied S $3p$ /TM $3d$ hybridized states. Their position and intensity
305 depend on their occupancy, the relative contribution of S and TM, and their position with respect to the core
306 level, thus being a general measure of covalence of the TM-S bond.⁶¹ Above this energy, the signals
307 correspond to transitions to higher states, such as S $3p$ /TM $4s$, p or those involving S $4p$, and the
308 photoionization of S atoms, involving complete ejection of the core electron to the continuum. Therefore,
309 the position of the absorption threshold is strongly dependent on the effective nuclear charge (Z_{eff}) on S,⁶¹

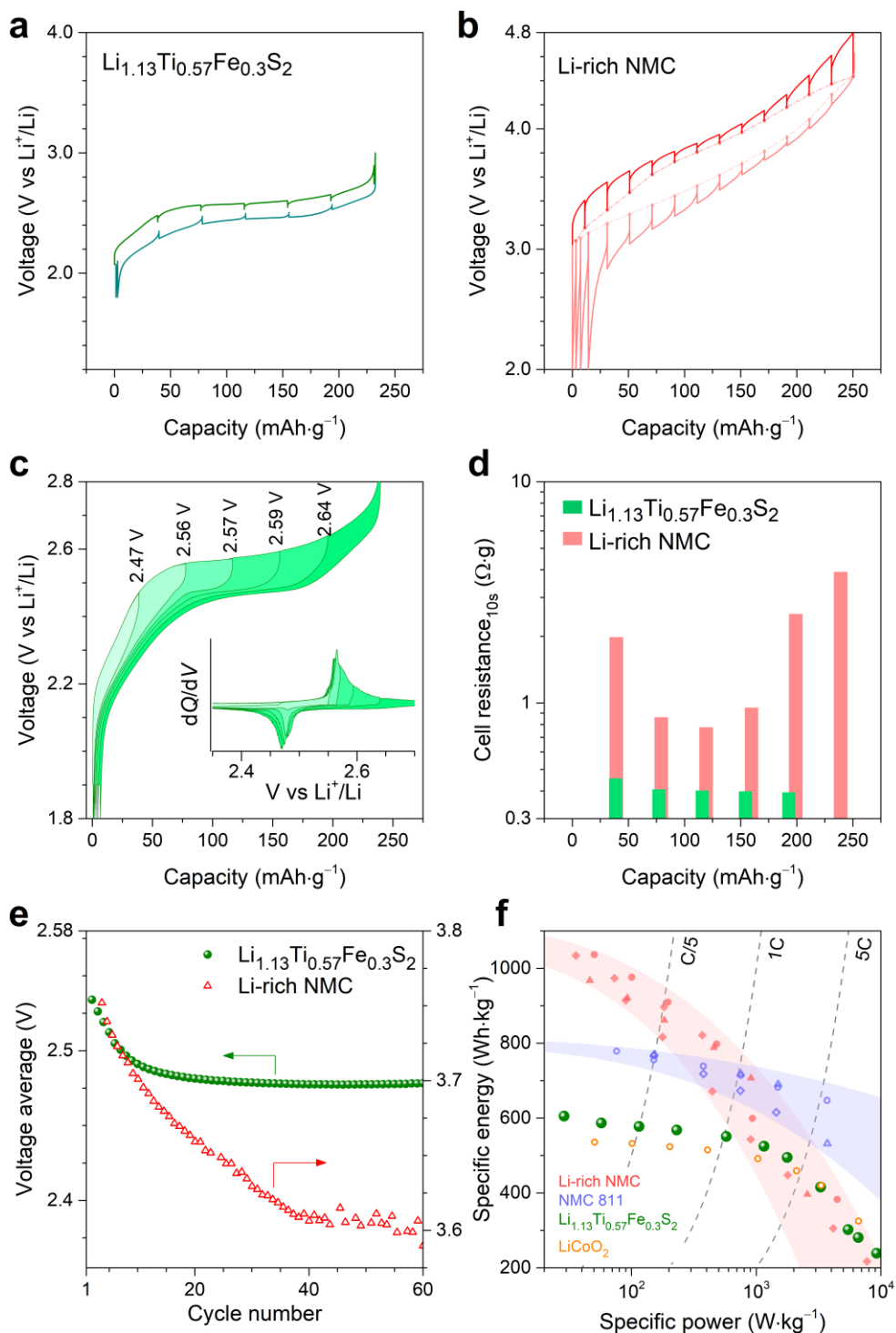
310 being a measure of redox transitions at the ligands. The spectra for pristine $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ consists in a
311 weak pre-edge at ~ 2465 eV (denoted as **A**) and a broad edge jump (denoted as **B**) located at ~ 2472 eV
312 similar to what is observed in amorphous rocksalt Li_2TiS_3 and hence characteristic of S^{2-} .⁴⁸ For the fully
313 charged state ($\sim \text{Li}_{0.1}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$), the spectrum (red curve in Figure 5e) undergoes notable changes with an
314 increase in amplitude of the pre-edge **A** and a ~ 1.2 eV shift of the **B** edge towards higher energy, and bears
315 resemblance to TiS_3 (dashed purple curve).⁶² Similarly, the opposite shift in the edge **B** is observed during
316 re-lithiation, as was reported for TiS_3 , and VS_4 .^{36,63} The 1.2 eV shift in **B** is therefore a clear indication of
317 the oxidation of S^{2-} into S^{n-} , $n < 2$. Similarly, the increase in intensity of pre-edge **A** is indicative of the
318 increase in density of unoccupied states just above the Fermi level with an S character, in agreement with
319 the expectation that the redox change is compensated by S $3p/\text{Fe } 3d$ electrons. The shift of the main
320 absorption edge also suggests that this compensation, and the resulting states, have a significant S character.
321 This unambiguously confirms the participation of S in the overall electrochemical activity of
322 $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ together with its reversibility since the S K -edge XANES spectra of the fully-discharged
323 and pristine samples nearly superimpose (Figure S6d).

324 To confirm the above observations S $2p$ core X-ray photoelectron spectroscopy (XPS) spectra
325 were also taken and are shown in Figure S6e. Clear variations of the spectra are observed upon charging-
326 discharging the samples. The S $2p_{3/2-1/2}$ XPS core spectrum can be fitted with a single doublet (160.7 - 161.9
327 eV) attributable to S^{2-} for the pristine material, as in the TiS_2 reference.⁶⁴ As the sample gets oxidized, the
328 spectrum markedly changes, with namely the appearance of one extra doublet at higher binding energies
329 (161.8 - 163.0 eV), which is indicative of the presence of oxidized S^{n-} ($n < 2$), in light of early previous
330 studies on TiS_3 that is well-known to contain partially oxidized sulfur.^{32,64} On discharge, the XPS spectrum
331 is almost restored to the pristine-like state, confirming the reversibility of the anionic redox process.

332 At this stage, mindful of the strong involvement of anionic redox in the charge compensation
333 mechanism of $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$, the next legitimate question pertains to the practicability of anionic redox
334 in sulfides. Using these newly designed Li-rich sulfides as model compounds, we investigated whether some
335 of the practical issues (large voltage hysteresis, sluggish kinetics and gradual voltage fade) that have so far
336 plagued the commercialization of analogous Li-rich layered oxides showing anionic redox activity^{12,6}, still
337 persist when oxygen is replaced by sulfur. To assess the practical figures of merit in Li-rich sulfides, we
338 first performed a galvanostatic intermittent titration technique (GITT) experiment (Figure 6a) after initial
339 seven cycles to stabilize the voltage profile. $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ shows the disappearance of voltage hysteresis
340 in the open-circuit voltage (OCV) throughout the cycle (only ~ 30 mV gap remains after just 30 mins of
341 relaxation). This is a significantly better scenario than in Li-rich NMC ($\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$), where a
342 severe OCV hysteresis up to 300 mV has been reported and further shown to be associated with oxygen
343 redox (Figure 6b).¹⁴ This performance is also better than the ~ 100 mV OCV hysteresis in $4d$ metal-based
344 $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ and approaches the favorable hysteresis-free situation experienced in $5d$ metal-based β -
345 Li_2IrO_3 .^{13,16} This observation clearly highlights that voltage hysteresis can be effectively mitigated by tuning
346 the ligand, and not just by choosing appropriate transition metals. The hysteresis was further studied by
347 progressive opening of voltage-windows during charge in subsequent cycles and the voltage profiles are
348 summarized in Figure 6c. Increasing the voltage cut-off does not lead to any noticeable increase in voltage
349 hysteresis. This contrasts with similar experiments on Li-rich NMC showing an onset of large hysteresis
350 upon full charging accompanied with lowering of the discharge potential around mid-SoCs (Figure S8a).
351 Furthermore, the corresponding dQ/dV curves (in the inset, Figure 6c) reveal that irrespective of upper cut-
352 off of charging voltage, in discharge the oxidative capacities are mostly recovered at ~ 2.5 V, therefore not
353 triggering any voltage hysteresis. This is quite contrary to Li-rich NMC, where oxidative capacities obtained

354 from anionic redox (i.e., charging above ~4.1 V) are only recovered partially at similar voltage upon
355 discharge (down to ~4 V). Further discharge to a lower voltage (below ~3.6 V) is necessary to regain the
356 remaining capacity, as the reduction of the oxidized Oⁿ⁻ species is split between high and low voltages,
357 causing a large voltage hysteresis (Figure S8b).¹⁴

358 Concerning the next issue of kinetics, we have previously shown how oxygen redox displays
359 sluggish kinetics.^{13,14} Hence, to check the same in sulfides, cell resistance was deduced from the voltage
360 drop during the first 10 s of the relaxation steps of the GITT experiment (Figure 6b). As revealed for
361 Li_{1.13}Ti_{0.57}Fe_{0.3}S₂, the electrochemical resistance remains quite low throughout the whole cycle (Figure 6d).
362 Whereas for Li-rich NMC, the resistance is significantly larger at all SoCs and increases at low and high
363 SoCs, which corresponds to the regions involving oxygen redox.¹⁴ Furthermore, electrochemical impedance
364 spectra (EIS) were collected at different SoCs of Li_{1.13}Ti_{0.57}Fe_{0.3}S₂, after each relaxation step during the
365 GITT experiment and the evolution of the EIS Nyquist plots is shown in Figure S9a,b. The charge-transfer
366 resistance, located in the mid-frequency regime of the spectra (characteristic frequency around 10 to 1 Hz),
367 remains very small and nearly constant throughout the cycle, irrespective of whether it is cationic or anionic
368 redox regime, as opposed to Li-rich oxides where the resistance builds up drastically with deeper oxidation
369 of oxygen.^{12,14} This clearly highlights the positive attribute of Li-rich sulfides concerning kinetics. The fast
370 kinetics was further confirmed with Li₁Ti_{0.5}Fe_{0.5}S₂ (y = 0.5) composition, which shows similar charge
371 transfer resistance and consequently similar cycling and rate performance (Figure S9c,d), despite having a
372 higher proportion of cationic redox capacity. Lastly, regarding the critical issue of voltage fade, we found
373 that it still afflicts Li-rich sulfides, though to a much lower extent, as shown in Figure 6e. The voltage fade
374 for Li_{1.13}Ti_{0.57}Fe_{0.3}S₂ can be divided in two regimes, starting first with a well-pronounced decrease from 2nd
375 cycle to the 7th (a drop of ~35 mV) followed by a stabilization afterwards to reach an overall drop of ~40
376 mV after 60 cycles (the maximum we have cycled). This again positively contrasts with Li-rich NMC that
377 shows a nearly continuous voltage fade upon cycling with an accumulated drop of ~150 mV after 60 cycles.
378 Overall, moving from oxygen to sulfur as the ligand turns out to be a correct strategy to partially mitigate
379 the practical bottlenecks of anionic redox. However, we need to keep in mind that this comes at the expense
380 of the overall energy density (Figure 6f) because of lower potential and higher molecular weight of sulfur.
381 A compromise could consist in combining the energy advantage of oxygen redox with the practicability of
382 sulfur redox. This task is not trivial bearing in mind the experienced difficulty in preparing 3d-metal-based
383 oxysulfides.



384

385 **Figure 6. Li-rich layered sulfide as a model material to study the practicability of anionic redox.** (a) Voltage profile of
 386 $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ in a two-electrode cell in the 8th cycle, recorded with a GITT protocol (C/5 rate with 30 min rests for equilibration).
 387 (b) Voltage profile of Li-rich NMC ($\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$) in a three-electrode cell in the 4th cycle, recorded with a GITT protocol
 388 (40 $\text{mA}\cdot\text{g}^{-1}$ pulses with 4 h rests for equilibration). (c) Voltage profiles obtained from the charge-window opening experiment
 389 (starting from 8th cycle). Inset shows the corresponding dQ/dV profiles. (d) Cell's electrochemical resistance (during charging)
 390 estimated simply by Ohm's law from the voltage drop in first 10 s of rest from the previous GITT experiment in (a). (e) Average
 391 voltage during long cycling of $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ and Li-rich NMC in Li-half cells. In each cycle, the average voltage is defined as the

392 mean of the average charge and discharge voltages that and was calculated by dividing the energy with the capacity obtained. (f)
393 Ragone plots of $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ and comparison with Li-rich NMC and Li-stoichiometric NMC ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$). Only values at
394 material-level are considered and values for the NMC-811 and the Li-rich NMC are adapted from *Reference*¹². LiCoO_2 is also
395 included in the comparison and the Li-rich layered sulfide appears at par with it.

396 Discussion

397 We have shown the feasibility, by partially substituting $\text{Ti}^{4+}/\text{Li}^+$ belonging in the metal layers of
398 $\text{Li}_{1.33}\text{Ti}_{0.67}\text{S}_3$ (commonly written Li_2TiS_3) with Fe^{2+} , to produce $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ phases showing
399 electrochemical activity due to cumulated cationic ($\text{Fe}^{2+/3+}$) and anionic ($\text{S}^{2-} / \text{S}^{n-}$, $n < 2$) redox processes.
400 Alike the Li-rich layered oxides having d^0 metals (Li_2TiO_3 , etc...), we found the feasibility to trigger Li
401 electrochemical activity in Li-rich layered sulfides having d^0 metals by the injection of metal substituents.
402 This does not come as a total surprise as such metal substitution modifies the U over Δ competition, so that
403 it falls within the domain to trigger reversible anionic redox activity as established from theoretical
404 calculations.⁴¹ The anionic redox activity upon oxidation was spectroscopically confirmed in
405 $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ via clear energy shifts in the S $L_{2,3}$ -edge EELS and XANES spectra as well as the onset of
406 a doublet signal in the S $2p_{3/2-1/2}$ XPS core spectra. Structure-wise on the other hand, our XRD and EELS
407 evidence did not suggest the local formation of very short S–S dimers (like in pyrites), but more
408 investigations focusing on the local structure are needed to unequivocally rule this out. For comparing with
409 oxides, let's recall that the XPS fingerprint of anionic redox activity in oxides was also the appearance of a
410 new component at slightly higher binding energy (531.5 eV) in the O $1s$ XPS core spectra that we assigned
411 to O^{n-} ($n < 2$).¹⁴⁻¹⁶ Interestingly, the binding energy of this component was independent of the structure and
412 composition as seen in various Li-rich oxides that show anionic redox activity, with or without evidences
413 of O–O shortening. This observation indicates that although XPS features have been widely used as the
414 spectroscopic signature of the anionic redox activity in various materials, caution has to be exercised when
415 interpreting XPS spectra.

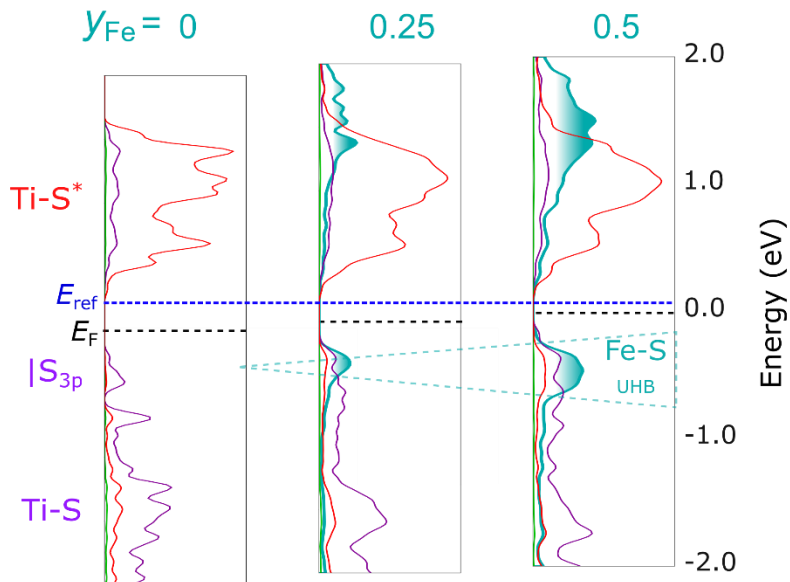
416 Besides, we found that $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ can deliver capacities as high as $245 \text{ mAh} \cdot \text{g}^{-1}$ with a near-
417 zero irreversible capacity during the first cycle as compared to $\sim 0.2 \text{ Li}$ for Li-rich $3d$ metal-based oxides
418 (Figure S8c,d). This is consistent not only with the absence of cationic migration in sulfides, in contrast to
419 some of the analogous oxides, but also with less severe changes observed between the first charge-discharge
420 voltage profiles in $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ as opposed to Li-rich NMCs that show a staircase charging curve
421 drastically changing to a S-shaped discharging curve. Lastly, part of the initial irreversibility in oxides is
422 associated to a small amount of oxygen release from the surface, either directly as O_2 gas or indirectly by
423 reacting with the electrolyte.^{3,65} This is quite unlikely to occur with S which is a softer element as compared
424 to O, therefore showing less reactivity and greater stability for the same degree of electrochemical oxidation.

425 We noted in the dQ/dV profile (recall Figure 3b) a systematic shift to lower potentials of the peaks
426 corresponding to concomitant cationic and anionic redox processes with increasing Fe-content in $\text{Li}_{1.33-}$
427 $_{2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$, while for instance the position of the peaks was found to remain independent of Sn
428 substitution in the $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$ series showing well-decoupled cationic and anionic redox.¹⁵ To understand
429 this behaviour, we calculated the spin-projected density of states (pDOS) for $y = 0, 0.25$ and 0.5 (these
430 compositions were chosen for ease of computation, see Methods) and plotted in Figure 7a. The electronic
431 structure of the parent $\text{Li}_{1.33}\text{Ti}_{0.67}\text{S}_2$ displays a charge transfer gap between the empty Ti d band (in red), split
432 by the crystal field, and the S band (in purple) formed of non-bonding S $3p$ states (denoted as $|\text{S}_{3p}$) that lies
433 above the Ti–S bonding states. Fe^{2+} substitution leads to the introduction of a partially filled d band (having
434 six electrons), which is split by d - d Coulomb repulsion (introduced by a correction term $U = 1.9 \text{ eV}$) into a
435 deep-lying Lower Hubbard band (LHB), with five spin-up electrons, and an Upper Hubbard Band (UHB)

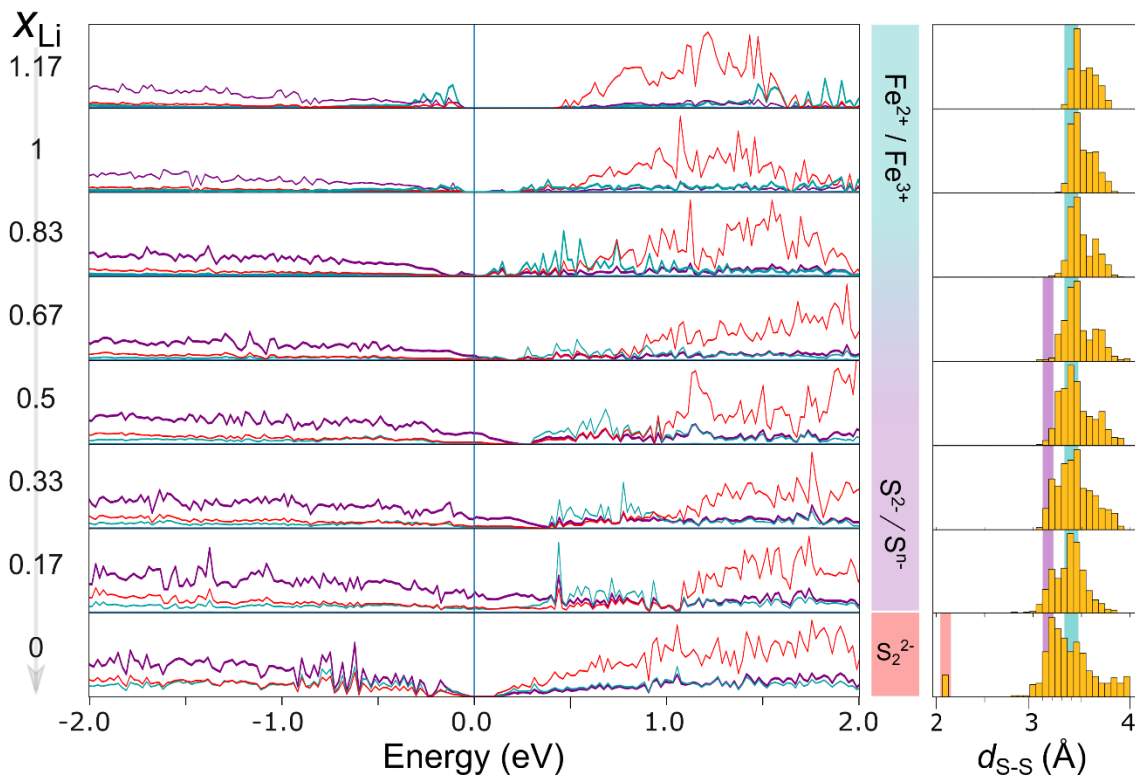
436 with one spin-down electron. This is consistent with the experimentally observed HS Fe²⁺ from Mössbauer
437 spectroscopy. The occupied states of the UHB lie above the |S_{3p} states. As the Fe content increases, the
438 number of these UHB states increases. If we take as a reference the energy (E_{ref}) of states that are not
439 expected to be directly affected by the Fe substitution, such as either the Ti- t_{2g}^* that is close to the Fermi
440 level (Figure 7a) or the S 3s core levels that are non-bonding and very deep in energy (see Figure S10a), we
441 observe that the highest occupied states are rising in energy with Fe content as indicated by the raising of
442 the Fermi level. This explains the experimental observation of voltage decrease with gradual Fe
443 introduction.

444 Next we asked whether the experimentally observed electronic and structural changes upon Li
445 removal could be supported by monitoring the evolution of pDOS and the corresponding theoretical S–S
446 distances. This is answered by calculating the pDOS of Li_xTi_{0.58}Fe_{0.25}S₂ ($1.17 > x_{\text{Li}} > 0.83$) that is summarized
447 in Figure 7b. At the beginning of charge ($1.17 > x_{\text{Li}} > 0.83$), the depletion of the Fe-UHB near the Fermi
448 level indicates that Fe gets oxidized, while the average S–S distance remains unaffected and thus confirming
449 that S acts as a spectator. This situation drastically changes upon further oxidation ($0.83 > x_{\text{Li}} > 0.17$) where
450 the pDOS indicates the depletion of the S band near the Fermi level, which implies S undergoes partial
451 oxidation. Over this composition range, the small decrease in some of the calculated S–S distances (marked
452 in purple background in the histograms) and the progressive closing of the band gap suggests that the holes
453 are delocalized over the S network through Fe–S interaction. The participation of S to the states right above
454 the Fermi level significantly increased upon oxidation, consistent with the increase in pre-edge intensity
455 observed by S K-edge XAS (Figure 5f).

a) Increasing Fe content in $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$



b) Decreasing Li content in $\text{Li}_x\text{Ti}_{0.58}\text{Fe}_{0.25}\text{S}_2$



456

457 **Figure 7. Correlating the experimental observations in $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ with theoretical calculations.** (a) Evolution of pDOS
 458 with increasing Fe content. Li, Ti, Fe and S contributions to bands are colored in light green, red, cyan and purple, respectively (b)
 459 Evolution of pDOS of $\text{Li}_{1.17}\text{Ti}_{0.58}\text{Fe}_{0.25}\text{S}_2$ with Li-removal. The panel in middle indicates the deduced redox processes. The
 460 corresponding theoretically obtained S-S distances are shown in the histograms at right. The distances were chosen using a
 461 distance cut-off of 4 Å, without renormalization.

462 At high states of charge, the top of the highly dispersed sulfur band gets raised above the bottom of
463 the empty Fe-UHB leading to electronic instability. This scenario triggers, if we simulate complete Li
464 removal ($x_{\text{Li}} \sim 0$), a reorganization of the network through the formation of true S–S dimers with a calculated
465 bond length of $\sim 2.1 \text{ \AA}$ (red background in the histogram). However, experimentally, full Li depletion is not
466 observed since our fully oxidized sample still contains 0.13 Li^+ ($\sim \text{Li}_{0.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$). In short, the
467 participation of S in the redox process could unambiguously be confirmed theoretically, hence explaining
468 the measured shortening of the S-S distances. However, the predicted dimerization at full charge could not
469 be confirmed experimentally because the fully delithiated phase was not obtained electrochemically. This
470 finding probably explains the excellent cycling reversibility of $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$, as opposed to TiS_3 ,
471 where the cleavage of the S–S dimers leads to huge rearrangements of the crystal structure, resulting to rapid
472 capacity fading with cycling.³⁰⁻³² Nevertheless, the question of $(\text{S}_2)^{2-}$ vs. S^{n-} ($n < 2$) upon complete
473 delithiation remains to be fully elucidated, which will likely trigger more detailed characterizations and
474 theoretical calculations on various sulfide materials in the future.

475 In summary, a new class of Li-rich layered sulfides $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ have been designed and
476 studied for their electrochemical behaviour as cathode materials. Within this series, the phase
477 $\text{Li}_{1.13}\text{Ti}_{0.57}\text{Fe}_{0.3}\text{S}_2$ offers the largest reversible capacity ($245 \text{ mAh}\cdot\text{g}^{-1}$) and we have shown, via
478 complementary Mössbauer, XANES, EELS, mRIXS and XPS spectroscopies, that this capacity mainly
479 originates from sulfur redox besides the cationic redox of Fe. When benchmarking against Li-rich NMCs,
480 this phase present several positive attributes such as (i) a nearly zero irreversible capacity during the initial
481 cycle, (ii) an overall voltage fade as low as 40 mV even after 60 cycles and (iii) low voltage hysteresis (35
482 mV), along with fast kinetics, as compared to Li-rich NMC showing an irreversibility of $\sim 0.2 \text{ Li}$, a voltage
483 fade of 150 mV and a hysteresis of 300 mV besides sluggish kinetics. Energy-wise, these Li-rich layered
484 sulfide positive electrodes display a specific energy of $\sim 600 \text{ Wh}\cdot\text{kg}^{-1}$ at the material-level while being
485 composed of earth-abundant elements (3d metals only). This is much lower than the $\sim 1000 \text{ Wh}\cdot\text{kg}^{-1}$
486 obtained for Li-rich NMC and thus they may not offer any real-world competitiveness against oxide
487 electrodes furthermore due to their low operating potential as well as the practical issues with the handling
488 of sulfides. Nevertheless, we believe that they could serve as excellent ‘model’ electrodes to study the
489 general properties of anionic redox chemistry and in exploring kinetics, especially via the realization of S-
490 based solid-state batteries that can enable playing with temperature as an extra dimension. Both low
491 hysteresis and structural integrity upon Li (de)intercalation are promising assets to design next-generation
492 cathodes provided we can overcome the energy density penalty pertaining to the use of sulfur as a ligand.
493 Preparing 3d-metal oxysulfides is an option if we ever overcome their synthesis difficulties. The door is
494 wide-open for chemists to take forward this new dimension of exploring the effect of the ligand in enhancing
495 the holistic performances of anionic redox in search for practical high-energy batteries.

496 Experimental Section

497 **Synthesis.** $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ samples were prepared by solid-state reaction of stoichiometric amounts of Li_2S (Alfa Aesar,
498 99.9%), TiS_2 (Sigma Aldrich, 99.9%) and FeS (Alfa Aesar, 99%). Homogeneously mixed and hand-grinded precursor powders
499 were filled in quartz tubes in an Ar-filled glovebox followed by sealing the tubes under vacuum ($\sim 10^{-5}$ mbar). The sealed tubes
500 were subsequently annealed at 750 °C for 36 h followed by quenching in water. The as-prepared samples were collected inside a
501 glovebox and hand-grinded prior to further use. In the whole process, air contact was avoided and subsequent processing was done
502 in an Ar-filled glovebox. TiS_3 , used as a reference for XAS, was prepared similarly, by reacting TiS_2 and elemental S (15 wt%
503 extra), in a vacuum sealed quartz tube at 550 °C, followed by cooling slowly.

504 **Structural Characterization.** Synchrotron X-ray powder diffraction (SXRD) patterns were collected at the 11-BM beamline of
505 the Advanced Photon Source (APS), Argonne National Laboratory. All SXRD data were collected in transmission mode with $\lambda =$
506 0.4127 Å, with the powder sealed in a quartz capillary of 0.7 mm diameter. Operando and *in situ* X-ray powder diffraction (XRD)
507 was performed in an airtight electrochemical cell equipped with a Be window. XRD patterns were recorded in reflection mode in
508 Bragg–Brentano geometry using a Bruker D8 Advance diffractometer equipped with a Cu- K_α X-ray source ($\lambda_1 = 1.54056$ Å, $\lambda_2 =$
509 1.54439 Å) and a LynxEye detector. The refinements of the patterns were done using the Rietveld method⁶⁶ as implemented in the
510 FullProf program⁶⁷.

511 **Electrochemical characterization.** $\text{Li}_{1.33-2y/3}\text{Ti}_{0.67-y/3}\text{Fe}_y\text{S}_2$ samples were cycled in galvanostatic mode in Li half-cells assembled
512 in Swagelok-type cells. The cathode materials were mixed with 20 wt% conductive carbon Super-P by hand-grinding for 5 min
513 prior to cycling (Figure S2d inset). LP30 (1M LiPF₆ in ethylene carbonate/dimethyl carbonate in 1:1 weight ratio) was used as the
514 electrolyte and was soaked in a Whatman GF/D borosilicate glass fiber membrane that was used as separator. Typical loadings of
515 10 mg of active materials were used and metallic Li was used as the negative electrode. The cells were assembled in an Ar-filled
516 glovebox and were cycled at a C/20 rate between 1.8 V and 3 V if not specified otherwise. Charged/discharged samples from the
517 Swagelok cells were recovered for *ex situ* characterizations by disassembling the cells inside glovebox, rinsed thoroughly with
518 anhydrous DMC and dried under vacuum. All electrochemical cycling and EIS measurements (in 10 mHz – 200 kHz frequency
519 range applying a 10 mV sinusoidal wave) were performed with BioLogic potentiostats.

520 **Mössbauer spectroscopy.** Room-temperature ⁵⁷Fe Mössbauer spectra were recorded in transmission geometry in the constant
521 acceleration mode and with a ⁵⁷Co(Rh) source with a nominal activity of 370 MBq. The velocity scale (± 4 mms⁻¹) was calibrated
522 at room temperature with α -Fe foil. The *in situ* cell was prepared with 32 mg.cm⁻² of active material mixed with 8 mg of carbon
523 black. The hyperfine parameters IS (isomer shift) and QS (quadrupole splitting) were determined by fitting Lorentzian lines to the
524 experimental data. The isomer shifts values are calculated with respect to that of α -Fe standard at room temperature. The obtained
525 operando spectra were fitted using a statistical method based on Principal Component Analysis (PCA). This approach is a
526 chemometric factor analysis tool able to determine the minimal particular structures in multivariate spectral data sets. Once the
527 number of principal components is determined by PCA, a Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS)
528 algorithm is used for the stepwise reconstruction of the pure spectral components which are necessary for interpreting the whole
529 multiset of operando Mössbauer spectra.⁶⁸

530 **Energy loss spectra (EELS).** The sample was prepared in an Ar-filled glove box by crushing the crystals in a mortar in DMC and
531 depositing drops of the suspension onto holey carbon grids. The samples were transported to the transmission electron microscope
532 (TEM) column while completely avoiding contact with air. High angle annular dark field scanning transmission electron microscopy
533 (HAADF-STEM) images and EELS spectra were obtained with a FEI Titan G3 electron microscope operated at 120 kV and
534 equipped with a monochromator and a Gatan Enfium ER spectrometer. Energy resolution measured by full width at half maximum
535 of the zero loss peak is 0.15 eV.

536 **X-ray absorption spectroscopy (XAS).** S K-edge, Fe L-edge and Ti L-edge X-ray absorption near edge spectroscopy (XANES)
537 measurements were performed at 4-ID-C beamline of APS at Argonne National Laboratory. Spectra were recorded simultaneously
538 under both the total electron yield (TEY) mode from the sample photocurrent at $\sim 10^{-9}$ Torr and total fluorescence yield (TFY) mode
539 using a silicon drift diode detector at a spectral resolution of ~ 0.2 eV, with a 2 s dwell time. The energy scales of the spectra were
540 calibrated with the references of Mo metal, Fe metal and SrTiO₃ measured simultaneously, for S, Fe and Ti edges, respectively.
541 Both TEY and TFY spectra produces similar spectra, and hence only TFY spectra (more bulk sensitive) has been reported here.

542 **Soft X-ray absorption spectroscopy (sXAS) and mapping of resonant inelastic X-ray scattering (mRIXS).** The S L-edge sXAS
543 and mRIXS experiments were performed in the iRIXS endstation of beamline 8.0.1 at the Advanced Light Source (ALS) of

544 Lawrence Berkeley National Laboratory.⁶⁹ The pristine powder and cycled electrodes were mounted in high purity Ar glove box
545 and transferred into the experimental vacuum chamber through a home-made kit to avoid any air exposure. The experimental energy
546 resolution of sXAS is better than 0.1 eV without considering the intrinsic core hole broadening (~0.2 eV). The energy resolution
547 along the emission energy in mRIXS is about 0.2 eV,⁶⁹ which is sufficient for separating the intrinsic S-L signals from the strong
548 C-K (2nd order) background that are different for about 10 eV. The X-ray exposure area on the samples were kept moving throughout
549 the mRIXS experiments to avoid irradiation damage.

550 **X-ray photoemission spectroscopy (XPS).** XPS spectra were collected on a sample (analyzed area = 300×700 μm²) with a Kratos
551 Axis Ultra spectrometer, using focused monochromatic Al Kα radiation ($h\nu = 1.4866$ keV). The pressure in the analysis chamber
552 was around 5×10^{-9} mbar. The binding energy scale was calibrated using the C 1s peak at 285.0 eV from the invariably present
553 hydrocarbon contamination (for the pristine sample), and using the S²⁻ position of the S 2p_{3/2} at 160.7 eV for a better accuracy (for
554 the other cycled samples). Peaks were recorded with constant pass energy of 20 eV. Core peaks were analyzed using a nonlinear
555 Shirley-type background.⁷⁰ The peak positions and areas were optimized by a weighted least-squares fitting method using 70 %
556 Gaussian, 30 % Lorentzian line shapes. Quantification was performed on the basis of Scofield's relative sensitivity factors.⁷¹

557 **Theoretical calculations.** Starting from a 221 supercell of Li₂TiS₃ obtained from SXRDR refinement, with honeycomb ordering of
558 Li/Ti in the metallic layer, we achieved a composition of Li_{1.17}Ti_{0.58}Fe_{0.25}S₂ (resp. Li₁Ti_{0.5}Fe_{0.5}S₂) by replacing 2 Li (resp. 4) and 1
559 Ti (resp. 2) atoms by Fe atoms. The atoms to replace were chosen to minimize the total Madelung energy of the final structure. To
560 delithiate, we iteratively removed the Li atoms according to their Madelung energy (assuming integer oxidation state for every ion),
561 using the Python Material Genome library.⁷² For each Li content, structures were then relaxed using the Vienna Ab-Initio Simulation
562 Package using ultra-soft PAW pseudo potentials and the Perdew-Burke-Ernzerhof functional with a generalized gradient
563 approximation.^{73,74} We added D3 correction to account for the van der Waals interaction⁷⁵ as well as a $U_{\text{eff}} = 1.9$ eV to account for
564 electron-electron interactions on Fe.⁷⁶ The forces on the atoms were converged to 10^3 eVÅ⁻¹ with a plane-wave energy cut-off of
565 600 eV and a well converged set of Kpoints.

566
567 **Acknowledgements:** S.S. thanks the Réseau sur le Stockage Electrochimique de l'Energie (RS2E) for
568 funding of the Ph.D. J.-M.T. acknowledges funding from the European Research Council (ERC)
569 (FP/2014)/ERC Grant-Project 670116-ARPEMA. Use of the 11-BM mail service of the APS at Argonne
570 National Laboratory was supported by the US Department of Energy under contract No. DE-AC02-
571 06CH11357 and is gratefully acknowledged. The sXAS and mRIXS experiments at BL8.0.1 used resources
572 of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-
573 AC02-05CH11231. The authors thank M. Saubanère & M-L. Doublet for fruitful discussions and the
574 laboratory Chimie Théorique Methodes & Modélisation (CTMM) at the Institut Claude Gerhardt Montpellier
575 (ICGM) for computational facilities.

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