LiFePO₄-Coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ Cathode Materials with Improved High Voltage Electrochemical Performance and Enhanced Safety for Lithium Ion Pouch Cells

Lei Zhu,¹,= Ting-Fang Yan,¹,= Di Jia,¹ Yong Wang,¹ Qiang Wu,² Hai-Tao Gu,¹ Yong-Min Wu,¹ and Wei-Ping Tang¹,²

¹State Key Laboratory of Space Power Technology, Shanghai Institute of Space Power-Sources (SISP), Shanghai Academy of Spaceflight Technology, Shanghai 200245, People’s Republic of China
²Research and Development Department, Deyang Weixia Lithium-Battery Technology Company Limited, Sichuan 61800, People’s Republic of China

The applicable nickel-rich cathode materials (LiNi₀.₅Co₀.₂Mn₀.₃O₂, NCM) under high cutoff voltage for high energy density lithium ion batteries shows a broad prospect, but creates enormous challenges for safety. In this work, the LiFePO₄-coated LiNi₀.₂Co₀.₆Mn₀.₂O₂ (NCM-LFP) composites were prepared on a large scale by the high-speed dispersion and mechanical fusion method, attempting to improve the electrochemical performance and safety of pouch full cells worked under a high cutoff voltage of 4.5 V. Performances have been greatly enhanced, especially for the heat generation during the charge process: the temperature rise of a 5Ah NCM-LFP/MCMB (mesocarbon microbeads) pouch cell was 18.7°C, much lower than that of a NCM/MCMB pouch cell (42.7°C). Also, no thermal runaway was observed of NCM-LFP/MCMB pouch cells at 100% state of charge (SOC) during the extrusion and metallic nail penetration tests. The results of ex-situ impedance measurement, high magnification transmission electron microscope (HR-TEM) and in-situ X-Ray Diffraction (XRD) during heating revealed that the enhanced high voltage safety was contributed to the suppressed structure evolution from layer to spinel to rock salt, as a result of a dense and uniform LFP protective layer on NCM.

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Experimental

Synthesis.—NCM and LFP (Wei Xu Co., Ltd., China) pristine materials were mixed to obtain NCM-LFP composites by a high speed dispersion and mechanical fusion method. During the preparation, LFP nanoparticles can be totally dispersed by shear force, and then introduced to the surface of NCM by mechanical friction. The NCM-LFP based full cell was demonstrated to show satisfactory electrochemical and safety performance under a high cutoff voltage of 4.5 V. That was attributed to the LFP coating layer, which had a significant impact on the structure transformation of NCM and the growth of SEI film on the electrode surface.

Materials characterization.—XRD (Rigaku D/max-2600PC, Japan) with Cu-Kα radiation source was applied for the in-situ observation of structure evolution. Samples were scanned over the 20 range of 10–80° with a scan rate of 2° min⁻¹ under different temperatures ranged from 25 to 585°C with a heating rate of 20°C min⁻¹. The particle morphologies were characterized using a scanning electron microscope (SEM, S-4800XL, HITACHI, Japan) and HR-TEM (JEM-2010F, Japan). The thermal stability of NCM and NCM-LFP cathode materials was observed by differential scanning calorimetry.

These authors contributed equally to this article.

E-mail: tangwp@sina.cn
(DSC, STA 449C, NETZSCH, Germany) and heated from 25 to 350 °C with a heating rate of 5 °C min⁻¹.

**Electrochemical measurements.**—Half coin cells and 5Ah pouch full cells with MCMB as anode materials were assembled, NCM and NCM-LFP were used as cathode active materials, respectively. The mixture containing 1 M LiPF₆ in an ethylene carbonate (EC) and dimethyl carbonate (EMC) solution (3:7, v/v) was applied as the electrolyte. The polypropylene membrane (Celgard 2325) was as the separator. The galvanostatic charge-discharge tests of half coin cells were carried out on a LAND battery test system, within the voltage range of 2.8–4.3 or 4.6 V vs. Li⁺/Li⁻ from 0.1 C to 5 C rate (1 C = 180 mAh g⁻¹). The tests of pouch cells were carried out within the voltage range of 2.75–4.2 or 4.5 V at 1 C (5 Ah). The test environment temperature was 25 °C. The electrochemical impedance spectroscopy test was performed using CHI1000C with a frequency range of 10⁻² to 0.01 Hz.

**Safety measurements.**—Accelerating rate calorimeter (ARC, THT, England) and LAND battery test system were simultaneously used to monitor the temperature and voltage variations of NCM/MCMB and NCM-LFP/MCMB pouch cells during the charging process and the thermal runaway process.

The extrusion and metallic nail penetration tests were carried out on NCM/MCMB and NCM-LFP/MCMB pouch cells charged to 4.5 V. For the extrusion test, the pressure was put in a direction perpendicular to the pouch cells until the voltage dropped to 0 V. For the metallic nail penetration test, the diameter of the steel needle was 8 mm and the penetrated speed was 28 mm s⁻¹.

**Results and Discussion**

The mass ratio of NCM: LFP is important for the electrochemical and safe performance of the composite. The SEM morphologies of NCM-LFP samples with different LFP contents (5 wt%, 10 wt%, 15 wt%, 20 wt%) were shown in Figure S1. When the LFP content was 5 wt%, most of the NCM surface was exposed, indicating LFP nanoparticles were too less to forming a protective layer. When it was up to 10 wt%, 15 wt% and 20 wt%, the NCM surface was totally covered by LFP nanoparticles. However, as the LFP content increased, the aggregation of additional LFP nanoparticles emerged at the surface of NCM-LFP electrode delivered a specific capacity of 144.6 mAh g⁻¹ at 5 C, with a capacity retention of 87.5%. While the NCM electrode delivered a specific capacity of 130.1 mAh g⁻¹, whose capacity retention was only 78.5%. When the cells worked at a high cutoff voltage of 4.6 V (vs. Li/Li⁺), more obvious evidences of enhanced rate performance were found in Figure 2b. The NCM electrode performed a palpable decrease in capacity from 0.2 C and the NCM-LFP electrode delayed it to 1 C. The NCM-LFP electrode delivered a capacity of 149.9 mAh g⁻¹ at 5 C, about 76.4% of the capacity at 0.1 C (196.3 mAh g⁻¹). However, the NCM electrode had a low capacity of 119.6 mAh g⁻¹ at 5 C, only 62.0% of the capacity at 0.1 C (192.8 mAh g⁻¹).

Figures 2c–2d showed the Nyquist plots of NCM and NCM-LFP electrodes under different states of charge during charging to 4.6 V (vs. Li/Li⁺), respectively. The semicircle in the high frequency region corresponded to the surface impedance Rsf, and the other one in the middle frequency region corresponded to the charge transfer impedance Rct.¹⁹ The charge transfer resistances were closely related to the charge transfer processes that took place in the electrodes. In Figure 2f, the Rct variation trends of the NCM and NCM-LFP electrodes were similar. Except the highest Rct value at the end of charge, there were two higher Rct values around 4.0 V and 4.3 V, in accordance with the charge transfer processes between Ni⁶⁺→Ni⁵⁺ and Ni⁵⁺→Ni⁴⁺ (Figure S3a-b).²¹ The value of Rsf varied with the associated value of Rct. That was because the ion diffusion was accompanied by the disintegration and/or reorganization of SEI film.²²,²³ The speciation of the transition metal elements (Ni, Mn, and Co) into different oxidation states occurred in the initial charging process, resulting in an irreversible capacity loss (Figure S3a-b). Because of the overlapping between the transition metals and the O²⁻ (2p) band, a high number of metallic species, i.e., NiO, MnO₂, CoO, Li₂CO₃, NiF₂, MnF₂, Li₂O, LiF₂, LiF, CoF₃ with some decomposed compounds from the electrolyte (e.g. ROCO₂Li, OF₂, and PO) generated on the surface of the cathode.²⁴ Due to the changed valance states of the transition metals during the charging process, the metallic species were constantly changing. That brought the frequent disintegration and/or reorganization of SEI film, and the Rsf value changed with it. Both the Rct and Rsf values decreased after the LFP modification, especially at the end of charging, where NCM electrode had a sharp increase in the value of Rct. The reduced impedance had positive consequences for building more favorable SEI film, thereby facilitating the Li⁺ diffusion, which might be responsible to the improved rate capability. Performances behaved in pouch cells would be strongly effective toward the commercial application. Hence, NCM/MCMB and NCM-LFP/MCMB pouch cells were assembled and tested.

![Figure 1.](image)
Figure 2. The rate performance of NCM and NCM-LFP electrodes under different cutoff voltages: (a) 4.3 V, (b) 4.6 V; Nyquist plots of (c) NCM and (d) NCM-LFP electrodes under different states of charge during charging to 4.6 V; The variation curves of (e) Rs and (f) Rct during the charge process.
Figure 3. (a) The cycling performance of 5 Ah NCM/MCMB and NCM-LFP/MCMB pouch cells at 1 C between 2.75–4.5 V; The charge and discharge curves of (b) NCM/MCMB and (c) NCM-LFP/MCMB pouch cells at different cycles.

Figure 3a showed the cycling performance of such pouch cells at 1 C in the voltage range of 2.75–4.5 V. The NCM/MCMB pouch cell presented a rapid capacity loss, with only 81.4% of the initial capacity left after 100 cycles. However, the NCM-LFP/MCMB pouch cell delivered a capacity retention of 90.0% at the same condition, indicating an apparently improved high voltage cycling performance, which was in agreement with the previous work. Figures 3b–3c compared the charge and discharge curves at different cycles. The voltage plateau of NCM declined at faster pace compared with NCM-LFP due to stronger polarization.

The above results demonstrated the electrochemical performance had been improved by the LFP coating. Next, much concern was paid to the safety situation. Heat of the pouch cells was quite significant toward the safety for application. The temperature and the heat generation power variations of NCM/MCMB and NCM-LFP/MCMB pouch cells during the charging process under different cutoff voltages were one key target to value the heat condition, as investigated in Figure 4. When the cutoff voltage was 4.2 V, there was a similar changing trajectory in the temperature and heat generation power variation curves. At the beginning of the charge, the value of heat

Figure 4. Temperature variation curves of NCM/MCMB and NCM-LFP/MCMB pouch cells under different cutoff voltages: (a) 4.2 V, (b) 4.5 V; Heat generation power variation curves of NCM/MCMB and NCM-LFP/MCMB pouch cells under different cutoff voltages: (c) 4.2 V, (d) 4.5 V.
generation power was lower than zero, indicated a little section of endothermal reaction occurred at 0–5% SOC. After that, all the reactions were exothermic at 5–100% SOC, and no reversible thermal reactions were observed. In other words, the heat production of NCM lithium ion batteries during charging mainly originated from irreversible heat of reaction and internal resistance. As shown in Figure 4a, the temperature of the NCM/MCMB pouch cell started to rise at 3.57 V, a little higher than that of the NCM-LFP/MCMB pouch cell (3.55 V). That might influenced by LFP, which had a low working potential. Then, the temperature of the NCM/MCMB pouch cell increased steadily with a decreased temperature rising rate from 3.57 V to 3.67 V (3.55–3.66 V for the NCM-LFP/MCMB pouch cell) and an increased temperature rising rate from 3.66 V to 3.76 V (3.67–3.76 V for the NCM-LFP/MCMB pouch cell). After that, until 4.2 V, the temperature rising rate decreased again, and temperature of pouch cells had a continuous rise. During the charging process, the temperature of the NCM/MCMB pouch cell increased by 12.2 °C while that of the NCM-LFP/MCMB pouch cell was 12.4 °C. The difference was not significant. In consistence with Figure 4a, the heat generation power variation curves in Figure 4c showed there were two peaks at 3.57 V and 3.76 V of the NCM/MCMB pouch cell, while 3.55 V and 3.76 V of the NCM-LFP/MCMB pouch cell. Both the highest heat generation power of the two pouch cells was 0.48W.

When the cutoff voltage was 4.5 V, before arrived at the cutoff voltage, Figures 4b and 4d depicted that both the temperature rising rate and the heat generation power were in the identical “up-down-up-down” changing trend with the case of 4.2 V. However, a huge difference emerged at the end of the charging process, the temperature of the NCM/MCMB pouch cell had a sharp increase. This phenomenon illustrated a great internal impedance, according with the results in Figure 2.26 During the charging process, the temperature of the NCM/MCMB pouch cell increased by 42.7 °C while that of the NCM-LFP/MCMB pouch cell was only 18.7 °C. The highest heat generation power of the NCM/MCMB pouch cell was 1.22 W while that of the NCM-LFP/MCMB pouch cell was 0.57 W, signifying the irreversible heat of reaction and internal resistance had been suppressed.

The thermal condition of NCM/MCMB and NCM-LFP/MCMB pouch cells during the discharging process was showed in Figure S3. The temperature of the cells was on the rise during the whole discharging process and the heat generation power was higher than zero, indicating the discharging process was an exothermic process. Besides, it was observed that the cells experienced a rapidly rising in temperature and heat generation power from 90% to 100% DOD, resulting from a rapid decrease of voltage at the end of the discharge process.27 The temperature of the NCM/MCMB pouch cell increased by 16.8 °C and 22.5 °C discharged from 4.2 and 4.5 V to 2.75 V, respectively. In the case of the NCM-LFP/MCMB pouch cell, the temperature rises dropped slightly, which were 16.2 °C (4.2 V) and 20.9 °C (4.5 V), indicating an improved safety. Therefore, satisfactory results of the high voltage safety could be expected.

In order to verify the safety and durability, the extrusion and metallic nail penetration tests were performed on NCM/MCMB and NCM-LFP/MCMB pouch cells charged to 4.5 V. At high SOC, the strong oxidized transition metal ions tended to react with the electrolyte violently, releasing oxygen and generating a large amount of heat. At this time, the destructive behaviors or short circuit could arouse sharp high temperature, which would cause the decomposition of cathode and then result in cell failure or even thermal runaway.28 Figures 5a–5b depicted the temperature and cell potential variations with time during the extrusion test. When the test continued for 1082 s, thermal runaway was observed in NCM/MCMB pouch cell. The voltage slumped to 0 V and the temperature reached 482.7 °C instantly. In contrast, there was no thermal runaway happened in NCM/MCMB pouch cell. The voltage dropped to 0 V until 4150 s, with the temperature up to 94.3 °C. Besides, the photographs from electrochemical impedance spectroscopy tests were shown in Figures 5c–5d. Normally, due to the excellent safety performance,29 the cell with pure LFP could pass the nail penetration test with no fire evidence.30,31 However, in the case of the cell with NCM, the result was dissatisfactory. When the nail pierced, the NCM/MCMB pouch cell quickly combusted. But then, for the NCM-LFP/MCMB pouch cell, surprisingly, until the nail penetrated the cell, there was no bulging, spark or flame observed, which revealed that the safety performance had been improved remarkably. Figures 5e–5f compared the characteristics monitored by ARC and LAND between NCM/MCMB and NCM-LFP/MCMB pouch cells during the thermal runaway. There were three main temperatures in the curves.25 (i) The cells were heated at the beginning of the experiment, and the voltage decreased, incrementally reaching the self-heating trigger temperature $T_1$, which was defined as safe usage temperature. (ii) Self-heating further elevated the cell temperature. When the rising rate was higher than 10 °C/min–1, it was considered to reach the thermal runaway trigger temperature $T_2$, and was defined as ultimate safe temperature. (iii) Once the thermal runaway happened, the temperature increased exponentially to a maximum ($T_{max}$). As shown in insert curves, the self-heating trigger temperature $T_1$ of NCM-LFP/MCMB was 74.8 °C, higher than 70.7 °C of NCM/MCMB. The value of $T_1$, mainly dominated by the decomposition of SEI film, higher $T_1$ meant more stable SEI film formed.33,34 Moreover, the thermal runaway trigger temperature $T_2$ of NCM-LFP/MCMB was 134.7 °C, also higher than 121.4 °C of NCM/MCMB, implying that the ultimate safe temperature of NCM based lithium ion batteries was increased by 13.3 °C.

For the purpose of finding out whether the cathode materials played a critical role in ameliorating the safety, the thermal decomposition temperatures of NCM and NCM-LFP charged to different cutoff voltages in full cells were measured by DSC test. Figure 6 showed when the cutoff voltage increased from 4.2 V to 4.5 V, the thermal decomposition temperatures both of NCM and NCM-LFP decreased. However, NCM-LFP showed less heat generation and a lower thermal decomposition temperature of 243.4 °C. 8.4 °C higher than that of NCM, implying that the thermal stability of cathode materials was improved.

The structural changes of NCM and NCM in the composite after 100 cycles under 2.75–4.5 V were analyzed by HR-TEM and fast Fourier transformation (FFT). Figure 7a presented the HR-TEM image of NCM particle, while Figures 7b–7c were FFT filtered TEM images recorded from different selected areas in Figure 7a. FFT results from different regions indicated that the bulk of the particle remained rhombohedral phase (Figure 7d, Region I), and that the structure change existed at about 20 nm from the surface. At a distance of 10–20 nm from the surface (outlined by red dotted square frame), spinel phase and rhombohedral phase coexisted in Region II (Figure 7e). While, only two symmetrical diffraction spots were observed at 10 nm from the surface (outlined by yellow dotted square frame), which indicated the existence of rock salt phase, referring to (11-1) planes of NiO and CoO (Figure 7f, Region III; Figure 7g, Region IV). As described in previous researches,35 the structural change of NCM was a result of cation mixing of Li$^+$ and Ni$^{2+}$, which arose from side reactions between Ni$^{4+}$ and electrolyte, especially at the end of charging. The existence of rock salt phase on the surface led to obstructed transmission of lithium ions, resulting in an increase in charge transfer impedance. Furthermore, the phase transition from rhombohedral to spinel to rock salt was accompanied by the release of oxygen, which incurred increased internal pressure of the cell and potential security concerns. The HR-TEM image and FFT filtered TEM images recorded from two selected areas of NCM particle in the NCM-LFP/MCMB composite are shown in Figures 7h–7j. Similarly, the corresponding FFT results demonstrated that the main structure of NCM in the composite maintained original layered structure (Figure 7k, Region I; Figure 7j, region II). Structure changes occurred at 10 nm from the surface (outlined by red dotted square frame), where the spinel phase was noticed in a mixed structure including both layer and spinel structure (Figure 7m, region III). Nevertheless, only at certain points (outlined by yellow dotted box), the spinel phase further transformed to the rock salt phase (Figure 7n, region IV), rather than forming a rock salt phase layer. Based on the analysis above, it was concluded that the dense LFP coating could effectively reduce the occurrence of side reactions, inhibit cation mixing and improve structural stability.
Figure 5. The extrusion test results of (a) NCM/MCMB and (b) NCM-LFP/MCMB pouch cells charged to 4.5 V; The metallic nail penetration test results of (c) NCM/MCMB and (d) NCM-LFP/MCMB pouch cells charged to 4.5 V; Thermal runaway curves of (a) NCM/MCMB and (b) NCM-LFP/MCMB pouch cells charged to 4.5 V.

Figure 6. DSC curves of NCM and NCM-LFP cathode materials charge to (a) 4.2 V and (b) 4.5 V.
Figure 7. (a) HRTEM image of the cycled NCM particle; FFT filtered TEM images recorded from (b) region II and (c) region III in (a); FFT results of (d) region I, (e) region II, (f) region III and (g) region IV in (a); (h) HRTEM image of the cycled NCM-LFP particle; FFT filtered TEM images recorded from (i) region III and (j) region IV in (h); FFT results of (k) region I, (l) region II, (m) region III and (n) region IV in (h).

The structural evolution trajectory during the thermal decomposi-
tion process of NCM and NCM-LFP at highly delithiated state was
intuitively monitored through in-situ XRD. Figure 8a presented that
the pristine NCM at 4.5 V exhibited a typical layered structure with R-
3m group. When the temperature was up to 205°C, the two splitting
peaks ((108) and (110)), which was an emblem of layered struc-
ture, began to disapper, portending a transition from rhombohedral
phase (R-3m) to spinel phase (Fd3m) and disappeared completely at
265°C. In the meantime, the characteristic (440) peak of spinel struc-
ture emerged.36 Sequentially, as the temperature rose to 405°C, (220)
and (422) peaks appeared, indicating that transition metal ions occu-
pied the tetrahedral sites in spinel phase, which could encourage the

transformation to rock salt phase.29 In the case of NCM-LFP in Fig-
ure 8b, the characteristic peak (440) of spinel structure appeared at
305°C, while (220) and (422) peaks appeared at 445°C. The phase
transition temperatures were 40°C higher than that of NCM. In con-
sistence with the HR-TEM results, the introduction of LFP helped
to improve structural stability of NCM, and the inhibition of phase
transformation played an important role in ameliorating safety.
The application of LFP coating, which had an outstanding thermal
stability, could protect NCM to avoid direct contact with electrolyte,
and less reaction heat generated due to less side reactions and oxygen
release. On the other hand, the thermal stability of NCM was enhanced
by stabilizing the structure, contributing to avoid the decomposition

Figure 8. In-situ XRD patterns heating from 25 to 585°C of (a) NCM and (b) NCM-LFP charged to 4.5 V.
of cathode materials and extricate lithium ion batteries from thermal runaway in extreme circumstances.

Conclusions

In summary, it is shown that the as-obtained NCM-LFP composite could improve not only the electrochemical performance, but also the safe reliability of NCM based lithium ion pouch cells at a high cutoff voltage of 4.5 V. 5 Ah NCM-LFP/MCMB pouch cells at highly delithiated state passed the extrusion and metallic nail penetration tests rather than thermal runaway, and the ultimate safe temperature was increased to 134.7 °C, 13.3 °C higher than that of NCM/MCMB pouch cells. The remarkable progress was contributed to the uniform and dense coating of LFP nanoparticles, which could protect NCM from contacting with electrolyte directly. In addition, it is demonstrated that there were two main reasons for the improvement: (i) The abatement of charge transfer impedance at high SOC was helpful to facilitate lithium ion migration and reduce the internal resistance of pouch cells; (ii) The postponed structure evolution from layer to spinel to rock salt led to the increased thermal decomposition temperature, which was a key factor for the enhanced safety. Therefore, we can foresee a broad application prospect of NCM-LFP composites as cathode materials in high energy density and high safety power lithium ion batteries.

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ORCID

Wei-Ping Tang https://orcid.org/0000-0003-1726-9105

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