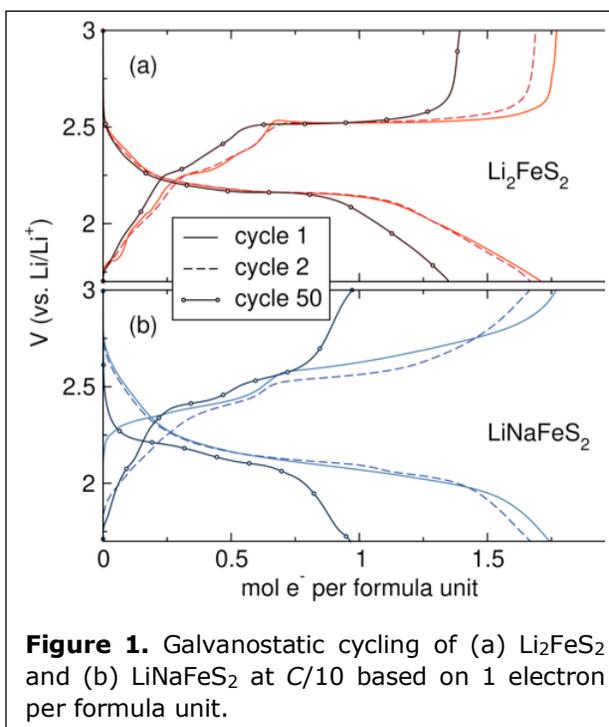


## Reversible Cation and Anion Redox in Lithium-rich Sulfide Battery Cathodes

Since the commercialization of lithium-ion batteries (LIBs) in the early 1990s, scientists and engineers alike have furthered our understanding of the fundamental electronic and structural processes that enable efficient energy storage for applications ranging from portable electronics and electric vehicles to the grid. However, current state of the art LIBs are reaching the theoretical limit with respect to capacity, a property largely limited by cathode materials based on a single electron transfer per transition metal as in the canonical  $\text{LiCoO}_2$ . As such, the development and fundamental understanding of new candidate cathode materials that can accommodate multielectron redox are of extreme interest in the field. To that end, researchers of the Center for Synthetic Control Across Length-scales for Advancing Rechargeables (SCALAR; a DOE Energy Frontiers Research Center) have characterized the charge storage mechanism in Li-rich layered sulfide  $\text{Li}_2\text{FeS}_2$  and a novel analog  $\text{LiNaFeS}_2$ , both of which can reversibly store  $\geq 1.5$  electrons per formula unit leading to high energy storage capacity.

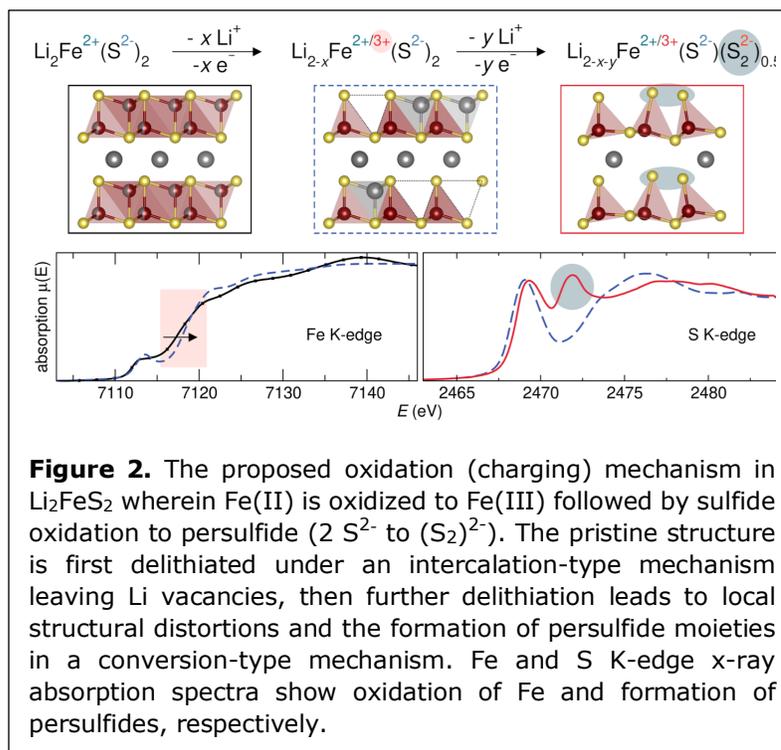
$\text{Li}_2\text{FeS}_2$  and  $\text{LiNaFeS}_2$  were synthesized through traditional solid-state methods. Both materials crystallize in the same structure with octahedral layers of Li or Na between tetrahedral layers of mixed-occupancy Fe/Li. The layered structure allows for fast removal and subsequent insertion of Li ions, which are processes that must be charge-balanced by redox on other atoms in the materials. Researchers found that the initial regions of the galvanostatic voltage profiles differed due to the deintercalation of Na from  $\text{LiNaFeS}_2$ , but both materials exhibit a long plateau at higher states of charge (Figure 1). The voltage profile on discharge is dissimilar to the charge profile, which points to a disparate mechanism from that during charging; nevertheless, the processes are observed to be highly reversible with extended cycling.

Combining the expertise and facilities of multiple groups in SCALAR, researchers were able to show unequivocally that the charge storage mechanism proceeds through a hybrid intercalation/conversion process enabled by redox on both Fe cations and S anions. Specifically, x-ray absorption spectroscopy experiments, which provide insight into oxidation state and local environment around the absorbing atom by hitting the sample with x-rays at element-specific energies, were performed at SSRL beam lines 4-1 and 4-3 at the Fe and S K-edges (Figure 2). The data show that at early states of charge (below 2.5 V, Figure 1), Li removal is being balanced by Fe(II) oxidation to Fe(III) accompanied by an increase in the covalency of the Fe–S interactions. Then, further removal of Li (i.e. from 2.5 V to 3 V, Figure 1) is balanced by oxidation of S, more specifically oxidation of sulfides to persulfide moieties ( $2 \text{S}^{2-}$  to  $(\text{S}_2)^{2-}$ ).



**Figure 1.** Galvanostatic cycling of (a)  $\text{Li}_2\text{FeS}_2$  and (b)  $\text{LiNaFeS}_2$  at  $C/10$  based on 1 electron per formula unit.

Li<sub>2</sub>FeS<sub>2</sub> and LiNaFeS<sub>2</sub> were shown to exhibit identical charge compensation mechanisms, but structural data indicated differences in the way the long-range order was responding to Li removal and insertion. Researchers performed *operando* x-ray diffraction on both materials throughout a full charge and discharge cycle and found that the two materials behaved differently. Li<sub>2</sub>FeS<sub>2</sub> exhibits signs of a single-phase mechanism consistent with lattice contraction concomitant with Li deintercalation at early states of charge, then in the plateau region of the voltage profile a two-phase mechanism is observed indicating a conversion-type mechanism. LiNaFeS<sub>2</sub> shows signs of a two-phase mechanism during the first plateau region and another during the high-voltage plateau. Additionally, the LiNaFeS<sub>2</sub> lattice contracts much more significantly due to the removal of the larger Na ions, which researchers suspect could explain the more pronounced capacity fade in LiNaFeS<sub>2</sub>. Despite the differences, however, analysis of the extended x-ray absorption fine structure from the x-ray absorption measurements show nearly identical trends in the Fe-S and Fe-Fe correlations between Li<sub>2</sub>FeS and LiNaFeS<sub>2</sub>, suggesting that on the local level, the structures behave similarly. With all data in hand, researchers hypothesize that the persulfide bonds are formed between corner-sharing FeS<sub>4</sub> tetrahedra as the layers distort to bring adjacent S atoms close enough together (Figure 2).



**Figure 2.** The proposed oxidation (charging) mechanism in Li<sub>2</sub>FeS<sub>2</sub> wherein Fe(II) is oxidized to Fe(III) followed by sulfide oxidation to persulfide (2 S<sup>2-</sup> to (S<sub>2</sub>)<sup>2-</sup>). The pristine structure is first delithiated under an intercalation-type mechanism leaving Li vacancies, then further delithiation leads to local structural distortions and the formation of persulfide moieties in a conversion-type mechanism. Fe and S K-edge x-ray absorption spectra show oxidation of Fe and formation of persulfides, respectively.

Future work will include high-resolution synchrotron x-ray diffraction and neutron diffraction experiments to more accurately determine the phases formed during cycling as well as detailed imaging to determine how the significant lattice contraction and expansion in LiNaFeS<sub>2</sub> may impact the particle morphology in the hopes of better understanding the capacity fade. In this work, researchers have gained understanding of the mechanisms that govern the reversible multielectron redox observed in Li<sub>2</sub>FeS<sub>2</sub> and LiNaFeS<sub>2</sub>. The discoveries made will inform the development of new materials for next-generation LIBs that utilize covalent metal-chalcogenide bonds to increase the available charge storage capacity.

### Primary Citation

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