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

Ryan Thorpe,* Sylvie Rangan, and Robert A. Bartynski†
Department of Physics and Astronomy and Laboratory for Surface Modification,
Rutgers University, 136 Frelinghuysen Road, Piscataway, New Jersey 08854, United States

Ryan Whitcomb
Department of Applied Physics, University of Michigan,
450 Church Street, Ann Arbor, MI 48109, United States

Ali C. Basaran, Thomas Saerbeck,‡ and Ivan K. Schuller
Department of Physics and Center for Advanced Nanoscience,
University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92039, United States

The phase evolution and morphology of the solid state FeF$_2$ conversion reaction with Li has been characterized using angle-resolved x-ray photoelectron spectroscopy (ARXPS). An epitaxial FeF$_2$(110) film was grown on a MgF$_2$(110) single crystal substrate and exposed to atomic lithium in an ultra-high vacuum chamber. A series of ARXPS spectra was taken after each Li exposure to obtain depth resolved chemical state information. The Li-FeF$_2$ reaction initially proceeded in a layer-by-layer fashion to a depth of $\sim$ 1.2 nm. Beyond this depth, the reaction front became non-planar, and regions of unreacted FeF$_2$ were observed in the near-surface region. This reaction progression is consistent with molecular dynamics simulations. Additionally, the composition of the reacted layer was similar to that of electrochemically reacted FeF$_2$ electrodes. An intermediary compound Fe$_x$Li$_{2-x}$F$_2$, attributed to iron substituted in the LiF lattice, has been identified using XPS. These measurements provide insight into the atomistics and phase evolution of high purity FeF$_2$ conversion electrodes without contamination from electrolytes and binders, and the results partially explain the capacity losses observed in cycled FeF$_2$ electrodes.

I. INTRODUCTION

Iron (II) fluoride-based nanocomposites are promising candidates as active materials in lithium ion conversion battery cathodes. Upon exposure to lithium ions in an electrochemical cell, FeF$_2$ is believed to undergo the following reversible reaction:4,5

$$2\text{Li}^+ + 2e^- + \text{Fe}^{(2+)}\text{F}_2 \rightarrow 2\text{LiF} + \text{Fe}^{(0)}.$$ (1)

Although FeF$_2$ is a bulk insulator with a band gap of about 2 eV,5 the use of FeF$_2$ nanoparticles embedded in a chemically inert conducting carbon matrix has been shown to increase the conductivity of FeF$_2$-based electrodes sufficiently to allow for efficient charge transport.1,2 Additionally, the volumetric expansion of FeF$_2$ upon lithiation is only 16%, which is small enough to avoid strain-induced damage to the cell during cycling.3 FeF$_2$ has a theoretical specific capacity of 571 mAh/g, while working devices have exhibited capacities as high as 350-450 mAh/g for several cycles.3,6 These values represent a significant improvement over the theoretical and practical capacities of modern LiCoO$_2$ electrodes, which are 272 mAh/g and 145 mAh/g respectively.7

This increase in charge storage is due to a fundamental difference in the reaction mechanism of iron fluoride particles. Conventional Li-ion intercalation batteries rely on the insertion/deinsertion of Li$^+$ ions into planar or columnar channels in a cathode material such as LiCoO$_2$.8 In practice, only $\sim$ 0.5 Li ions per formula unit can be inserted and removed from the cathode without significantly altering the crystalline structure of the LiCoO$_2$ and destroying the structural integrity of the cathode. Conversely, the Li-FeF$_2$ conversion involves extensive morphological and structural transformations as FeF$_2$ is converted to metallic Fe and LiF. This reaction transfers two Li ions, and hence two electrons, per formula unit.4,5,9,10

Despite the apparent advantages of using FeF$_2$ cathodes, their implementation has thus far been limited by capacity fading and high voltage hysteresis upon cycling. These issues have been attributed in part to limited lithium mobility within the FeF$_2$/Fe/LiF composite and to a loss of active material from parasitic reactions.4,10 Recent molecular dynamic (MD) simulations by Ma and Garofalini11,12 have suggested that the FeF$_2$(110) and (001) crystalline faces react differently upon exposure to lithium. The FeF$_2$(001) orientation exposes [001] channels in which the kinetic barrier for Li ion diffusion is less than 0.05 eV. These channels facilitate lithium diffusion into the bulk of the FeF$_2$, which allows the conversion reaction to proceed rapidly from the surface to the bulk of the material. Conversely, the FeF$_2$(110) surface has a high ($\sim$ 1 eV) kinetic barrier for Li transport into the bulk, which causes the conversion reaction to initiate in a layer-by-layer fashion. However, as the reaction proceeds several layers into the FeF$_2$ surface, grain boundaries between Fe nanoparticles and LiF provide pathways for lithium diffusion into the crystal. These interfacial regions then become preferential nucleation points for the
sub-surface conversion reaction, causing a non-planar reaction front as the conversion reaction proceeds into the FeF$_2$(110) crystal.

In order to bridge the gap between these MD simulations and bulk measurements of electrochemically cycled FeF$_2$ electrodes, it is necessary to study high-purity FeF$_2$ samples in the absence of electrolytes, binders, and separators which affect cell performance. To this end, high-purity epitaxial FeF$_2$(110) thin films were grown and exposed to atomic lithium in an ultra-high vacuum chamber. The (110) orientation has the lowest surface energy of the FeF$_2$ crystalline faces, so this surface is expected to dominate the nanocrystalline FeF$_2$ composites used in electrochemical cells. The resulting solid state reaction was then characterized by angle-resolved x-ray photoelectron spectroscopy (ARXPS) in order to produce a nanometer-scale model of the reaction progression. The results obtained from these ARXPS measurements indicate that the reaction front initially progresses in a layer-by-layer fashion, forming a planar interface between the reacted overlayer and the unreacted FeF$_2$ substrate. This is consistent with MD simulations for small lithium exposures. However, when the reacted layer reached a depth of $\sim 1.2$ nm into the film, the reaction front deviated from this planar geometry and the reacted overlayer acquired a non-uniform thickness. This behavior is consistent with a model in which preferential reaction nucleation occurs in the sub-surface regions of the FeF$_2$(110) crystal. The chemical composition of the reaction products and the phase evolution of the FeF$_2$ film agree with results of pair distribution function (PDF), galvanostatic intermittent titration technique (GITT), and XPS studies of cycled FeF$_2$ electrodes, which found evidence of the formation of an intermediate compound identified as Fe$_x$Li$_{2-2x}$F$_2$.\textsuperscript{1,6}

II. EXPERIMENTAL METHODS

A. Sample Preparation

Epitaxial FeF$_2$(110) films were grown on MgF$_2$(110) single crystal substrates by electron beam evaporation of FeF$_2$ powder (Cerac Inc.) at a rate of 0.05 nm/s. The temperature of the MgF$_2$ substrates was maintained at 300°C to enhance the crystallinity of the film. During deposition, the chamber pressure was less than 2 $\times$ 10$^{-7}$ Torr. The FeF$_2$ structure and crystallinity were investigated using x-ray reflectometry (XRR), x-ray diffraction (XRD), and helium ion microscopy (HIM). The x-ray data was acquired using a D8 Discover Bruker rotating anode diffractometer with Cu K$\alpha$ ($\lambda = 1.54\AA$) radiation. The film was exposed to air during the transfer from the growth chamber to the ultra-high vacuum analysis chamber. In order to remove adsorbates from the surface, the FeF$_2$ film was degassed at 300°C in ultra-high vacuum (UHV) for 30 minutes. This temperature was sufficiently high to remove most surface impurities without reducing the FeF$_2$ film.

Atomic lithium was deposited onto the surface of the FeF$_2$ film at room temperature using a lithium getter source (SAES Getters). The lithium source was well degassed prior to exposure, and the pressure in the vacuum chamber was kept below 5 $\times$ 10$^{-9}$ Torr during lithiation. The Li exposure rate was estimated to be 0.07 nm/min, which was chosen to be slow enough to prevent the accumulation of metallic Li at the surface of the FeF$_2$ film.

B. Angle-Resolved XPS

X-ray photoelectron spectroscopy measurements were performed using a Thermo Scientific ESCALAB 250Xi using a monochromated Al K$\alpha$ x-ray source with an energy of 1486.6 eV. The total resolution of the instrument was 0.5 eV. To obtain angular resolution, the half-angle of acceptance of the electron analyzer was set to 10$°$ and the sample was rotated with respect to both the x-ray source and detector from 0$°$ to 50$°$ in 5$°$ increments. In this work, the emission angle is measured with respect to the surface normal.

In order to minimize the buildup of electrical charge during XPS measurements, charge compensation was performed using a dual beam flood source of low-energy Ar$^+$ ions and 1 eV electrons. Spectra taken before and after these measurements showed no x-ray or ion induced damage. A small amount of peak broadening attributed to differential charging was observed after prolonged lithium exposures, likely due to the inhomogeneity in the conductivity of the conversion reaction products. The C 1s spectral component at -284.8 eV arising from adventitious carbon was chosen as a binding energy reference.\textsuperscript{13} XPS spectra were analyzed by subtracting Shirley backgrounds and fitting the remaining core level features with Voigt profile components,\textsuperscript{14} or, in the case of Fe 2p spectra, with broadened reference spectra taken from pure FeF$_2$ and Fe metal samples.

Angle-resolved XPS (ARXPS) makes use of the nanometer-scale inelastic mean free path (IMFP) of electrons in solid media to obtain depth resolved chemical and elemental information from samples whose surface roughness is less than 1-2 nm. For a thin (<5 nm) overlayer of material A (thickness d) on a substrate B, the ratio $R$ of XPS intensities from species A and B is well approximated by

$$R(\theta, d) = \frac{I_A}{I_B} = \frac{I_A^\infty}{I_B^\infty} \left[ \frac{1 - \exp(-d/\lambda_A \cos \theta)}{\exp(-d/\lambda_B \cos \theta)} \right]$$

where $\lambda_{ij}$ is the IMFP in material j for electrons emitted from material i, $\theta$ is the electron emission angle measured with respect to the surface normal, and $I_{ik}^\infty$ is the XPS intensity of an infinitely thick layer of material k.\textsuperscript{15} To increase the precision of the ARXPS analysis, an effective attenuation length (EAL) was substituted for each IMFP in Equation 2 in order to account for elastic scattering of photoelectrons at large emission angles.\textsuperscript{16-18} EALs were...
calculated as a function of emission angle and overlayer thickness for each compound using the NIST Electron EAL Database. Equation 2 can be simplified by assuming that the EAL is constant:

\[ R(\theta, d) \approx R^\infty \left[ \exp\left(\frac{d}{\lambda \cos \theta}\right) - 1 \right] \]  

(3)

where \( R^\infty = I_A^\infty / I_B^\infty \). This expression is then linearized by rearranging terms and taking the natural logarithm:

\[ \ln (1 + R/R^\infty) \approx d/\lambda \cos \theta. \]  

(4)

To calculate the thickness and uniformity of the reacted layers as precisely as possible, Equation 2 was used. Since this equation has no analytical solution for \( d \), a multi-layer model of the Li-FeF\(_2\) reaction was constructed and used to predict the variation of \( R \) as a function of \( \theta \). The details of this model will be explained further in the subsequent section. Data will be analyzed using Equation 4 so that it can be presented in a linearized form.

III. RESULTS AND DISCUSSION

A. Characterization of the FeF\(_2\)(110) Film

![XRR - FeF\(_2\) As Grown](image-url)

FIG. 1: X-ray reflectometry data from the as-grown FeF\(_2\)(110) film indicating a film thickness of 42.7 nm and a surface roughness of \( \sigma = 0.7 \) nm.

Figure 1 shows x-ray reflectometry (XRR) data from the as-grown FeF\(_2\)(110) thin film. The fit to the XRR data was performed with MOTOFIT software by assuming a slab model density profile (Figure 1: inset). The film thickness was assumed to have a Gaussian distribution with a standard deviation \( \sigma \). These measurements indicate an FeF\(_2\) film thickness of 42.7 nm and a surface roughness of \( \sigma = 0.7 \) nm. Additionally, helium ion microscopy images of the film indicated that the lateral dimensions of the FeF\(_2\) domains were 10-15 nm.

After transferring the FeF\(_2\)(110) film to the XPS chamber and annealing at 300°C to remove surface contamination, a series of normal emission XPS spectra was taken to measure the purity and stoichiometry of the film. These spectra are shown in Figure 2. The Fe 2p core level spectrum (inset (a)) is composed of broad 2p\(_{3/2}\) and 2p\(_{1/2}\) states at binding energies of -711 eV and -725 eV and small satellite features whose centroids are at \( \sim 6 \) eV higher binding energy than the main doublet peaks. The F 1s core level spectrum (inset (b)) is composed of a single feature at -685 eV. These Fe 2p and F 1s features are consistent with previous studies of high purity FeF\(_2\) thin films and powders. Normalizing the F 1s and Fe 2p intensities by their respective Scofield factors and detector functions yielded a F:Fe ratio of (1.8 \pm 0.1):1, confirming the stoichiometry of the film. The O 1s core level spectrum (inset (c)) is composed of three peaks. The main peak at a binding energy of -530 eV is attributed to FeO, which formed due to the oxidation of the FeF\(_2\) film in air. The F:O ratio suggests that only the topmost layer of FeF\(_2\) was oxidized. The smaller O 1s peaks at -531.5 and -532 eV are attributed to hydroxyl and water contamination on the surface of the sample. These intensities are consistent with one monolayer of surface contamination. The C 1s spectrum (inset (d)) exhibits a large component at -284.8 eV and two smaller components at -287.5 and -289.0 eV. These are indicative of adventitious carbon contamination, and their total intensity is consistent with slightly less than one monolayer of contamination on the surface of the film. Despite the surface contamination present on the FeF\(_2\) film, the formation of lithium oxides, hydroxides, and carbonates was not observed upon exposure to lithium. Indeed, the O 1s and C 1s spectra were unchanged after the lithium deposition, and hence these contaminants were not believed to significantly affect the Li-FeF\(_2\) reaction. It should be noted in subsequent sections that, due to its energy overlap with the Fe 3p core level, the Li 1s peak was not evaluated in this work.

B. Chemical State Analysis

The FeF\(_2\)(110) film was exposed to Li in intervals ranging from 5 to 20 minutes at a rate of about 0.07 nm/min, for a total lithiation time of 160 minutes. After each lithiation, a series of XPS spectra was acquired. In order to extract quantitative chemical information from the XPS data, a least squares fit was performed for each Fe 2p spectrum using a linear combination of reference spectra taken from pure Fe metal and FeF\(_2\) samples (Alfa Aesar). Figure 3 shows a normal emission Fe 2p XPS spectrum after 35 minutes of total Li exposure. The XPS data, shown as black dots, exhibits multiple peaks corre-
responding to different chemical states of iron. The Fe$^{2+}$ (FeF$_2$, red) and Fe metal (Fe$^0$, gray) reference spectra were not sufficient to fit the data, suggesting the formation of an intermediate compound during the conversion reaction. To account for this missing intensity, an additional spectral component was constructed from the final (160 minute) lithiation spectrum by subtracting Fe metal and FeF$_2$ components from the Fe 2p data. The details of this procedure are presented in Section SII of the Supplemental Material. The resulting lineshape, shown in yellow in Figure 3, exhibited 2p doublet peaks at binding energies of -709 eV and -723 eV and intense satellite features at -716 eV and -730 eV.

The peak positions and lineshape of this chemical species are not consistent with any known iron fluoride, oxide, or oxyfluoride compounds. However, several recent studies provide insight into the possible nature of this compound. First, recent pair distribution function (PDF) studies of electrochemically cycled FeF$_2$ by Ko and coworkers observed an expansion of the LiF rocksalt lattice upon delithiation. This was attributed to the incorporation of iron in the LiF lattice to form Fe$_x$Li$_{12-2x}$F$_2$, with $x$ estimated to be between 0.4 and 0.5. Additionally, MD simulations by Ma and Garofalini predicted the formation of a ternary Fe-Li-F compound upon the lithiation of both FeF$_2$(110) single crystals and FeF$_2$ nanoparticles. Consequently, the additional Fe 2p component observed in the lithiated FeF$_2$ spectrum is attributed to the ternary compound Fe$_x$Li$_{12-2x}$F$_2$.

The Fe$_x$Li$_{12-2x}$F$_2$ spectral component was necessary to fit every Fe 2p spectrum acquired after the initial lithiation, and its integrated intensity was found to be between 85% and 110% that of the Fe$^0$ component for every Li exposure, which is consistent with $x \approx 0.5$. This chemical species was also identified in XPS spectra of electrochemically cycled FeF$_2$ electrodes. Using $x \approx 0.5$, this compound can be written as Fe$_{0.5}$LiF$_2$, and hence an alternative FeF$_2$ conversion reaction pathway can be described by

$$\text{Li} + \text{FeF}_2 \rightarrow \text{Fe}_{0.5}\text{LiF}_2 + 0.5\text{Fe}. \quad (5)$$

In the following sections, it will be assumed that $x = 0.5$, and this chemical compound will be referred to as Fe$_{0.5}$LiF$_2$. Since the amount of Fe$_{0.5}$LiF$_2$ was observed to increase monotonically with each Li exposure, this compound is believed to be a stable product of the FeF$_2$ conversion reaction.
C. ARXPS of the Li-FeF$_2$ Reaction

XPS was used to determine the changes in FeF$_2$ film stoichiometry after each lithium exposure. Figure 4(a) shows the normal emission Fe 2p spectra acquired after each lithium exposure. The spectra have been normalized to their maximum intensities to allow for a visual comparison. The bottom spectrum in Figure 4(a) is the same as the Fe 2p spectrum shown in Figure 2. Upon exposure to lithium, new features appeared at binding energies of -707 eV and -720 eV, attributed to the 2p$_{1/2}$ and 2p$_{1/2}$ electronic states of iron metal. The intensity of these features increased monotonically as a function of Li exposure while the FeF$_2$ intensity decreased simultaneously, in accordance with the conversion reaction proposed in Equation 5. The topmost Fe 2p spectrum, acquired after 160 minutes of total Li exposure, mainly exhibits Fe$^0$ and Fe$_{0.5}$LiF$_2$ features with FeF$_2$ accounting for only 12% of the spectral intensity.

In order to obtain depth-resolved information from the lithiated FeF$_2$ film, a series of angle-resolved XPS spectra was taken at 5° increments after each lithiation. Figure 4(b) shows one such series acquired after 35 minutes of total Li exposure and the three Fe 2p components required to fit each spectrum. These spectra are representative of the ARXPS data acquired after each lithiation step and are presented as an example. The heights of the features in order to enhance their visual differences. At normal emission ($0^\circ$), the Fe 2p spectrum exhibits features from FeF$_2$, Fe$^0$, and Fe$_{0.5}$LiF$_2$ chemical states. As the electron emission angle increases, the integrated intensity of the FeF$_2$ component decreases relative to the Fe$^0$ component. Conversely, the Fe$_{0.5}$LiF$_2$ component maintains a 1:1 ratio with the Fe$^0$ component for all angles. This suggests that the Fe$^0$ and Fe$_{0.5}$LiF$_2$ species formed an overlayer atop the FeF$_2$ film. Since no angular variation in the Fe$^0$:Fe$_{0.5}$LiF$_2$ ratio was observed for any Li exposure, only the Fe$^0$:FeF$_2$ ratio was necessary to calculate the thickness and uniformity of the reacted Fe$_{0.5}$LiF$_2$+Fe$^0$ overlayer. Hence, the Fe$^0$:FeF$_2$ ratio ($R$) was analyzed after each lithium exposure. Figure 5 shows the evolution of $R$ as the function of emission angle after 5 minutes (a) and 35 minutes (b) of total lithium exposure. The solid and dashed lines represent fits to the data that correspond to uniform reacted overlayers and whose (artificially extrapolated) y-intercepts are at the origin.

For both 5 minute and 35 minute Li exposures, the value of $R$ (shown as black dots in Figure 5) increases as a function of $\theta$, again consistent with an overlayer of Fe and Fe$_{0.5}$LiF$_2$ on the FeF$_2$ substrate. The error bars shown were calculated from the residuals of the Fe 2p fit and do not account for the uncertainty caused by variations in the position/shape of the x-ray beam spot as the sample was tilted. For the 5 minute exposure, shown in Figure 5(a), the fit to the data (solid red line) was obtained from Equation 2 by considering a uniformly thick reacted overlayer consisting of stoichiometric amounts of Fe and Fe$_{0.5}$LiF$_2$.

The ARXPS model assumed that the number of photo-electrons passing through each species was proportional to the specific volume of that species. This is mathematically equivalent to dividing the overlayer vertically into discrete regions of Fe$_{0.5}$LiF$_2$ and Fe, as illustrated in Figure 6(a). For small overlayer thicknesses ($d <$ 5 nm), this approximation should be accurate since the typical dimensions of the Fe nanoparticles are expected to be between 2-5 nm.$^{5,11,12}$ Consequently, the particles should extend from the sample surface to the reaction interface, as shown in Figure 6(b). Hence, the agreement between the data and the uniformly thick overlayer model ($r^2 = 0.958$) suggests that the conversion reaction front was planar for 5 minutes of lithium exposure. The reacted overlayer thickness is estimated to be 0.5 ± 0.1 nm, which is consistent with the conversion of about one bi-layer of FeF$_2$. The reaction front remains uniform for overlayer thicknesses up to 1.2 ± 0.1 nm. More information about the ARXPS model for this and subsequent lithium exposures is presented in Section SIV of the Supplemental Material.

Figure 5(b) shows the $R(\theta, d)$ curve (black data points) obtained after 35 minutes of total Li exposure, and two fits based on Equation 2 assuming a uniformly thick reacted overlayer (solid red line) and a reacted overlayer with non-uniform thickness (dashed red line). The model with a non-uniform overlayer thickness agrees well with the data ($r^2 = 0.978$) and is described in more detail below. For this and subsequent Li exposures, the reaction model was modified to account for a non-planar interface between reacted and unreacted materials, as shown in Figure 6(c). The best agreement between the measured and predicted $R(\theta, d)$ curves was obtained for models in which ($87 \pm 2$)% of the reaction front area proceeded to a depth of $D = 3.8 \pm 0.3$ nm, while the remaining ($13 \pm 2$)% remained at a depth of $d =$ 1.2 ± 0.1 nm, as shown in the idealized and realistic models in Figure 6(a) and (b) respectively. In other words, ($13 \pm 2$)% of the near-surface FeF$_2$ remained unreacted after the reaction front proceeded beyond 1.2 nm into the film. Again, this variation in the reacted overlayer thickness is consistent with MD simulations.$^{11}$

Figure 7 shows the linearized $R(\theta, d)$ plots, which were constructed from the approximation shown in Equation 4. By plotting $\ln(1 + R/R_\infty)$ vs. $\theta$, the curves that correspond to uniform reacted overlayers should appear as straight lines whose slopes are proportional to the overlayer thickness and whose (artificially extrapolated) y-intercepts are at the origin.

Using this simple method of analysis provides an intuitive explanation of the relationship between the $R(\theta, d)$ curves and the diagrams in Figure 6. The values of $d$, $D$, and the percentage of unreacted FeF$_2$ covered by a thin overlayer are summarized in Table I. For small Li exposures (overlayer thicknesses less than $\sim$ 1.2 nm), the reaction front proceeds uniformly through the film. Consequently, the data corresponding to 5 minutes (0.5 nm) and 15 minutes (1.2 nm) of total Li exposure are well-fit
FIG. 4: (a) Evolution of the normal emission Fe 2p XPS spectra from FeF₂(110) before and after sequential Li exposures. (b) Angular dependence of the Fe 2p spectrum after 35 minutes of total Li exposure. The spectra have been normalized by height in order to accentuate the differences between their lineshapes.

FIG. 5: The Fe²⁺:FeF₂ ratio \( R \) versus electron emission angle after 5 minutes (a) and 35 minutes (b) of total lithium exposure. The solid (dashed) curves are fits based on models with reacted overlayers of uniform (variable) thickness.

by \( R(\theta, d) \) curves derived from uniformly thick overlayer models (shown as solid red lines). For greater overlayer thicknesses, the reaction front becomes non-planar, and hence the curves corresponding to \( > 25 \) minutes (2.5 nm and thicker) are not well fit by uniformly thick overlayer models, but instead by models with non-uniform overlayers (dashed red lines). When the reaction front proceeds deeper than the escape depth of the Fe 2p photoelectrons (\( D > 10 \) nm), the film appears as a mixture of Fe, Fe₀₂₅LiF₂, and unreacted FeF₂. At these large lithium exposures, the XPS data no longer varies with emission angle, and hence no information can be garnered about the depth of the reaction front. However, the amount of unreacted FeF₂ is observed to slowly decrease from \((13 \pm 2)\% \) to \((8 \pm 1)\% \), as seen by the increase in the Fe:FeF₂ ratio between the \( > 12 \) nm and \( > 20 \) nm curves in Figure 7. For these \( R(\theta, d) \) curves, the low intensity of the FeF₂ component in the Fe 2p spectra causes a large uncertainty in the value of \( R \). However, the position and shape of the x-ray beam on the sample also contributed to the error, which likely caused the \( R \) values for the \( 0° \) data points to differ significantly from the \( R(\theta, d) \) fits. Despite the low coefficient of determination for the 160 minute data \( (r^2 = 0.322) \), the consistent increase in the \( R \) values indicates a reduction of FeF₂ in the near-surface region.

These ARXPS results show that the progression of the conversion reaction into the FeF₂(110) surface occurs in three distinct phases. At low lithium exposures the reaction front is planar, and hence the reacted region forms
This is consistent with MD simulations, and can be understood intuitively since the [110] channels into the FeF$_2$(110) film have a high kinetic barrier for Li transport which prevent lithium diffusion directly into the bulk of the film. Consequently, reaction front remains planar until the reacted overlayer reaches a thickness of $\sim$ 1.2 nm. Upon further lithium exposures, the reacted overlayer thickness becomes non-uniform and can be modeled by a thick ($> 2.5$ nm) Fe$^{0}$/Fe$_{0.5}$LiF$_2$ overlayer occupying $\sim$ 87% of the FeF$_2$ surface, while the remainder of the overlayer remains $\sim$ 1.2 nm thick. This can also be interpreted as 13% of the near-surface FeF$_2$ remaining unreacted. One possible mechanism causing this non-planar reaction front is preferential Li diffusion along the Fe$^{0}$/Fe$_{0.5}$LiF$_2$ interfaces, resulting in localized regions in which Li is able to reach the underlying FeF$_2$ and react. Lastly, when the reacted overlayer becomes thicker than $\sim$ 7.5 nm, the percentage of unreacted FeF$_2$ is observed to decrease from 13% to 8% upon further lithium exposures. The persistence of these unreacted FeF$_2$ regions suggest that the FeF$_2$ becomes trapped within the Fe$_{0.5}$LiF$_2$ matrix. This loss of active cathode material could partially explain the capacity losses observed in cycled FeF$_2$ cells.

IV. CONCLUSION

Epitaxial FeF$_2$(110) thin films were exposed to atomic Li in an ultra-high vacuum environment as a solid state analogue for the discharge of FeF$_2$ conversion batteries. Chemical state analysis using XPS showed the presence of an iron compound identified as Fe$_{0.5}$LiF$_2$, which agrees with prior distribution function and XPS measurements of electrochemically cycled FeF$_2$ electrodes. ARXPS of the lithiated FeF$_2$ showed that the reaction initially proceeded in a layer-by-layer manner. This is attributed to the low diffusivity of lithium into FeF$_2$ (110) channels. When the reacted region became thicker than 1.2 nm, a uniformly thick overlayer on the FeF$_2$(110) substrate.
grain boundaries between the metallic Fe\(^0\) and Fe\(_{0.5}\)LiF\(_2\) facilitated preferential Li diffusion into the film, leading to a non-planar reaction front and hence regions of unreacted FeF\(_2\), in agreement with MD simulations.\(^{11}\)

This work shows that the FeF\(_2\)(110) crystalline face is reactive with Li despite the high kinetic barrier for Li diffusion directly into the crystal. However, the incomplete reduction of FeF\(_2\) in the near surface regions suggests that FeF\(_2\) might become trapped in the Fe\(_{0.5}\)LiF\(_2\) matrix that forms upon lithiation. This could lead to a loss of active conversion material and hence a loss in capacity upon cycling as seen in FeF\(_2\) conversion materials. Additionally, the formation of Fe\(_{0.5}\)LiF\(_2\) prevents iron ions in the cathode from being fully reduced upon lithium exposure, further diminishing the charge storage capacity of FeF\(_2\) electrodes.

In order to gain more insight into the reactivity of FeF\(_2\), additional ARXPS studies will be performed on the FeF\(_2\)(001) surface. A thorough characterization of the Fe\(_{0.5}\)LiF\(_2\) compound with TEM to determine its structure and location in lithiated FeF\(_2\) will be crucial in developing a complete understanding of the Li-FeF\(_2\) reaction. Additionally, a comprehensive study of the effect of Li exposure rate would shed light on the nature of the kinetic limitations of the Li-FeF\(_2\) reactions. Lastly, the use of thin FeF\(_2\) films on conducting substrates could also allow for scanning tunneling microscopy imaging of the FeF\(_2\) surface after small Li exposures. This would further elucidate the mechanism by which Li reacts with both the (110) and (001) surfaces.

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**Associated Content**

More information about the identification of the Fe\(_{0.5}\)LiF\(_2\) XPS component and the model used to generate \(R(\theta, \delta)\) curves is reported in the Supporting Information. XPS spectra from electrochemically cycled FeF\(_2\) cathodes and from lithiated iron oxide powders are also presented.

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