Design of Surface Protective Layer of LiF/FeF₃ Nanoparticles in Li-Rich Cathode for High-Capacity Li-Ion Batteries

Taolin Zhao^a, Li Li^a, Renjie Chen^{a}, Huiming Wu,^b Xiaoxiao Zhang^a, Shi Chen^a, Man Xie^a,*

Feng Wu^{a}, Jun Lu^{b*}, Khalil Amine^{b*}*

*a. School of Chemical Engineering and the Environment, Beijing Key Laboratory of
Environmental Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*

b. Chemical Sciences and Engineering Division, Argonne National Laboratory, IL 60439, USA

ABSTRACT

Advanced lithium-ion batteries for renewable energy storage applications have become a major research interest in recent years. Much better performance can be realized by improvements in the material surface design, especially for the cathode materials. Here, we present a new design for a surface protective layer formed via a facile aqueous solution process in which a nano-architected layer of LiF/FeF₃ is epitaxially grown on bulk hierarchical Li-rich cathode Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂. Coin cell tests of this material in the voltage range of 2–4.8 V indicated a high reversible capacity (260.1 mAh g⁻¹ at 0.1C), superior rate performance (129.9 mAh g⁻¹ at 20C), and excellent capacity retention. Differential scanning calorimetry showed good thermal stability. The enhanced capacity and cycling stability are attributed to the suppression of interfacial side reactions as well as the conversion reaction resulting from the introduction of LiF/FeF₃ as a surface protective layer.

KEYWORDS

Lithium-ion battery, nanoparticle, surface protective layer, iron fluoride, Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂

1. Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronics and are a prime candidate as the power source for electric vehicles because of their superior performance characteristics, namely, long cycle life, high energy and power densities, and no memory effect.¹⁻⁵ The cathode material provides the lithium source for Li extraction (charging) and insertion (discharging) processes associated with the oxidation and reduction of transition metal ions,⁶ and is the key limiting component to further development of LIBs. Thus, improved design of cathode materials is critical for further application of LIBs.

Nowadays, due to the limited availability and cost of cobalt, cathodes with little or no cobalt are being intensively investigated. Among the candidate cathodes, Li-rich materials with a layered structure,⁷⁻¹⁰ such as $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ (LLNMO), can deliver much higher capacity than the traditional cathode materials. Nevertheless, several fundamental challenges still need to be settled: high initial irreversible capacity losses, resulting from removing Li_2O at the first charge;¹¹ capacity and voltage fading on cycling; and low rate capability due to the layered-to-spinel transformation on cycling.¹² To date, researchers have made great efforts to improve the structural stability and the electrochemical performance of these layered Li-rich cathodes through surface modification. Up to now, the coating materials investigated include carbon, metal oxide (TiO_2 , V_2O_5 , Al_2O_3 , CeO_2 , ZrO_2 , SiO_2 , ZnO), metal fluoride (AlF_3), and metal phosphate (AlPO_4).¹³⁻¹⁶ The benefits of surface modification include stabilizing the electrode-electrolyte interface, improving the ionic or electronic conductivity, decreasing cationic disorder in crystal sites, suppressing phase transition, and reducing the electrolyte acidity. Remarkable improvements in reversible capacity, cycle life, and rate capability are realized from the

decreased resistance and interfacial side reactions.^{17, 18} Despite these advantages, the gravimetric energy density decreased due to the addition of a non-electrochemical active coating layer.

To solve the limitation of the present coating technology, researchers have pursued a novel design route, namely, the combination of an electrochemical conversion reaction cathode and extraction/insertion cathode. In recent years, conversion reaction cathode material has demonstrated high energy storage.^{19–22} For example, theoretically, FeF_3 ^{23–25} can react with three Li^+ ions and deliver a high capacity of 712 mAh g^{-1} at an average potential of $\sim 2.7 \text{ V}$ ²⁶, which equals a very high theoretical energy density, 1950 Wh kg^{-1} . In addition, its discharge products, LiF and Fe nanodomains, can act as a protective layer to restrain the electrolyte decomposition on the cathode surface and enhance the cycle stability. To our knowledge, little work has been done on the conversion reaction into the protective layer for further enhancement of LIB performance.

In this work, we have developed a facile aqueous solution process to prepare a LiF/ FeF_3 /LLNMO composite with active protective layer (see scheme 1). In preparing this composite, an ultrathin protective layer (UPL) provides a much higher reversible capacity and excellent rate capability, while a thicker protective layer (TPL) provides significantly improved cycling performance (see Experimental). In this composite, the electrochemical performance benefits from the conversion reaction of FeF_3 as well as the merits of LiF serving as a surface protective layer. Thus, our prepared LiF/ FeF_3 /LLNMO composite shows considerable potential as a candidate cathode material for high energy density LIBs.

2. Experimental Detail

The pristine material $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ (LLNMO) was synthesized via a typical co-precipitation method, and the synthesis mechanism is illustrated in Scheme 1. Nickel sulfate

hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), sodium hydroxide (NaOH), and ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were used as the starting reagents to prepare $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursor in a water-jacketed continuous stirring tank reactor. A 2 M transition metal solution with a Ni/Mn atomic ratio of 1:3 was pumped into the reactor under N_2 atmosphere. At the same time, a 2 M NaOH solution and a desired amount of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution were fed into the tank reactor to control the pH value at 11. The reaction temperature was maintained at $60\text{ }^\circ\text{C}$, and the stirring speed was controlled at 1000 rpm. The obtained precursor was well mixed with Li_2CO_3 and then calcined at $900\text{ }^\circ\text{C}$ for 15 h to produce the cathode material LLNMO. The LiF/FeF_3 surface coating layer was obtained as follows. Select amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NH_4F were separately dissolved in deionized water. A select amount of LLNMO powder was dispersed in the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. The NH_4F solution was then added into this mixture drop by drop for 3 h. Then, the resulting mixture was heated to $80\text{ }^\circ\text{C}$ and stirred vigorously until the solution was evaporated to dryness. The obtained powder was calcined at $400\text{ }^\circ\text{C}$ in a tube furnace in Ar atmosphere for 5 h and then cooled to room temperature at a rate of $2\text{ }^\circ\text{C min}^{-1}$ to produce the LiF/FeF_3 -modified $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$. Samples were prepared with 1 wt.% and 5 wt.% coating amount and are referred to in this paper as “ultrathin protective layer” (UPL) and “thick protective layer” (TPL), respectively.

The structural analysis of the composite powders before and after the LiF/FeF_3 coating was carried out by X-ray diffraction (Rigaku Ultima IV-185) with $\text{Cu-K}\alpha$ irradiation source. The source tension and current were 40 kV and 40 mA, respectively. Data were acquired with a step size of $0.5^\circ\text{ min}^{-1}$ over a 2θ range of 10° – 80° . The morphology of the prepared samples was inspected by a field-emission scanning electron microscope (Quanata 200f). Elemental mapping and the chemical composition of the prepared samples were determined with energy dispersive

X-ray spectroscopy. The crystal orientation was detected with a transmission electron microscope (JEM-2010). X-ray photoelectron spectroscopy (XPS, PHI Quantera) was used to detect the surface chemical state of the samples. Thermal experiments were carried out in a differential scanning calorimeter (Q2000 V24.10 Build 122) using a temperature scan rate of 5 °C min⁻¹ under an air atmosphere.

For cell testing, the cathode electrodes were prepared by coating a mixture in N-methyl-2-pyrrolidone containing 80% cathode material, 10% acetylene black, and 10% poly-vinylidene fluoride binder onto Al current collector foil. After drying overnight at 80 °C in a vacuum oven, the electrodes were punched into disks with diameter of 1.1 cm. Coin cells (type 2025) were assembled with the cathode electrodes as-prepared, metallic lithium foil as counter electrode, Celgard 2400 membrane as separator, and 1 M lithium hexafluorophosphate (LiPF₆) dissolved in ethyl carbonate and dimethyl carbonate (1:1 in volume) as electrolyte. The cells were assembled and tested in a glove box filled with high-purity argon. The charge/discharge tests were performed galvanostatically using a Land battery test system (Land CT2001A, Wuhan, China) in the voltage range of 2.0–4.8 V at different current rates (1C = 200 mA g⁻¹). That is, the constant current charge step was followed by an additional constant voltage charge step until the current density dropped to half of its initial value.

3. Results and Discussion

We prepared LLNMO and the LiF/FeF₃/LLNMO composites using a combination of co-precipitation and the aqueous solution method illustrated in Scheme 1. By tailoring experimental conditions during co-precipitation, we obtained a hydroxide precursor Ni_{0.25}Mn_{0.75}(OH)₂ with hierarchical structure involving two levels of particle agglomeration (1–2 μm and 10 μm). The morphologies of the precursor analyzed by FE-SEM are shown in Figure 1(A1, A2, A3). The

primary structure, including irregular nanoparticles and nanoplates, was assembled into secondary particles (“first agglomeration”) with average size of 1–2 μm . Then, the second agglomerates were obtained with an average size of around 10 μm by the combination of several first agglomerates.

After calcining the mixture of hydroxide precursor and lithium carbonate at high temperature, we synthesized LLNMO with hierarchical structure composed of the micro-sized plates and particles (1–2 μm), as shown in Figure 1(B1, B2). Its crystal structure (Figure 2C) was evaluated by XRD, and results are given in Figure 3A. Except for the superlattice peaks between 20° and 23° , all the other peaks of the diffraction patterns are consistent with the well-crystallized layered hexagonal $\alpha\text{-NaFeO}_2$ structure and the space group $R\bar{3}m$, similar to the typical layered crystal structure of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (Figure 2D). The low-intensity peaks between 20° and 23° , which can be indexed to the monoclinic unit cell $C2/m$,^{27,28} are characteristic of a Li_2MnO_3 -type structure (Figure 2E) with LiMn_6 (Ni-substituted) cation arrangements in the transition metal layers. Good electrochemical performance of the LLNMO can be predicted as a result of the thin nanoplates and nanoparticles, as well as a reasonable packing density due to the macroporous structure, even if there is no protective layer.²⁹

Based on the synthesis of LLNMO, a surface protective layer was introduced by a facile aqueous solution method. The inert Ar atmosphere used in the calcination process was aimed at avoiding the transformation of fluorides to oxides. No visible difference can be observed from the FE-SEM images in Figure 1(C1, C2, D1, D2), demonstrating that the introduction of the surface protective layer has little impact on the particle morphology. In addition, no obvious FeF_3 structure, illustrated in Figure 2A, was detected in XRD patterns (Figure 3A) of the UPL and TPL samples due to the trace amount present. However, the LiF structure can be observed in

the XRD patterns of both samples, especially the TPL sample, which can be attributed to the outward diffusion of lithium in the calcination process. The presence of LiF phase is confirmed by the peaks at 38.7° and 45° in the two inset enlarged images in Figure 3A and its crystal structure is shown in Figure 2B.

Rietveld refinement results of all the materials are presented in Figure 3B and Table 1. The high-symmetry $R\bar{3}m$ space group was used for the refinement of the crystal structure rather than the low-symmetry $C2/m$ space group. Therefore, the superlattice reflections region from 20° to 23° has been excluded. We obtained satisfactory refinement results, as indicated by the low R values in Table 1. Obviously, the c-lattice parameters of both UPL and TPL are larger than those of LLNMO, which provides wider Li slab spacing for Li^+ extraction/interaction in the composites.^{30, 31} Therefore, better cycling stability of UPL and TPL samples can be predicted from the Rietveld refinements.

We also employed TEM to elucidate the surface layer and analyze the elemental compositions of all the samples. Figure 4(A1, A2, A3) presents TEM and HR-TEM images of LLNMO along with a SAED image in Figure 4(inset A2), which show superlattice reflection and fundamental reflection of layered Li-rich materials.³² The surface of LLNMO appears clean and smooth. Well-defined equidistant fringes in the bulk crystal confirm the layered order structure of the LLNMO material prepared in this study, consistent with the SAED image. In the bulk material, we observed distinct domains of different crystalline orientation, indicating a polycrystalline structure of the primary particles. The interplanar spacing of the lattice fringe is measured to be 0.47 nm, which is well indexed to the [003] planes of layered Li-rich structure. Compared with LLNMO, UPL and TPL have identical layered fringes in the bulk, while their surfaces have quite different morphologies, as shown in Figures 4(B1, B2, B3) and Figure 4 (C1, C2). A uniform

and smooth coating was observed for both of them. The ultrathin layer of UPL is crystalline and estimated to be 5 nm thick, as compared with 50 nm thick for the TPL. As further characterized, the outer nanostructure of UPL clearly presents two different fine lattice fringes. Part of interplanar spacing of the lattice fringes is measured to be 0.27 nm, which is well indexed to the [104] plane of FeF_3 structure, indicating FeF_3 was indeed successfully coated on the surface of LLNMO. The other part of the interplanar spacing (0.20 nm) corresponds to the [220] plane of cubic LiF structure. In addition, the EDS mappings in Figure 5 indicate uniform element distributions of Mn, Ni, Fe, O, and F in UPL and TPL, respectively.

With the confirmation of the existence of LiF/ FeF_3 on the LLNMO surface, XPS was applied to probe the surface chemical states of the materials. Figure 6 gives the O 1s, F 1s, Li 1s, Mn 2p, Ni 2p, and Fe 2p multiplex spectra for the electrodes. For all three samples, the Ni 2p $3/2$ XPS spectra have a binding energy of 854.9 eV, in agreement with Ni^{2+} in $\text{Li}[\text{Li}_{1/3-2x/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ compounds.³³ The Mn 2p $3/2$ peak fits well with a binding energy of 642.4 eV, which is in a good agreement with the typical value of Mn^{4+} oxidation state (642.4 eV) in manganese-based layered compounds.³⁴ From the above data, it is believed that the valences of Ni and Mn of all the samples are +2 and +4, respectively.

In Figure 6, the F1s spectra at 684.7 eV can be assigned to F-M bonding, such as the F-Fe bond in FeF_3 ³⁵ and the F-Li bond in LiF.³⁶ These results indicate the presence of LiF/ FeF_3 phase, which is consistent with the binding energy of 714.4 eV for the Fe-F bond in Fe spectra³⁷ and that of 56.3 eV for the Li-F bond in Li spectra.³⁸ Moreover, the lower binding energy peak at 529.6 eV for the O element is considered to be relative to the O^{2-} in the layered oxide, and its intensity decreases as the coating layer increases. That behavior may be due to the atom arrangement in the second calcination process. According to previous studies, the higher binding

energy peak at 532eV is mainly attributed to impurities like OH⁻ or adsorbed oxygen, and the impurities will increase with more coating layer. All the data imply that the LiF/FeF₃ phase is present on the surface of the UPL and TPL samples.

The electrochemical conversion reactions of FeF₃ are as follows:

As shown in Figure 7A, Li⁺ is first inserted into the FeF₃ framework via a two-phase reaction to form Li_{0.5}FeF₃ and then via a single-phase reaction to form LiFeF₃, which is reported to decompose to form LiF and Fe metal after reacting with another two Li⁺ ions. The reconversion of LiF and Fe is also quite intriguing because a capacity equivalent to three Li⁺ ions per Fe is obtained. Two different speculations have been proposed about the cause, that is, a “FeF₂-like” structure or a defect trirutile FeF₃ instead of the initial FeF₃ structure.^{39, 40} Despite the different speculations, the conversion reaction is believed to be reversible, which could be also responsible for the enhanced reversible capacity.

Considering the structural compatibility between the two phases, the materials modified by LiF/FeF₃ are expected to have good structural stability and electrochemical performance for several reasons. First, the ultrathin outer nano-architecture layer not only behaves as an effective protective jacket, but also can react with Li⁺ through a conversion reaction and provide extra discharge capacity. Second, along with the continuous changes during cycling of FeF₃, the intermediate product LiF can act as a surface protective layer, together with the LiF phase produced through the outward diffusion of lithium in the calcination process. Meanwhile, LiF can reduce the metal dissolution and suppress the increase in the charge transfer resistance,

thereby improve the cyclic performance of the electrode materials. These unique features will have a beneficial impact on the structural stability and the electrochemical performance of the modified materials.

Galvanostatic charge/discharge tests were performed with coin cells cycled between 2.0 and 4.8 V at the 0.1C rate. A pristine LLNMO cathode was tested along with UPL and TPL cathodes. For all the samples, Figure 8A shows a typical first charge/discharge profile of Li-rich cathode material, composed of a sloping curve below 4.5 V and a plateau around 4.5 V during charging and continuous sloping curves during discharging. As illustrated in Figure 7B, at the first charge, the extraction of Li^+ from Li_2MnO_3 phase above the 4.5 V voltage plateau is accompanied by the oxygen release, that is, the Li_2O component is removed, resulting in the electrochemical activation of the Li_2MnO_3 component and a high irreversible capacity loss.¹¹ However, this conversion reaction was not observed for the initial discharge process due to the merging of the voltage profiles of the LLNMO. Furthermore, the UPL cathode delivered a higher first discharge capacity than that of the pristine LLNMO (291.8 vs. 269 mAh g^{-1}), mainly benefiting from the suppression of interfacial side reactions between electrolyte and active material and the extra capacity provided by the conversion reaction of FeF_3 . The relatively thick coating layer (50 nm) of the TPL cathode could not benefit from the transfer of electrons and is responsible for the lower first discharge capacity (229.1 mAh g^{-1}). In addition, while the discharge capacities of the LLNMO and UPL cathodes decreased slightly after the first cycle, they increased in the following two cycles for the TPL cathode, which could be attributed to the thick protective layer and the slow activation of the bulk Li-rich component.

Figure 8C shows the cycling stability of all the cathode materials over 60 cycles. The UPL cathode attained a reversible discharge capacity of 260.1 mAh g^{-1} and showed a capacity

retention of 89.14% after 60 cycles. These values are much higher than the discharge capacity of 216.4 mAh g⁻¹ and the capacity retention of 80.4% for LLNMO. The TPL cathode achieved the best cycling capability, with a discharge capacity of 234.5 mAh g⁻¹ and capacity retention of 102.4%, benefiting from the thicker protective layer and less interfacial side reaction. In brief, both cathodes with the surface protective layer LiF/FeF₃ benefit from less side reaction and reversible conversion reaction of FeF₃, resulting in higher reversible capacity and better cycling performance.

Differential capacity vs. voltage plots for the different cathodes at various cycle numbers at 0.1C are shown in **Figure 8B**. After the initial electrochemical activation of the Li₂MnO₃ component above 4.4 V, a dominant reversible redox reaction slightly around 3 V occurs and becomes apparent as the redox reaction peaks of the layered structure weaken gradually.⁴¹ This behavior is interpreted to mean that the layered structure of the samples is transformed to a spinel component on cycling to yield an unexpected layered-spinel intergrowth structure. The spinel peak position of the UPL cathode was obviously higher than that of the pristine LLNMO. This observation, together with the voltage fade changes shown in **Figure 8D**, indicate that less spinel structure was formed after introducing the ultrathin coating layer. However, the thicker layer of LiF/FeF₃ will lower the discharge voltage because of the low reaction potential (~2.7 V) of the conversion reaction, as is apparent from the charge/discharge profiles at various rates (**Figure 8D**).

As shown in **Figures 9(A, B)**, although the capacity decreases with increased rate due to the increasing polarization, both UPL and TPL cathodes exhibited a good rate capability between 2.0 and 4.8 V. The rate property of pristine LLNMO was also evaluated under the same test condition for comparison. Among the three cathodes, UPL exhibited the highest discharge

capacities at various moderate rates. Although structural transformation suffered on cycling at these rates, a discharge capacity of 196.8 mAh g^{-1} was achieved at the 1C rate after 100 cycles; even at 5C, the discharge capacity was 170.3 mAh g^{-1} . In addition, the TPL cathode had the best cycling stability at various rates, because of less side reaction and the wider Li^+ transport path.

The LiF/FeF_3 coating thickness plays a very important role on the electrochemical performances of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ cathode. An ultrathin coating layer can accelerate the transition of electrons and Li^+ and suppress the surficial side reactions, and thus improve the rate capability. As for the thick coating layer, it can better suppress the side reactions and thus the cathode material shows outstanding cycle ability. But thicker coating layer may have a negative effect on the electrons transport and Li^+ diffusion, leading to a larger impedance.

Figure 9C shows the EIS profiles of the electrodes at open circuit potential. The impedance spectra are composed of a high-frequency semicircle and a low-frequency slope, as in standard Nyquist plots. The intercept of the semicircle with the horizontal axis (Z') at the highest frequency refers to the uncompensated ohmic resistance of the electrolyte (R_Ω), and the diameter of the semicircle represents the charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}). The rising line in the low-frequency section is related to the Warburg impedance (Z_W), which is associated with the diffusion of Li^+ into the bulk material.⁴² The ohmic resistance (R_Ω) and “faradaic impedance” (the combination of R_{ct} and Z_W) reflect the kinetics of the cell reactions.⁴³ Obviously, the R_{ct} value of the UPL cathode is about 75Ω , which is smaller than that of the other two cathodes, indicating good reaction kinetics as well as good electrochemical performance. The EIS spectra at charged state of 4.1 V at various cycles for the UPL cathode are shown in Figure 9D. The semicircle at high frequency stands for the resistance for Li^+ diffusion in the surface layer (R_{SEI}), and the semicircle at low frequency reflects the reaction kinetics (R_{ct}).

Compared with the spectrum of the first cycle, the R_{SEI} after 60 cycles decreased to 13 Ω , and the R_{ct} increased from 60 Ω to 75 Ω , demonstrating lower polarization.

Figure 10A compares the high-rate performance of all the cathodes at rates of 10C and 20C and voltage range between 2.0 and 4.8 V. Similar curve shapes to that at moderate rate are observed from the 25th charge/discharge profiles of all the cathodes. Fast extraction/insertion of Li^+ at high rates damages the fragile structure of pristine LLNMO, resulting in the obvious capacity fade on cycling.^{27, 44} Surprisingly, the UPL cathode delivers stable reversible capacities of 141.7 mAh g⁻¹ at 10C and 129.9 mAh g⁻¹ at 20C, while the corresponding values for the TPL cathode are 129.5 mAh g⁻¹ and 125.9 mAh g⁻¹. Compared with that of the UPL and LLNMO cathodes, the lower discharge voltage and the gradually rising trend of reversible capacity for the TPL cathode can be related to the relatively low reaction potential of the conversion reaction, the slow activation of the bulk component, and the protective layer that stabilizes the internal structure. The superior reversible capacity and good cycling stability at high rates for the UPL and TPL cathodes were attributed to the good charge transfer kinetics and structural features from the LiF/FeF₃ protective layer and the conversion reaction.

Thermal stability and safety of electrode materials are important to large-scale commercial applications of LIBs. **Figure 10B** exhibits the DSC profiles of the electrodes recovered from all three cells charged to 4.8 V. Although the onset temperatures of thermal reactions for the three cathode materials were very close (225 °C), the major exothermal reactions of the UPL and TPL materials occurred at 271.46 °C and 288.47 °C, respectively, compared with the 265.12 °C for the pristine LLNMO. On the other hand, the heat generation was reduced after LiF/FeF₃ surface modification. Especially for the TPL cathode, the total generated heat was estimated to be 303.6 J g⁻¹, which is much lower than that of LLNMO (398.94 J g⁻¹). We propose that the thermal

stability of the UPL and TPL cathodes originated from the FeF_3 phase in the surface region due to the good thermal stability of FeF_3 .⁴⁵

As shown above, the outstanding reversible capacity and rate capability of the UPL cathode and the much improved cycling stability of the TPL cathode result from the surface protective layer LiF/FeF_3 on the bulk LLNMO, that is, the combination of the extraction/insertion cathode (LLNMO) and the conversion reaction cathode (FeF_3 layer). Our as-prepared hierarchical composite with a nano-architected protective layer delivers fast Li^+ transportation in the bulk layered structure and extra capacity via the conversion reaction. As a protective layer, LiF , together with the new reaction product LiF during discharging of the conversion reaction, can protect the layered bulk material from erosion by electrolytes and restrain the bulk active mass loss. Moreover, a smaller amount of LiF/FeF_3 coating on the bulk LLNMO can not only serve as the protective layer to suppress the interfacial side reaction (Figure 10C) and provide electrochemically active surface, but also diminish the voltage fading and form less spinel phase during cycling.

4. Conclusion

In summary, we report a thermally stable cathode material with improved electrochemical performance for the Li-ion battery that combines conversion and intercalation electrode chemistry based on LiF/FeF_3 and $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ (LLNMO). The test results demonstrate that this novel cathode composite attains high electrochemical performance in terms of reversible capacity and cycle stability life as well as rate capability. Such performance is associated with the active surface protective layer LiF/FeF_3 . In addition, the employment of iron in the layer and the cobalt-free bulk material make the composite promising for LIB cathodes with high energy and power and low cost for energy storage in the near future.

5. Acknowledgement

The experimental work of this study was supported by the Chinese National 973 Program (2015CB251100), the National Science Foundation of China (NSFC51302014), Beijing Nova Program (Z121103002512029), Beijing Excellent Talents Plan funding and the New Century Educational Talents Plan of the Chinese Education Ministry (NCET-12-0050). This work was also supported by the U.S. Department of Energy under Contract DE-AC0206CH11357 with the main support provided by the Vehicle Technologies Office, Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE). The authors especially thank US-China Electric Vehicle and Battery Technology between Beijing Institute of Technology and Argonne National Laboratory.

Corresponding author

E-mail address: chenrj@bit.edu.cn (R. Chen); wufeng863@bit.edu.cn (F. Wu); junlu@anl.gov (J. Lu) and amine@anl.gov (K. Amine)

6. References

- (1) Armstrong, A. R.; Bruce, P. G. *Nature* **1996**, *381*, 499–500.
- (2) Armstrong, A. R.; Lyness, C.; Panchmatia, P. M.; Islam, M. S.; Bruce, P. G. *Nat. Mater.* **2011**, *10*, 223–229.
- (3) Ceder, G.; Chiang, Y. M.; Sadoway, D. R.; Aydinol, M. K.; Jang, Y. I.; Huang, B. *Nature* **1998**, *392*, 694–696.
- (4) Chiang, Y.-M. *Science* **2010**, *330*, 1485–1486.

- (5) Gu, M.; Belharouak, I.; Genc, A.; Wang, Z.; Wang, D.; Amine, K.; Gao, F.; Zhou, G.; Thevuthasan, S.; Baer, D. R.; Zhang, J. G.; Browning, N. D.; Liu, J.; Wang, C. *Nano Lett.* **2012**, *12*, 5186–5191.
- (6) Goodenough, J. B.; Kim, Y. *Chem. Mater.* **2010**, *22*, 587–603.
- (7) Hong, J.; Seo, D.-H.; Kim, S.-W.; Gwon, H.; Oh, S.-T.; Kang, K. *J. Mater. Chem.* **2010**, *20*, 10179–10186.
- (8) Zhao, T.; Chen, S.; Li, L.; Zhang, X.; Chen, R.; Belharouak, I.; Wu, F.; Amine, K. *J. Power Sources* **2013**, *228*, 206–213.
- (9) Zhao, T.; Li, L.; Chen, S.; Chen, R.; Zhang, X.; Lu, J.; Wu, F.; Amine, K. *J. Power Sources* **2014**, *245*, 898–907.
- (10) Lu, Z.; Beaulieu, L. Y.; Donabarger, R. A.; Thomas, C. L.; Dahn, J. R. *J. Electrochem. Soc.* **2002**, *149*, A778–A791.
- (11) Armstrong, A. R.; Holzapfel, M.; Novák, P.; Johnson, C. S.; Kang, S.-H.; Thackeray, M. M.; Bruce, P. G. *J. Am. Chem. Soc.* **2006**, *128*, 8694–8698.
- (12) Yu, D. Y. W.; Yanagida, K. *J. Electrochem. Soc.* **2011**, *158*, A1015–A1022.
- (13) Wu, Y.; Vadivel Murugan, A.; Manthiram, A. *J. Electrochem. Soc.* **2008**, *155*, A635–A641.
- (14) Zheng, J. M.; Li, J.; Zhang, Z. R.; Guo, X. J.; Yang, Y. *Solid State Ionics* **2008**, *179*, 1794–1799.
- (15) Gao, J.; Kim, J.; Manthiram, A. *Electrochem. Commun.* **2009**, *11*, 84–86.

- (16) Wu, Y.; Manthiram, A. *Solid State Ionics* **2009**, *180*, 50–56.
- (17) Myung, S.-T.; Amine, K.; Sun, Y.-K. *J. Mater. Chem.* **2010**, *20*, 7074–7095.
- (18) Chen, Z.; Qin, Y.; Amine, K.; Sun, Y. K. *J. Mater. Chem.* **2010**, *20*, 7606–7612.
- (19) Armand, M.; Tarascon, J. M. *Nature* **2008**, *451*, 652–657.
- (20) Cabana, J.; Monconduit, L.; Larcher, D.; Palacin, M. R. *Adv. Mater.* **2010**, *22*, E170–E192.
- (21) Wang, F.; Robert, R.; Chernova, N. A.; Pereira, N.; Omenya, F.; Badway, F.; Hua, X.; Ruotolo, M.; Zhang, R.; Wu, L.; Volkov, V.; Su, D.; Key, B.; Whittingham, M. S.; Grey, C. P.; Amatucci, G. G.; Zhu, Y.; Graetz, J. *J. Am. Chem. Soc.* **2011**, *133*, 18828–18836.
- (22) Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J. M. *Nature* **2000**, *407*, 496–499.
- (23) Badway, F.; Cosandey, F.; Pereira, N.; Amatucci, G. G. *J. Electrochem. Soc.* **2003**, *150*, A1318–A1327.
- (24) Badway, F.; Pereira, N.; Cosandey, F.; Amatucci, G. G. *J. Electrochem. Soc.* **2003**, *150*, A1209–A1218.
- (25) Plitz, I.; Badway, F.; Al-Sharab, J.; DuPasquier, A.; Cosandey, F.; Amatucci, G. G. *J. Electrochem. Soc.* **2005**, *152*, A307–A315.
- (26) Li, H.; Balaya, P.; Maier, J. *J. Electrochem. Soc.* **2004**, *151*, A1878–A1885.

- (27) Thackeray, M. M.; Kang, S.-H.; Johnson, C. S.; Vaughey, J. T.; Benedek, R.; Hackney, S. *A. J. Mater. Chem.* **2007**, *17*, 3112–3125.
- (28) Kim, J.-S.; Johnson, C. S.; Vaughey, J. T.; Thackeray, M. M.; Hackney, S. A.; Yoon, W.; Grey, C. P. *Chem. Mater.* **2004**, *16*, 1996–2006.
- (29) Wang, D.; Belharouak, I.; Zhou, G.; Amine, K. *Adv. Funct. Mater.* **2013**, *23*, 1070–1075.
- (30) Kang, K.; Ceder, G. *Phys. Rev. B* **2006**, *74*, 094105.
- (31) Kang, K.; Meng, Y. S.; Bréger, J.; Grey, C. P.; Ceder, G. *Science* **2006**, *311*, 977–980.
- (32) Meng, Y. S.; Ceder, G.; Grey, C. P.; Yoon, W. S.; Jiang, M.; Bréger, J.; Shao-Horn, Y. *Chem. Mater.* **2005**, *17*, 2386–2394.
- (33) Tran, N.; Croguennec, L.; Labrugère, C.; Jordy, C.; Biensan, P.; Delmas, C. *J. Electrochem. Soc.* **2006**, *153*, A261–A269.
- (34) Shaju, K. M.; Subba Rao, G. V.; Chowdari, B. V. R. *Electrochim. Acta* **2002**, *48*, 145–151.
- (35) Li, C.; Yin, C.; Mu, X.; Maier, J. *Chem. Mater.* **2013**, *25*, 962–969.
- (36) Liu, J.; Manthiram, A. *J. Mater. Chem.* **2010**, *20*, 3961–3967.
- (37) Myung, S.-T.; Sakurada, S.; Yashiro, H.; Sun, Y.-K. *J. Power Sources* **2013**, *223*, 1–8.
- (38) Hong, J.; Lim, H.-D.; Lee, M.; Kim, S.-W.; Kim, H.; Oh, S.-T.; Chung, G.-C.; Kang, K. *Chem. Mater.* **2012**, *24*, 2692–2697.
- (39) Li, L.; Meng, F.; Jin, S. *Nano Lett.* **2012**, *12*, 6030–6037.

- (40) Yamakawa, N.; Jiang, M.; Key, B.; Grey, C. P. *J. Am. Chem. Soc.* **2009**, *131*, 10525–10536.
- (41) Johnson, C. S.; Li, N.; Lefief, C.; Vaughey, J. T.; Thackeray, M. M. *Chem. Mater.* **2008**, *20*, 6095–6106.
- (42) Tan, K.; Reddy, M.; Rao, G.; Chowdari, B. *J. Power Sources* **2005**, *141*, 129–142.
- (43) Tan, G.; Wu, F.; Li, L.; Chen, R.; Chen, S. *J. Phys. Chem. C* **2013**, *117*, 6013–6021.
- (44) Xu, B.; Fell, C. R.; Chi, M.; Meng, Y. S. *Energy Environ. Sci.* **2011**, *4*, 2223–2233.
- (45) Zhou, M.; Zhao, L.; Okada, S.; Yamaki, J.-i. *J. Power Sources* **2011**, *196*, 8110–8115.

Figures and Tables

Scheme 1. Schematic diagram of synthetic route for LLNMO/UPL/TPL composite.

Table 1 Crystallographic parameters of Rietveld refinements for the LLNMO, UPL, and TPL

Sample	Crystallographic Parameters				
	a (Å)	c (Å)	R_p	R_{wp}	R_{exp}
LLNMO	2.8597(2)	14.2441(5)	9.93	12.6	4.25
UPL	2.8612(3)	14.2588(9)	7.89	10.1	3.59
TPL	2.8570(3)	14.2741(1)	14.6	18.5	4.62

Figure 1. Field emission scanning electron microscopy (FE-SEM) images of the hydroxide precursor $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ (A1, A2, and A3), LLNMO (B1 and B2), UPL (C1 and C2), and TPL (D1 and D2).

Figure 2. The crystal structures of (A) rhombohedral FeF_3 ($R3c$), (B) cubic LiF ($Fm-3m$), (C) $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$, (D) layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($R\bar{3}m$), and (E) monoclinic Li_2MnO_3 ($C2/m$).

Figure 3. (A) X-ray powder diffraction (XRD) of pristine LLNMO, UPL, and TPL along with the standard patterns: (a) layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($R\bar{3}m$), (b) monoclinic Li_2MnO_3 ($C2/m$), (c) cubic LiF ($Fm\bar{3}m$), and (d) rhombohedral FeF_3 ($R3c$). (B) Rietveld refinement results of all three materials.

Figure 4. Transmission electron microscopy (TEM) and high-resolution (HR) TEM images of LLNMO (A1, A2, and A3), UPL (B1, B2, and B3), and TPL (C1, C2); Selected area electron diffraction (SAED) pattern of LLNMO (inset A2).

Figure 5. SEM image and EDS elemental distribution mapping of UPL (A). TEM image and EDS elemental distribution mapping of TPL (B).

Figure 6. X-ray photoelectron spectroscopy (XPS) analysis of (a) Li 1s, (b) Ni 2p, (c) Mn 2p, (d) Fe 2p, (e) O 1s, and (f) F 1s.

Figure 7. (A) The conversion reaction mechanism of FeF_3 , and (B) the extraction/insertion of Li^+ in bulk material LLNMO.

Figure 8. Electrochemical performance of pristine LLNMO, UPL, and TPL cathodes: (A) initial three charge/discharge profiles at 0.1C, (B) differential capacity curves at various cycles, (C) capacity retention for 60 cycles at 0.1C, and (D) charge/discharge profiles over 60 cycles.

Figure 9. (A) Capacities at 0.5C, 1C, 2C, and 5C rates after three charge/discharge cycles at 0.1C for pristine LLNMO, UPL, and TPL cathodes; (B) their charge/discharge voltage profiles at 5th and 100th cycles, (C) their electrochemical impedance spectroscopy (EIS) profiles at open circuit potential; and (D) EIS profiles of UPL cathode at charged state of 4.1 V for 1st and 60th cycles.

Figure 10. (A) High-rate cycle performance of pristine LLNMO, UPL, and TPL cathodes at 10C and 20C and the charge/discharge profiles at 25th cycle at various rates; (B) differential scanning calorimetry (DSC) profiles of pristine LLNMO, UPL, and TPL cathodes charged to 4.8 V; and (C) illustration of protective mechanism of LiF/FeF₃ nanoparticles.

Taolin Zhao obtained her Bachelor's Degree in Environmental Engineering from Yanshan University. She is currently a Ph.D. candidate in School of Chemical engineering and Environment in Beijing Institute of Technology (BIT), China. Her research interests are synthesis chemistry, nano science and the cathode materials of LIBs.

Prof. Li Li has been working at Beijing Institute of Technology (BIT) since 2004 after graduation. Her research interests are electrochemical energy storage& conversion technology and recycling technique&life-cycle analysis for spent secondary batteries. As the principal investigator, Dr. Li successfully hosted the National Key Program for Basic Research of China, National High Tech 863 project, National Natural Science Foundation, etc. She has authored/co-authored over 80 research papers and filed 20 patents and patent applications in China.

Renjie Chen is a Professor in the School of Chemical Engineering and the Environment at Beijing Institute of Technology (BIT). His research focuses on electrochemical energy storage and conversion technology. He was a post-doctoral fellow in Department of Chemistry at Tsinghua University and a visiting professor in Department of Materials Science and Metallurgy at University of Cambridge. As the principal investigator, Prof. Chen successfully hosted the National Key Program for Basic Research of China, National High Tech 863 project, National Natural Science Foundation, etc. He has (co-) authored over 70 research papers and filed 18 patents and patent applications.

Huiming Wu received his Ph.D. in Materials Science and Engineering from Zhejiang University in 2007. Currently, he is an assistant materials scientist at Chemical Sciences and Engineering Division in Argonne National Laboratory, USA. His research interests focus mainly on developing high energy electrode cathode materials for lithium ion batteries.

Xiaoxiao Zhang received her Bachelor's Degree in Environmental Engineering from Qingdao University of Science and Technology in 2009 and received her Master of Engineering degree from Beijing Institute of Technology (BIT) in China. She is currently a PhD candidate under supervision of Prof. Feng Wu in BIT. Her research interests focus on recycling of spent LIBs, electrode materials for LIBs and lithium oxygen battery.

Dr. Man Xie is an associate professor of School of Chemical Engineering and the Environment, Beijing Institute of Technology (BIT), China. Her research interests focus on the high-power lithium ion batteries and sodium-ion batteries. Dr. Xie hosted and participated in National Youth Project, National Key Program for Basic Research of China (973 projects) and National High Tech 863 project. She has authored/co-authored over 20 research papers and filed 6 patents and patent applications in China.

Prof. Shi Chen was born in Beijing in 1961 and has been working at Beijing Institute of Technology (BIT) since 1986. Prof. Chen is the vice dean of the School of Chemical Engineering and the Environment. His research interests are low cost electrode materials for lithium ion batteries. As the principal investigator, Prof. Chen successfully hosted the National High Tech 863 project, National Natural Science Foundation, etc. He has authored/co-authored over 50 research papers and awarded 8 patents.

Prof. Feng Wu was born in Beijing in 1951 and has been working at Beijing Institute of Technology (BIT) since 1982 after graduation. Prof. Wu is the director of the Professor Commission of the School of Chemical Engineering and the Environment, the director of Green Energy Research Institute and the vice president of China Battery Industry Association. His research interests are the new electrode materials and electrolytes for green secondary batteries. As the chief scientist, he hosted the National Key Program for Basic Research of China (973 projects) “Basic Research on New Rechargeable Batteries and Related Materials” since 2002. He published over 500 papers and awarded 45 patents. In 2012, he was awarded the IBA Research Award for outstanding research of battery material and systems for electric vehicles.

Dr. Jun Lu is a chemist at Argonne National Laboratory. His research interests focus on the electrochemical energy storage and conversion technology, with main focus on beyond Li-ion battery technology. Dr. Lu earned his bachelor degree in Chemistry Physics from University of Science and Technology of China (USTC) in 2000. He completed his Ph.D. from the Department of Metallurgical Engineering at University of Utah in 2009 with a major research on metal hydrides for reversible hydrogen storage application. He is the awardee of the first DOE-EERE postdoctoral fellow under Vehicles Technology Program from 2011-2013. Dr. Lu has authored/co-authored more than 110 peer-reviewed research articles and has filed over 15 patents and patent applications.

Dr. Khalil Amine is a Distinguished Fellow and the Manager of the Advanced Battery Technology programs at Argonne National Laboratory, where he is responsible for directing the research and development of advanced materials and battery systems for HEV, PHEV, EV, satellite, military and medical applications. Dr. Amine currently serves a member of the U.S. National Research Council on battery related technologies. Among his many awards, Dr. Khalil is a 2003 recipient of Scientific America's Top Worldwide Research 50 Research Award, a 2009 recipient of the US Federal Laboratory Award for Excellence in Technology Transfer, and is the four-time recipient of the R&D 100 Award, which is considered as the Oscar of technology and innovation. In addition, he was recently awarded the ECS battery technology award and the international battery association award. Dr. Amine holds or has filed over 130 patents and patent applications and has over 280 publications. From 1998-2008, Dr. Amine was the most cited scientist in the world in the field of battery technology.

Table of Contents Graphic