The Solid State Conversion Reaction of Epitaxial FeF$_2$(110) Thin Films with Lithium Studied by Angle-Resolved X-Ray Photoelectron Spectroscopy: Supporting Information

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SI. HELIUM ION MICROSCOPY OF THE IRON FLUORIDE FILM

FIG. S1: Helium Ion Microscope image of the as-grown FeF$_2$(110) thin film showing 10-15 nm lateral domain size and a film thickness of $\sim$ 50 nm.

Figure S1 shows an image of the as-grown FeF$_2$(110) film as taken by a Zeiss ORION Helium-Ion Microscope (HIM) operating at an accelerating voltage of 35 kV, a beam current of 1 pA, and a 1 $\mu$s dwell time. During imaging, the sample surface was oriented at a 45$^\circ$ angle with respect to the ion beam in order to simultaneously image the surface and cross section of the film. Three distinct regions are visible in this image: a textured region at the top of the image, a narrow band in the center, and a uniform layer at the bottom. These features are attributed to the FeF$_2$(110) surface (with $< 1$ nm corrugations), the bulk FeF$_2$ layer, and the MgF$_2$ substrate respectively. This image confirms that the FeF$_2$ film is about 50 nm in thickness and suggests that the film is composed of 10-15 nm domains.

SII. IDENTIFICATION OF IRON CHEMICAL SPECIES

FIG. S2: Fe 2p XPS spectrum of the FeF$_2$(110) sample after 160 minutes of total Li exposure. The satellite features of the Fe$_x$Li$_{2-2x}$F$_2$ component are clearly visible, and are not fit by any combination of iron fluoride or oxide reference spectra.

Figure S2 shows a Fe 2p core level spectrum obtained from the FeF$_2$ surface after exposure to atomic Li for 160 minutes. The Fe 2p spectral components arising from FeF$_2$ and Fe$^0$ were both taken from reference spectra, and were not sufficient to fit the data. In particular, the presence of the satellite features at binding energies of -716 eV and -730 eV, labeled in Figure S2 was not consistent with any known iron fluoride or oxide species.$^{1-4}$ An additional component was then constructed, and subsequently identified as Fe$_x$Li$_{2-2x}$F$_2$, using the Fe 2p spectrum taken after the final Li exposure (160 min), as shown in Figure S2. This was chosen as the spectrum with the highest ratio of Fe$_x$Li$_{2-2x}$F$_2$:FeF$_2$.

Identification of the Fe$_x$Li$_{2-2x}$F$_2$ component was accomplished via comparisons with previous studies. Ko and coworkers have previously observed an expansion in the LiF rock salt lattice upon delithiation of an
FeF₂ cathode. This was attributed to the formation of FeₓLi₂₋₂xF₂.

![Fe 2p XPS spectrum from a cycled FeF₂ cathode showing the same spectral components as the thin film sample.](image)

FIG. S3: Fe 2p XPS spectrum from a cycled FeF₂ cathode showing the same spectral components as the thin film sample.

The formation of FeₓLi₂₋₂xF₂ was also observed in recent ex situ XPS measurements of electrochemically cycled FeF₂ electrodes. Figure S3 shows the peak fitting scheme used for a delithiated electrode in this previous work. These measurements showed that the FeₓLi₂₋₂xF₂ did not fully dissociate upon the delithiation of the electrode, and hence this ternary compound might be partially responsible for the capacity losses observed in FeF₂ cells.

**SIII. EVOLUTION OF IRON PEAKS**

The reduction of the FeF₂ film upon exposure to lithium was quantified by fitting the Fe 2p peak with a sum of Fe⁰, FeF₂, and FeₓLi₂₋₂xF₂ components. Figure S4 shows the evolution of the normal emission Fe 2p spectra for several different lithium exposures. The spectra have been normalized by their maximum intensities in order to highlight their visual differences. From these spectra, it can be seen that the relative intensities of the Fe⁰ and FeₓLi₂₋₂xF₂ components increase monotonically as a function of lithium exposure, while the FeF₂ intensity simultaneously decreases. The Fe:FeₓLi₂₋₂xF₂ ratio increases slightly as a function of exposure, from 0.85 after 5 minutes of exposure to 1.10 after 160 minutes.

![Fe 2p spectra of the FeF₂ film taken at normal emission after each lithium exposure.](image)

FIG. S4: Fe 2p spectra of the FeF₂ film taken at normal emission after each lithium exposure.

**SIV. ARXPS DETAILS**

The model used to fit the R(θ, d) curves consisted of an infinitely thick film of FeF₂ with an inhomogeneously thick overlayer of FeₓLi₂₋₂xF₂ and Fe metal, as shown in Figure S5. In order to model the attenuation of the FeF₂ photoelectrons, the overlayer was divided vertically into four different types of regions: (1) thick Fe⁰, (2) thick FeₓLi₂₋₂xF₂, (3) thin Fe⁰, and (4) thin FeₓLi₂₋₂xF₂. The relative coverages of Fe⁰ and FeₓLi₂₋₂xF₂ were determined by the ratio of the specific volume of each species, such that 85% of the surface was covered by FeₓLi₂₋₂xF₂ and 15% by Fe⁰. This columnar geometry of overlayer compounds is consistent with the Fe⁰ and FeₓLi₂₋₂xF₂ spectral intensities being equal for all angles and overlayer thicknesses.

The FeF₂ signal was then calculated from the following
FeF$_2$ has a P4$_2$/mnm rutile (tetragonal) structure with lattice constants $a = b = 4.697$ Å and $c = 3.309$ Å at room temperature. Each Fe$^{2+}$ ion in the bulk is bound to six F$^-$ ions in a distorted octahedral configuration with metal-ion distances of 2.03 Å and 2.10 Å. The FeF$_2$ [110] channels have nearly square cross sections and are located between the octahedra in the lattice. This square cross section measures 2.10×2.10 Å, from the centers of the fluorine ions at the boundaries. Including the radii of the F$^-$ ions, the cross section of the [110] channel is approximately 0.6 Å, which is smaller than the diameter of either Li$^0$ or Li$^+$. This geometrical argument supports the assertion that lithium cannot diffuse into the FeF$_2$(110) surface. In comparison, the FeF$_2$ [001] channels are 3.43×3.43 Å from the centers of the bounding ions and 2.18×2.18 Å including the ionic radii, which is large enough to accommodate either Li$^0$ or Li$^+$ diffusion.

### Table SII: Summary of relevant atomic and ionic radii from Shannon$^3$ and Slater$^4$

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<th>Element</th>
<th>Charge</th>
<th>Radius (pm)</th>
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