Final Scientific/Technical Report for Low Cost, High Capacity Non-Intercalation Chemistry Automotive Cells

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Executive Summary

Commercial Li-ion batteries typically use Ni- and Co-based intercalation cathodes. As the demand for improved performance from batteries increases, these cathode materials will no longer be able to provide the desired energy storage characteristics since they are currently approaching their theoretical limits. In addition, the Ni- and Co-containing batteries may negatively affect ecology due to the Ni and Co toxicity. These metals also may have negative human health impacts associated with the production, processing, and use of Ni and Co, which may cause adverse respiratory, pulmonary, and neurological effects as well as cancer in those exposed. Additionally, the uneven distribution of Co in the earth crust (with most Co mining located in developing countries) and the insufficient use of suitable personal protection equipment in many of the Co mines has created major health and safety concerns. Development of new types of commercially-viable, environmentally friendlier cathode materials will allow for development of lighter, smaller, and safer batteries for use in electric vehicles, personal devices, and for storage of energy from renewable sources such as wind and solar.

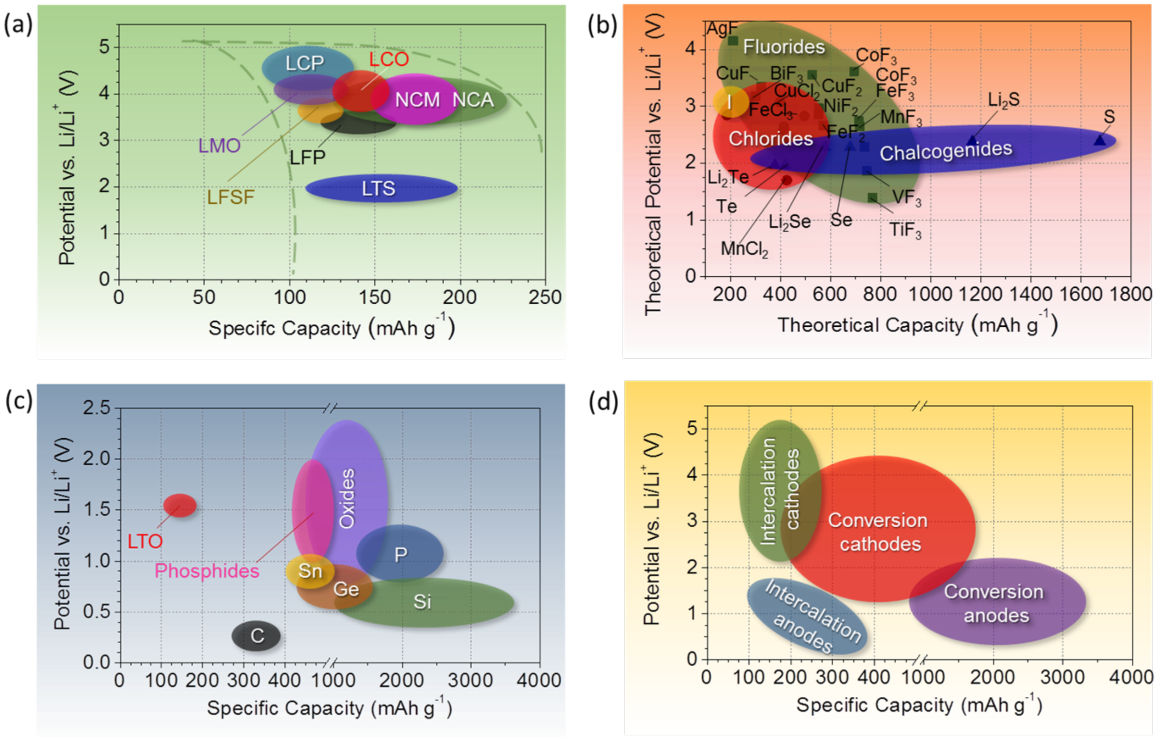

Figure 1. Schematic representation of fundamental electrochemical performance characteristics for intercalation-type and conversion-type active materials for anodes and cathodes in Li-ion batteries. [Reproduced from N. Nitta, F. Wu, J.T. Lee and G. Yushin "Lithium Ion Battery Materials: Present and Future", Materials Today, 2015, 18 (5), 252-264].

Conversion cathode materials are prime candidates for improvement of Li-ion batteries. On both a volumetric and gravimetric basis they have higher theoretical capacity than intercalation cathode materials (Figure 1). As a result, they may offer higher volumetric and higher specific energy characteristics to rechargeable Li and Li-ion cells when used in combination with Si-based or Li-based anodes (Figure 2-3). In addition, conversion-type cathode materials may comprise less expensive and more abundant elements, which are safer and friendlier to the environment. Development of conversion cathode materials that utilize earth-abundant metals will make batteries less-toxic, cheaper, more socially-responsible, and the supply-chain more reliable than Co-based cathodes.

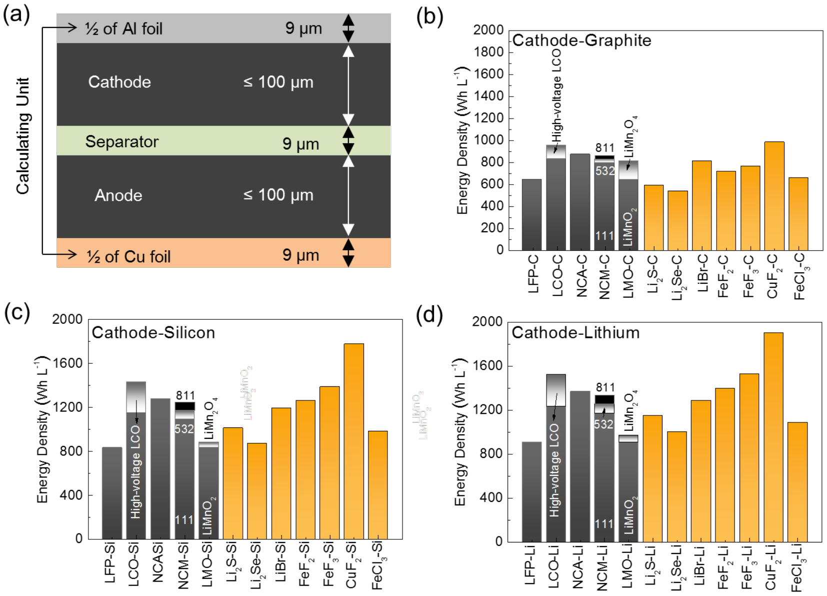

Figure 2. Estimations of the volumetric energy densities that may be achievable in a unit stack (cell repeat unit) composed of half of 9 micron Al and Cu foil, 9 micron polymer separator and the thickest electrode being 100 micron [Reproduced from F. Wu and G. Yushin "Conversion cathodes for rechargeable lithium and lithium-ion batteries", Energy & Environmental Science, 2017, 10, 435-459].

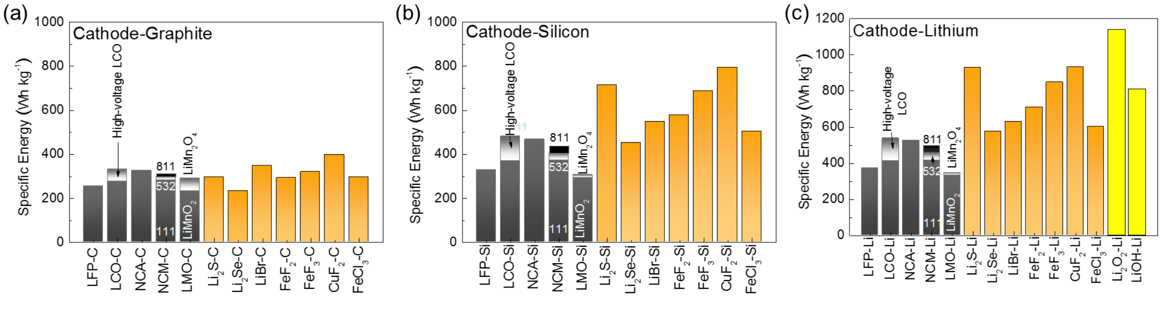

Figure 3. Estimations of the specific energy densities that may be achievable in a unit stack (cell repeat unit) composed of half of 9 micron Al and Cu foil, 9 micron polymer separator and the thickest electrode being 100 micron [Reproduced from F. Wu and G. Yushin "Conversion cathodes for rechargeable lithium and lithium-ion batteries", Energy & Environmental Science, 2017, 10, 435-459].

Compared to S cathodes, selected metal fluoride (MF_x) cathodes (e.g., CuF_2) offer higher specific energy density and dramatically higher volumetric energy density to battery cells. Compared to air cathodes (e.g., considering a more realistic case of LiOH cathode), MF_x cathodes (e.g., FeF_3 and CuF_2) offer higher specific energy density and dramatically higher volumetric energy density. Unfortunately, cells containing MF_x cathodes typically have very short cycle life, or are mostly considered to be just primary cells due to multiple challenges. The cathode reaction that takes place during cell discharge is the conversion of MF_x to LiF and M (Figure 4). Phase separation of the LiF and metal can cause large voltage hysteresis, low rate capability, or isolation and loss of active material. MF_x and LiF have low electronic and ionic conductivities that also contribute to large voltage hysteresis and low rate capability. Additionally, metal salts that are soluble in electrolyte can form due to side reactions during cell cycling. This can lead to migration of the soluble cathode-derived compounds through the separator to the anode, which reacts chemically and decreases cell capacity.

We sought to address the challenges associated with metal fluorides through nanostructured material design and synthesis. We hypothesized that nanoparticles of MF_x encapsulated in a matrix material should overcome the challenges associated with MF_x cathodes. The small size-scale prevents large phases of LiF and M from forming, and a matrix containing conductive material allows access of electrons and Li-ions to the material. This should lead to lower voltage hysteresis and increased reversibility. Encapsulation of the MF_x nanoparticles in the matrix prevents diffusion of any soluble metal salt that may form during cell cycling.

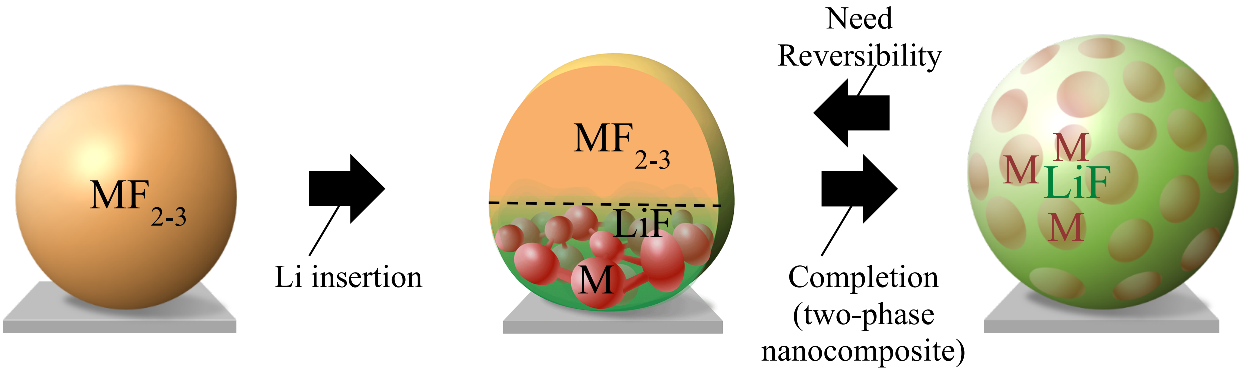

Figure 4. Material design approach to a conversion cathode material. Prevention of separation of M and LiF phases will increase reversibility [Reproduced from F. Wu and G. Yushin "Conversion cathodes for rechargeable lithium and lithium-ion batteries", Energy & Environmental Science, 2017, 10, 435-459].

Through all stages of synthesis and electrochemical testing, we have designed processes that are readily scalable and a cathode material that is fully compatible with already existing cell manufacturing infrastructure to serve as a drop-in replacement of current Li-ion battery cathode materials. This drop-in approach will lead to cheaper and faster deployment of new technology.

A major goal of this project was to develop and demonstrate Li-ion cells based on Si-comprising anodes and metal fluoride (MF_x) comprising cathodes. Pairing the high-capacity MF_x cathode with a high-capacity anode, such as an alloying Si anode, allows for the highest possible energy density on a cell level. We aimed to demonstrate the use of the MF_x cathode not only with impractical and difficult to scale (with current technology) Li-metal anodes typically used for proof-of-concept studies, but with a commercially-viable anode material Sila Nanotechnologies is currently scaling for production and commercial use.

After facing and overcoming multiple material synthesis and electrochemical instability challenges, we succeeded in fabrication of MF_x half cells with cycle stability in excess of 500 cycles (to 20% or smaller degradation) and full cells with MF_x-based cathodes and Si-based anodes with cycle stability in excess of 200 cycles (to 20% or smaller degradation) at room temperature. Future work is required to achieve cycle stability in excess of 1,500 cycles in full cells (e.g., for automotive applications) when cycled in a broader temperature window. Future work is also required to reduce the volume fraction of inactive components of the cells and increase cell-level energy and power densities.

Summary of Project Activities

This project proposed to create and demonstrate a metal fluoride (MF_x) conversion cathode material that would overcome the pitfalls that have prevented use of these materials (such as low cycling stability, very slow rate capability, low energy efficiency, low capacity utilization, etc.) and eventually allowing for fabrication of commercially viable cells with higher energy density and capacity. The goal of this project was to pair these high capacity metal fluoride cathodes with a high capacity anode, such as a Si-based anode, realizing even higher energy density than possible with conventional anode materials.

The initial phase of the project focused on the development and characterization of a MF_x-comprising (nano)composite materials where nanoscale phases would help overcome the voltage hysteresis, phase separation, active material dissolution and low conductivity usually associated with metal fluoride cathode materials. In the simplest proof-of concept case, we could incorporate MF_x nanoparticles into the pores of porous carbon materials. We started the project with such a composite design. Together with our sub-contractors at Georgia Tech, we also started synthesis with less energy-dense and easier to produce FeF_2-based composite materials. The porous carbon in this example provides electronic conductivity and also defines the size of the nanoparticles, as they are confined in carbon pores.

In one of the earlier simple synthesis approaches, we utilized a solution of $FeSiF_6$ as a FeF_2 precursor. A Process Flow like that schematically shown in Figure 3 was utilized in the composite fabrication. The porous carbon powders were mixed with the $FeSiF_6$ solution and put under reduced pressure to facilitate diffusion of the solution into the pores of the porous carbon. As the solvent evaporated, the $FeSiF_6$ precipitated into the nanoscale pores, forming nanoparticles of $FeSiF_6$. To make sure $FeSiF_6$ precipitations take place within the carbon pores only (and thus prevent their nucleation and growth on the outer surface of the particles), while achieving high particle-to-particle uniformity, several criteria were satisfied. First, the carbon was selected to be sufficiently hydrophilic to warrant complete pore wetting by the precursor solution. Second, it was critical to make sure that the concentration of $FeSiF_6$ does not exceed the solubility limit before capillary forces pull all the liquid into the pores. Finally, it was important to agitate the powders during drying to make sure high particle-to-particle uniformity is achieved. After successful and uniform infiltration was achieved, the $FeSiF_6$/carbon composite was then heated to 240 ˚C, upon which SiF_4 gas evolved, leaving a composite of porous carbon containing FeF_2 nanoparticles.

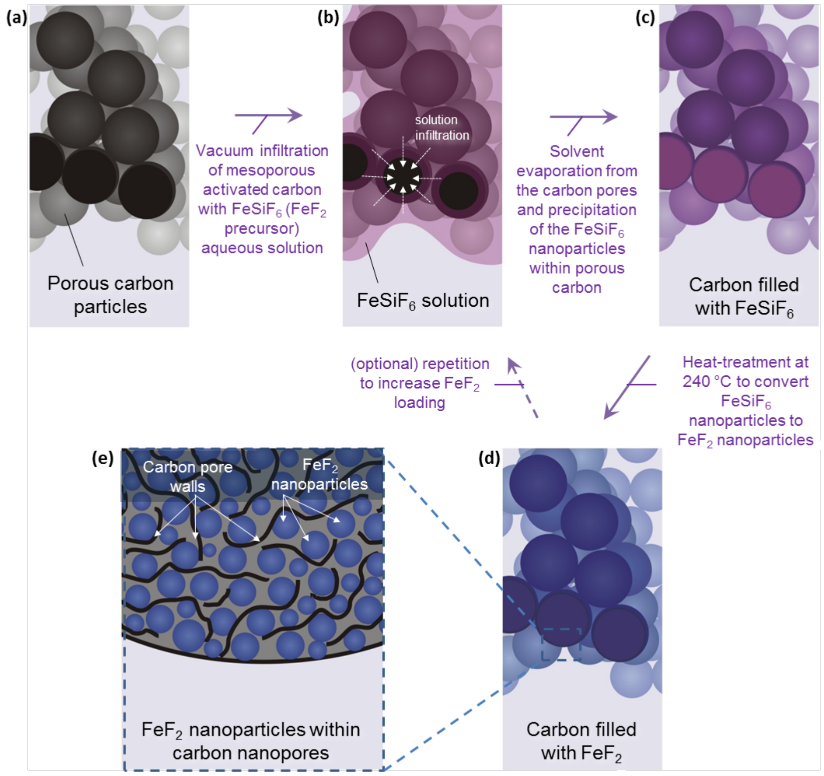

Figure 5. Schematic representation of synthesis of a FeF_x/carbon composite material. [Reproduced from W. Gu, O. Borodin, B. Zdyrko, H.-T. Lin, H. Kim, N. Nitta, J. Huang, A. Magasinski, Z. Milicev, G. Yushin "Lithium-Iron Fluoride Batery with In-Situ Surface Protection", Advanced Functional Materials, 2016, 26, 1507-1516].

Figure 6 shows an illustrative example of typical composites produced according to the procedure of the Figure 5. The smooth surface of the FeF_2 infiltrated AC particles (compare Figure 6a and 6d) indicates a good efficiency of such a synthesis procedure, where no nanoparticles present outside the carbon pores. X-ray diffraction studies were regularly used to confirme the presence of the desired phase (e.g., FeF_2 nanoparticles in this example) and the lack of any crystalline impurities. Transmission electron microscopy (TEM) studies (as well as energy dispersive spectroscopy, EDS, scans) were regularly used to further confirm the uniformity infiltration of FeF_2 and other metal fluorides within the porous carbon particles.

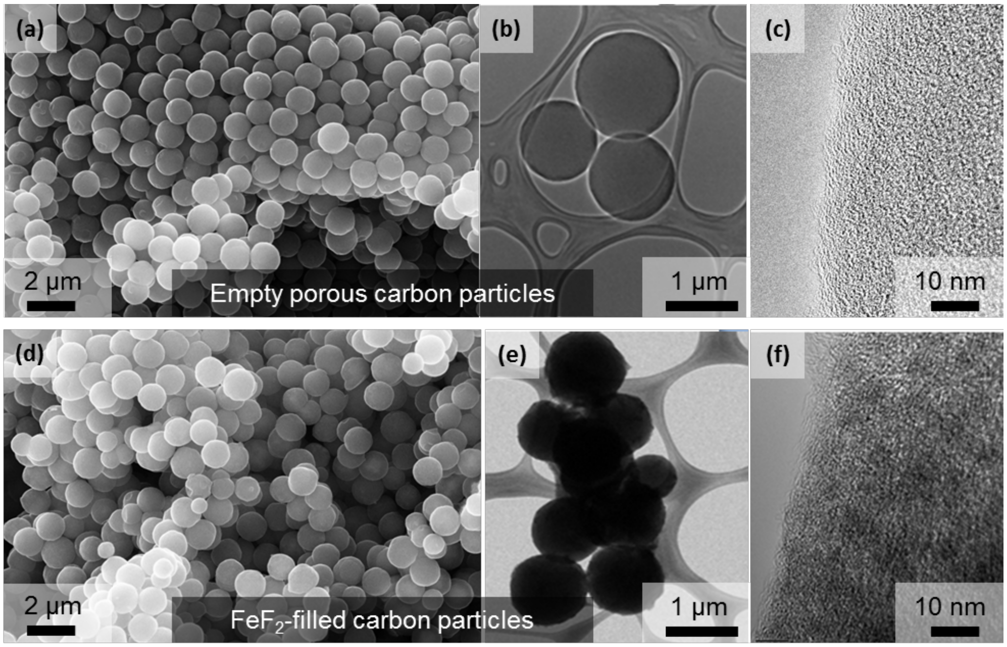

Figure 6. Porous carbon particles before and after infiltration with FeF_2 nanoparticles [Reproduced from W. Gu, O. Borodin, B. Zdyrko, H.-T. Lin, H. Kim, N. Nitta, J. Huang, A. Magasinski, Z. Milicev, G. Yushin "Lithium-Iron Fluoride Batery with In-Situ Surface Protection", Advanced Functional Materials, 2016, 26, 1507-1516].

MF_x-based nanostructured composite materials (including FeF_2-based ones shown in Figure 6) require development and optimization of very different slurry, coating, and electrolytes compared to conventional intercalation-type lithium metal oxide cathode materials. This is because such composites exhibit different density, different morphology and in some cases very different surface chemistry.

Many of the initial electrochemical tests on various coatings were conducted in half cells, where metal fluoride cathode was paired with lithium metal anode. Furthermore, most of such initial tests were conducted in a coin cell format.

In order to make an electrode from a cathode material, the material is mixed with binder, conductive additive, and a dispersant. The slurry is coated onto an electronically conductive substrate and dried. Once a general composition was found that formed slurries and electrode coatings from a particular MF_x-based nanocomposite powder (with its particular size, morphology, composition, solvent-accessible specific surface area, density and surface chemistry) some of the mixing methods were varied. Figure 7 shows an example comparison of two half cells where the cathode slurries were mixed in two different ways, but both the active (nanocomposite) material and the inactives (binders, conductive additives) within electrodes are of the same composition and ratios. Although both cells showed similar capacity, one had significantly lower voltage hysteresis and internal resistance. This figure emphasizes the importance of the slurry mixing method to create the electrode with a more uniform dispersion of the active material, binder, and conductive additives, which typically yields lower resistance of electron and ion transport (and thus leading to lower voltage hysteresis).

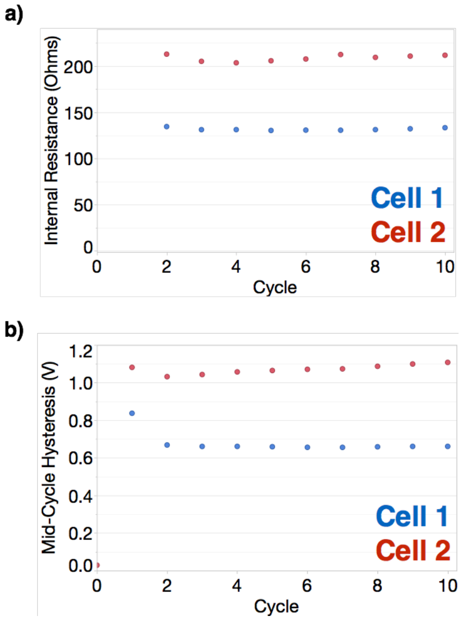

Figure 7. Comparison of two half cells containing MF_x electrodes made by two different methods for mixing the slurry using identical active material, showing a significant impact of the electrode processing on performance: a) internal resistance measured during cycling; b) voltage hysteresis between charge and discharge.

Achieving good slurry uniformity was also found to be critically important for the cell stability, particularly in the case of full cell testing where local matching of the anode and cathode capacity is most critical.

Electrolyte composition was found to be another important factor. In particular, in case of cells with a simpler type of MF_x-based cathodes where MF_x nanoparticles come in direct contact with liquid electrolyte, electrolyte impact on cell stability was most instrumental.

Furthermore, all - the salt concentration, the salt composition and solvent composition were found to be critically important for maximizing the cell performance.

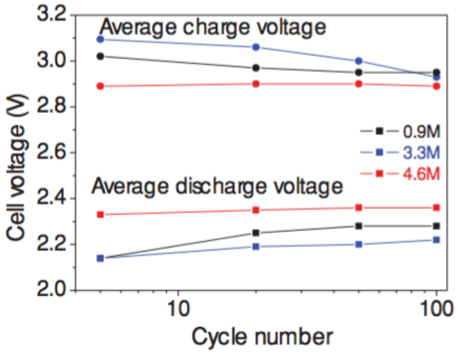

Figure 8. Impact of salt concentration on the electrochemical stability and voltage hysteresis in FeF_2-C/Li cells [Reproduced from W. Gu, O. Borodin, B. Zdyrko, H.-T. Lin, H. Kim, N. Nitta, J. Huang, A. Magasinski, Z. Milicev, G. Yushin "Lithium-Iron Fluoride Batery with In-Situ Surface Protection", Advanced Functional Materials, 2016, 26, 1507-1516].

Traditional Li-ion batteries typically utilize $LiPF_6$ salt in organic carbonate solvents with a variety of other additives. We found that non-traditional electrolyte salt and solvent may provide higher capacity and cycle stability. For example, lithium bis(fluorosulfonyl)imide salt (LiFSI) in 1,2-dimethoxyethane solvent show promising performance characteristics. Higher salt concentration may reduce the dissolution of cathode active material and thus favor better performance characteristics. Figure 8 shows an example comparison of three cells containing different concentrations of LiFSI. All show remarkable cycle stability and capacity utilization compared to prior results with metal fluoride cathodes, but the cell with the highest concentration electrolyte shows a marked improvement over cells with lower concentrations of LiFSI. Analysis of the electrodes after cycling shows that the highest concentration electrolyte provided the most effective protective surface layer. This layer prevents Fe-based salts from dissolving and contributing to capacity fade. As shown in other examples (Figure 9 and Figure 10), the voltage hysteresis for the 4.6 M electrolyte is quite low (for metal fluorides) and stable throughout cycling. Although the observed 0.6 V hysteresis is not yet near the values observed for intercalation cathode material (< 0.2 V), this is significantly better than previously observed for metal fluoride cathode material.

Figure 10 shows an example of the long-term cycling that may be achieved in MF_x-cathode based cells. This particular example demonstrates our ability to greatly exceed the milestones outlined at part of the project goals. This cell, in particular, shows >600 cycles before degradation to less than 80% of the initial capacity, where the initial capacity milestone was >65% of theoretical. The project goals were exceeded substantially despite higher current densities than have been utilized with metal fluoride cathodes in the past. Figure 10 further shows that performance of nanoconfined MF_x cathodes result in much longer cycle stability and higher capacity utilization of FeF_2 at higher current densities. Prevention of phase separation of Fe and LiF inside nanopores prevents phase separation and contributes to the stability, low voltage hysteresis, and allows for higher current densities to be used. The formation of stable surface protective layer (in this example – originating from a high concentration LiFSI/DME electrolyte likely) prevents dissolution of Fe-salts, also contributing to greatly improved cycle stability.

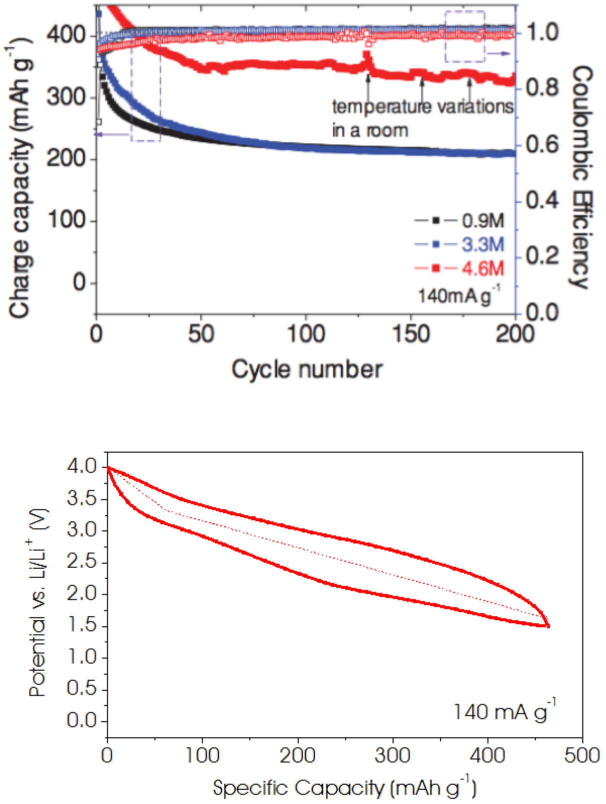

Figure 9. Example of cycle stability and a charge-discharge curve in FeF_2-C/Li cells. Capacity is normalized by the FeF_2 mass in the cathode [Reproduced from W. Gu, O. Borodin, B. Zdyrko, H.-T. Lin, H. Kim, N. Nitta, J. Huang, A. Magasinski, Z. Milicev, G. Yushin “Lithium-Iron Fluoride Batery with In-Situ Surface Protection”, Advanced Functional Materials, 2016, 26, 1507-1516].

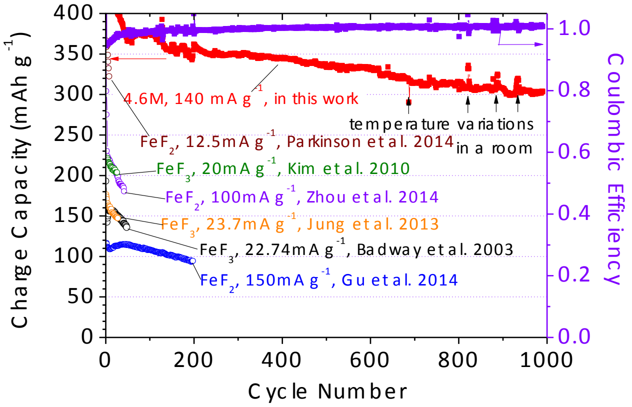

Figure 10. Stability of FeF_2-C / Li half cells in comparison with selected prior art studies [Reproduced from W. Gu, O. Borodin, B. Zdyrko, H.-T. Lin, H. Kim, N. Nitta, J. Huang, A. Magasinski, Z. Milicev, G. Yushin "Lithium-Iron Fluoride Batery with In-Situ Surface Protection", Advanced Functional Materials, 2016, 26, 1507-1516].

Other, more energy-dense MF_x materials were more challenging to produce using the same methodology, therefore work on the synthesis, improvement, and understanding of these materials continued throughout the project. For example, for other metal salts, the production, infiltration, and conversion of $MSiF_6$ to MF_x were not straight-forward. We also explored other soluble fluorine-containing metal salts that can be infiltrated into a porous matrix material and may be converted directly to MF_x. Examples of such salts included the salts of BF_4 and AlF_4. Decomposition of such salts and the subsequent removal BF_3 or AlF_3 might be expected to leave MF_x. Unfortunately, with this approach we faced difficulties with synthesis and infiltration of the precursor salts as well as clean conversion of the precursor salts to MF_x. Some of our tested approaches explored the use of gaseous fluorine-containing sources. In order to safely handle such fluorine-containing gases, a semi-automated tool was designed and built. This tool allowed precise control of temperature, pressure, and gas flow rate, as well as recording the information for later processing and analysis. Safety systems prevent exposure of workers or the environment to fluorine or fluorine-containing gases. This tool allowed for testing and understanding a large variety of conditions in a reproducible manner.

Fortunately, by the end of the project, we were able to successfully develop an alternative synthesis route to produce MF_x-based nanocomposite materials for a variety of metals and oxidation states. In such composites, MF_x are incorporated within a conductive matrix material, which significantly enhances stability and rate performance of MF_x-comprising cathodes.

The major goal of this project was not only to demonstrate half cells, but to pair MF_x-based cathodes with a high-capacity Si-based anode, allowing for the significant gains in energy density on a cell level. This required development of a cell platform that was compatible with both electrodes.

Sila Nanotechnologies, Inc. (with the financial assistance of the prior ARPA-E support) has developed Si-based anode powder, which exhibit minimal particle-level volume changes during cycling and thus exhibits stable solid electrolyte interphase (SEI) and excellent cycle stability in full cells. Figure 11 shows an example of the electrode-level thickness changes in Si anode produced in 2015 at Sila and cycled against lithium iron phosphate (LFP) cathode in matched full cells. Figure 12 shows examples of cycle stability achieved in matched full cells with Si anode matched in capacity against LFP and lithium nickel cobalt manganese oxide (NCM) cathodes. Note that no pre-lithiation and no "excess cathode" was used in the construction of such cells. Also note that these anodes comprised 100% of Sila material with no graphite particles mixed.

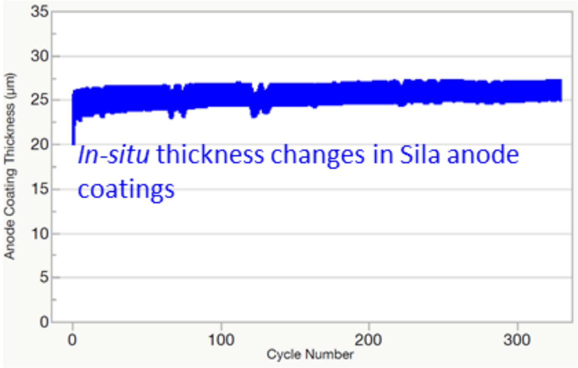

Figure 11. Example of the low thickness changes in Si-based anodes produced in 2015 at Sila facilities and cycled in matched full cells with intercalation-type LFP cathode.

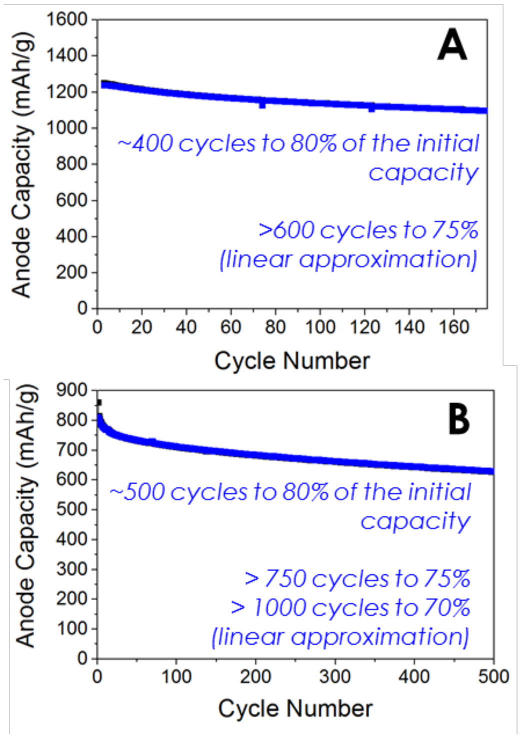

Figure 12. Example of the cycle stability of two Si-based anodes produced in 2015 at Sila facilities and cycled in matched full cells with intercalation-type cathodes (commercial LFP and NCM powder-based, respectively). Note – no pre-lithiation and no "excess cathode" was used in the construction of such cells. Also note that these anodes comprised 100% of Sila material with no graphite particles mixed. Cell A show 400 cycles to 80% of the initial capacity and > 600 cycles to 75% of the initial capacity, while Cell B shows 500 cycles to 80% of the initial capacity and > 1000 cycles to 70% of the initial capacity.

Cell A of Figure 12 shows 400 cycles to 80% of the initial capacity and >600 cycles to 75% of the initial capacity, while Cell B shows 500 cycles to 80% of the initial capacity and >1000 cycles to 70% of the initial capacity. The anodes in these cells comprised up to 22.5 wt. % inactives (binder and conductive additives). However, newer Si anodes show substantially better performance characteristics (e.g., better cycle stability) while requiring only 6 wt. % or even smaller fraction of inactive components.

Figure 13 shows example of rate performance of full cells with Sila Si-based anodes matched with LFP cathodes. The Sila Si-based anode powder offers comparable (or better) rate capability to high-performance graphites used in state of the art commercial cells.

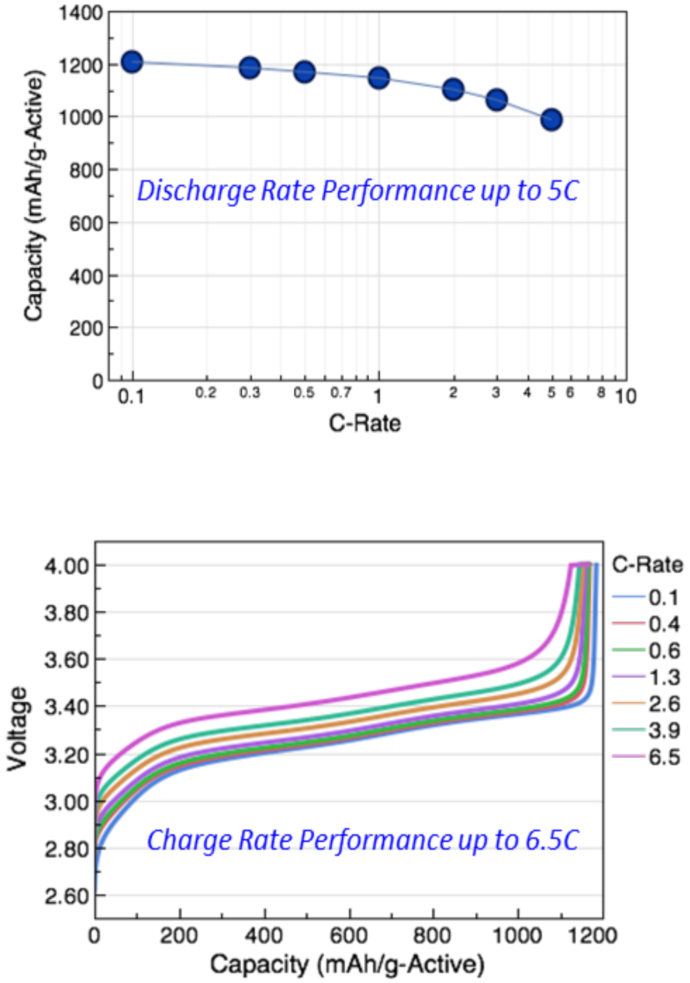

Figure 13. Example of the rate performance of a Si-based anode produced in 2015 at Sila facilities and cycled in matched full cells with intercalation-type (commercial LFP powder-based) cathode.

Promising performance characteristics of MF_x-based cathodes and Si-based anodes allowed us to conduct optimization studies on full cells comprising these types of conversion-type chemistry in both electrodes.

Figure 14 shows an example of three selected cells with Si anodes and MF_x-based cathodes. Cell 1 exhibits close to theoretical capacity at the initial cycle, but fades relatively quickly. Still on a relative scale, this capacity fade is slow compared with previously studied metal fluoride cathodes cycled in full cells, reaching 82 cycles before falling below 80% of its initial capacity (Figure 14b). Cell 2 shows very stable cycling, reaching 250 cycles before falling below 80% of the maximum capacity, but it has a very low maximum capacity, at only a small fraction of the theoretical value. Cell 3 showed the best performance traits of both of the prior cells, with high theoretical capacity at the initial cycle, and retaining 80% of the initial capacity for 330 cycles.

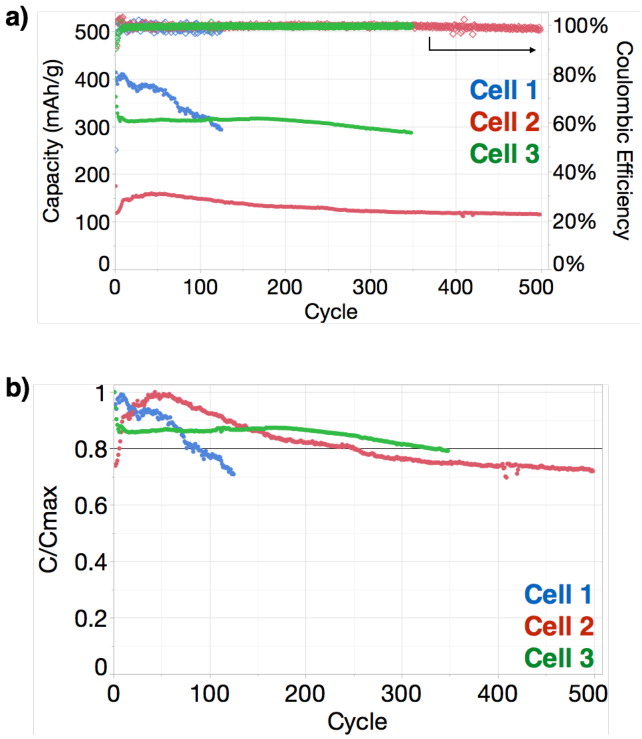

Figure 14. Comparison of full cells comprising a MF_x-based cathode and a Si-based anode. Capacity is normalized per gram of active cathode material: a) capacity and coulombic efficiency for three selected cell designs and compositions; note Capacity is represented with full circles and coulombic efficiency with empty diamonds; b) capacity as a fraction of the maximum cell capacity for several cell designs and compositions.

The full cell performance our team achieved with Si anodes and MF_x-based cathodes is clearly impressive. We have achieved gravimetric capacities of MF_x significantly higher than that of intercalation cathode materials, and the cycle stability has reached levels that are useful for many applications that would benefit from higher energy density cells. We believe the MF_x cathode materials that have been developed and demonstrated as part of this project are extremely promising as a new high energy density cathode material. The strides forward that have been achieved for both capacity, cycle stability, and voltage hysteresis are attributed to addressing the multiple problems that have previously prevented metal fluorides from being a viable rechargeable cathode material. By nano-confining the MF_x materials, the phase separation that happens during a conversion reaction only took place at a nanoscale, preventing large voltage hysteresis and loss of active material. Additionally, by finding an electrolyte that is compatible with both the MF_x cathode and Sila Si anode, the formation of a stable SEI could be achieved, which yielded stable cycling performance.

Future studies will be directed towards further performance improvements and targeted to meet the requirements of electric vehicles (EVs) and other applications requiring improved specific and volumetric energy storage characteristics. We aim to substantially improve cycle stability, rate performance and energy efficiency of this cell chemistry.

Products

Publications:

1) G. Yushin et al., "Conversion Cathodes: Lithium–Iron Fluoride Battery with In Situ Surface Protection" *Advanced Functional Materials* v 26 (10), p. 1507–1516 (2016)
2) G. Yushin et al. "Electrolytes for Core-Shell Cathodes in Lithium–Metal Fluoride Cells" (in preparation for 2017 submission; title is subject to change)

Networks or collaborations: Georgia Institute of Technology, Army Research Laboratory

Inventions/Patent Applications: G. Yushin et al. "Stable Lithium Fluoride-Based Cathodes For Metal And Metal-Ion Batteries" US Patent Application US20170018768

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