

Supporting information for:

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

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1 The positioning of the X-ray Raman Scattering (XRS) incident beam on the *post mortem*
2 $\text{Li}_2\text{FeSiO}_4$ electrode samples was verified by the presence of Li 1s peak at ≈ 55 eV, depicted
3 in Fig. S1.

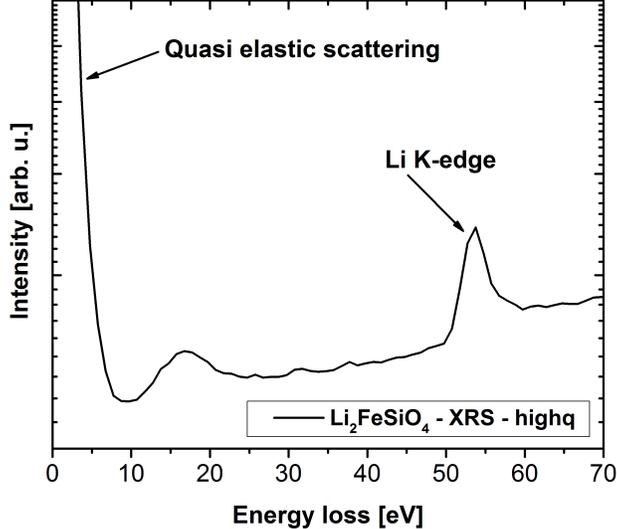


Figure S1: XRS quasi elastic scattering and Li K-edge of a $\text{Li}_2\text{FeSiO}_4$ *post mortem* electrode sample.

4 The experimental spectra contains combined information of all electron orbitals of oxygen
 5 and those of overlapping neighbours with K-edge energy region. To deconvolute the exper-
 6 imental spectra and investigate the origin of the oxygen K-edge pre-edge feature, partial
 7 density of states (DOS) calculations for the $\text{Li}_2\text{FeSiO}_4$ using FEFF9 code were carried out.
 8 The projection of individual DOS of Fe $4p, 3d$, Si $3p$, and oxygen $2p$ are shown in Fig. S2.
 9 The projection highlights that the oxygen K-edge pre-edge peak, observed in experimental
 10 spectra, originates primarily from Fe $3d$ states.

11 The total DOS obtained via FEFF9 calculation for the oxygen K-edge of $\text{Li}_2\text{FeSiO}_4$ com-
 12 pared to experimental XRS spectra of pristine sample A are depicted in Fig. S3.

13 The *operando* XANES of iron K-edge study during first charge and held at elevated
 14 potential 4.8 V for several hours, reveal no sign of oxidation of iron beyond the Fe^{3+} state,
 15 see Fig. S4. It should be noted that the pristine sample contained a slight share of Fe^{3+}
 16 originating from phase impurities.

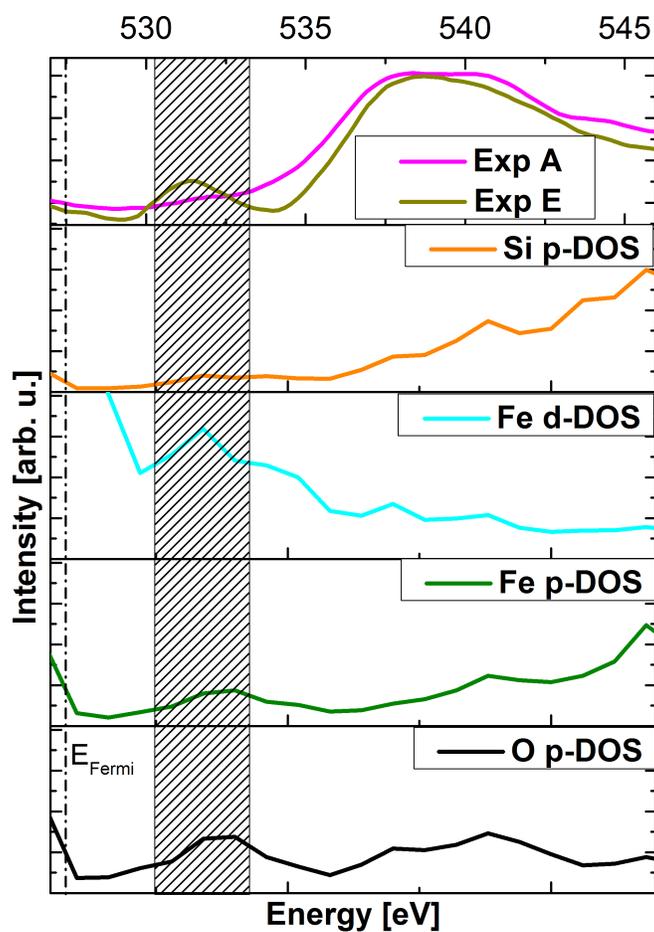


Figure S2: From bottom to top: Projection of density of states of O $2p$, Fe $4p$, $3d$ and Si $3p$ compared to experimentally obtained spectra of O K-edge at pristine (A) and EOC (E) state. Dash-dotted line marks the Fermi energy.

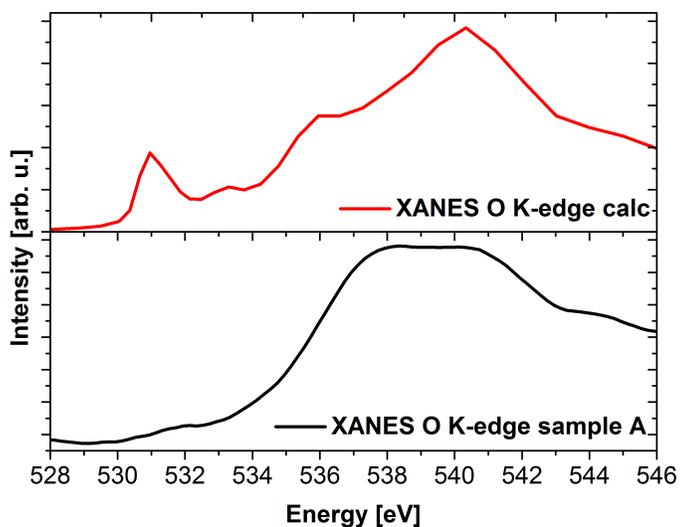


Figure S3: Comparison of O K-edge XANES spectra obtained experimentally via XRS (bottom) and total DOS obtained through FeFF9 calculations (top).

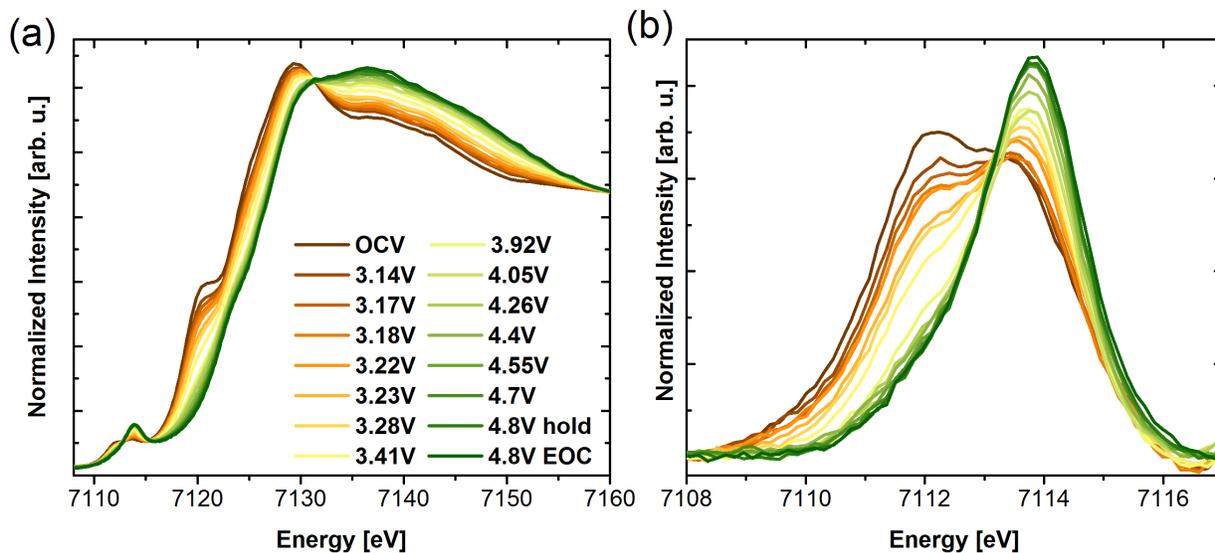


Figure S4: *Operando* Fe K-edge XANES (a) complete spectra (b) and pre-edge peaks during first charge (delithiation) and holding at elevated potential 4.8 V.