Thermal Synergy Effect between LiNi0.5Co0.2Mn0.3O2 and LiMn2O4 Enhances the Safety of Blended Cathode for Lithium Ion Batteries

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ABSTRACT: The layer-structured LiNi0.5Co0.2Mn0.3O2 (LS23) with high specific capacity and the spinel LiMn2O4 (LMO) with excellent thermostability complement each other in a blended cathode for better heat stability and electrochemical performance. The delithiated LMO starts to react with electrolyte at 160–200 °C to cause structural instability, and the delithiated LS23 generates massive heat when its temperature is raised above 275 °C with the electrolyte present, but we found that the blended cathode shows a remarkable improvement in thermal stability since the reaction at 160–200 °C between LMO and the electrolyte disappears, and the total heat generated from the reaction between LS23 and the electrolyte is drastically reduced. The reaction between LMO and the electrolyte at 160–200 °C causes structural instability of LMO as a self-accelerating attack from HF. With LS23 present, this reaction is eliminated because the H+ from HF and Li+ in LS23 undergo exchange reaction to prevent further generation of HF. The presence of LMO, however, reduces the total heat generated by LS23 reacting with the electrolyte at high temperature. This thermal synergy between LMO and LS23 not only improves the thermal safety of the blended cathode but also preserves their structures for better electrochemical performance.

KEYWORDS: LiNi0.5Co0.2Mn0.3O2, LiMn2O4, electrolyte, synergistic effect, self-accelerating

1. INTRODUCTION

High energy lithium ion battery (LIB)—the most reliable and efficient energy storage device—has attracted enormous interest from the automobile industry for electric powered vehicle applications, and has become ever increasingly important in the portable electronic industry.1–6 One of the major concerns of the LIB application in electric vehicles is its safety, particularly when it is assembled into a large battery pack and operated at elevated temperatures.7–9 Studies have shown that when the temperature is raised above 80 °C, a thermal runaway is likely being triggered, resulting in battery venting, burning, or explosion.10–12 Among all the components inside a lithium ion battery, it is well documented that the cathode materials determine the thermal characteristics of the cell because the cathode materials, most of them being transition metal oxides with high redox potentials, are strong oxidants and can easily oxidize organic electrolyte components when the battery is fully charged and/or at high temperature.7,13 The reaction between the cathode and the electrolyte generates heat faster than the cell can dissipate it, which results in either the cell becoming pressurized for explosion or internal thermal runaway for burning, thus the safety of the cell is in great danger.14–16

The past decade has witnessed extensive research efforts in improving LIB electrochemical performance and cycle stability, particularly in modification of cathode materials, such as lattice doping with stable metal ions,17–19 surface modification of cathode particles with lithium ion conducting oxides or phosphate materials,20–22 and morphological control by synthesis design.23,24 Nevertheless, the thermal stability of the cathode materials with the electrolyte are usually neglected.

In order to satisfy the demands of electric vehicles (EV), hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and large-scale industrial production, cathode materials with lower cost, high thermostability, and power densities have attracted much attention in recent years.25 The top two candidate systems are the LiNi1−xSixCo1−yMnxO2 and LiMn2O4 (LMO).9,26,27 Thorough studies on the electrochemical and physicochemical properties of the intercalation...
compounds used as LIB cathode materials revealed that the layer-structured transition metal oxides (especially solid state solution compounds LiNi$_x$Co$_{1-x}$Mn$_2$O$_4$) and three-dimensional transition metal oxide spinel LiMn$_2$O$_4$ are complementary to each other: rock salt layer-structured LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ exhibits high specific capacity, high cycling stability, but low rate capability and low thermal stability at delithiated stage and/or elevated temperature; LiMn$_2$O$_4$ shows moderate specific capacity, high rate capability, and high thermal stability at the delithiated stage, but low structural stability. The low thermal stability of the cell with LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ as cathode is due to its strong oxidation power at delithiated stage toward the organic electrolyte and the low structural stability of LMO arises from the reaction between HF in the electrolyte and LMO accompanying with manganese dissolution. Studies have shown that with the increasing nickel content in LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ the capacity of material is improved. However, the capacity attenuation and resultant thermostability problems are as follows. Among these materials, the cycle stability and capacity of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (L523) is acceptably expected to slightly lower thermostability. And another competitive LiMn$_2$O$_4$ has better thermostability and lower capacities than L523.

One kind of material can not satisfy practical requests on good heat stability, high capacity, and excellent rate capacity and so on, at the same time. So blended materials composed by two or more than two different materials were attempted to obtain comprehensive performance by cooperating with their advantages. For example, people have attempted to blend Li[Ni$_{0.33}$Co$_{0.33}$Mn$_{0.33}$]O$_2$ and LiMn$_2$O$_4$ as a blended cathode for lithium ion batteries, and results show that this composite material has good thermostability. But the cause of this synergistic effect is still unclear.

In this work, we chose LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (L523) as our layer-structured cathode material as a component of the blended cathode materials. We investigated their cycling stabilities, rate capabilities, and thermal stabilities of L523 and LMO blended cathode materials with different mixing ratios. Indeed, the blended materials exhibit complementary electrochemical performance of L523 and LMO to each other. We also observed the disappearance of the thermal reaction between LMO and the electrolyte at 160–200 °C by delithiated L523 as well as the greatly reduced total heat generated from the oxidation of the electrolyte by delithiated LMO. It is apparent that there is a thermal synergistic effect between L523 and LMO, which is responsible for the better thermal stability of the blended materials, compared to L523 or LMO. However, this synergistic effect of the blended materials—LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ and LiMn$_2$O$_4$ has not been fully understood. In order to shed light on this phenomenon and for the sake of which component in the electrolyte is responsible for the exothermic reaction between the cathode and the electrolyte, we studied the electrochemical properties and thermal stabilities of a series of blended cathode materials and simulation experiments to discover the origins of these thermal reactions and elucidate the reaction mechanism of the synergistic effect.

2. EXPERIMENTAL SECTION

2.1. Materials Preparation. LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (L523) was purchased from Ningbo Jinhe New Materials Co., Ltd.; LiMn$_2$O$_4$ (LMO) was purchased from Qingdao LNCM Co., Ltd. The blended materials were obtained by ball milling method (FRITSCH Pulverisette 14) from a mixture of LS23 and LMO. The mixture of the powders was milled for 20 min at 150 r per minute. LS23 and LMO were blended by the weight ratios of 7:3, 1:1, 3:7, and the samples obtained were labeled thus as 7−3, 1−1, and 3−7, respectively.

2.2. Preparation for the Samples of Delithiated Cathode Used for DSC/TGA Measurements. The button cell was first cycled for one cycle and then charged to 4.6 V state at 0.5 C; the charged cell was taken apart to get electrode materials film in an Ar-filled glovebox; the film was washed several times with DMC and naturally dried inside the glovebox, and finally the electrode materials scraped from film and electrolyte were sealed together in a gold-plated stainless steel crucible in the glovebox. The ratio of electrolyte to electrode materials was 1 μL of electrolyte per milligram of electrode materials. During the process of testing, a stainless steel crucible system is in a closed state to ensure no other contamination and mass loss.

2.3. Materials Characterization. Field emission scanning electron microscopy (SEM, HITACHI S-4800) was used to characterize the morphology of samples, and energy dispersive X-ray spectroscopy (EDS, OXFORD 7593-H, an accessory of SEM) was carried out to analyze the surface elemental distribution of particles with 20 kV acceleration voltage. The DSC/TG (STA 449 F3 Jupiter Netzsch) was used to measure the thermal stability of electrodes from 50 to 350 °C at a heating rate of 5 °C/min.

2.4. Electrochemical Measurements. The electrochemical performances of these materials were evaluated with CR2016 type coin cell configuration. The working electrode film was obtained by spreading a slurry of 85 wt % active material, 8 wt % acetylene black, 2 wt % graphite black, and 5 wt % polyvinylidene difluoride (PVDF) binder dispersed in N-methyl pyrrolidione (NMP) solvent onto an aluminum foil. After drying in a vacuum oven at 100 °C overnight, the electrode was punched out and roll-pressed. CR2016 type coin cells were assembled by sandwiching a porous polyethylene separator between the electrode and Li metal foil in a high-purity Ar-filled glovebox. The electrolyte was 1.0 M LiPF$_6$ salt dissolved in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a weight ratio of 1:1. The cells were charged with a constant-current and constant-voltage mode (CC−CV) and discharged with specified constant current between 3.0 and 4.3 V at room temperature on battery testers (NEWARE BTS type battery charger, Shenzhen, China). Taking 1 C as an example, the cells were first charged galvanostatically to 4.3 V, after 4.3 V was reached, the voltage was kept at 4.3 V until the current decreases gradually from 1C to 0.1C (constant voltage charge step). The current values at various rates were calculated based on the specific capacity of LS23 (150 mAh·g$^{-1}$) and LMO (110 mAh·g$^{-1}$) given by manufactures; while for the composite samples of 7−3, 1−1, and 3−7, the specific capacities were calculated based upon LS23 and LMO weight proportionally. All the tests were conducted at 25 °C unless specified. The mass loading for all the cells was controlled in about 6 mg·cm$^{-2}$.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization and Electrochemical Performance. The SEM images of LS23 (a, b), LMO (c), 7−3 (d), 1−1 (e), and 3−7 (f) samples are shown in Figure 1, respectively. The particles of the LS23 are sphere-like with sizes ranging from 5 to 15 μm (Figure 1a) and composed by many nanoparticles with crystalline facets (Figure 1b). The LMO particles are of irregularity (Figure 1c), aggregating by little granules. After the blending, the LS23 and LMO are uniformly distributed, as shown in Figure 1d−f, and it is difficult to distinguish between LS23 and LMO. To further illustrate the distribution of LMO and LS23, EDS spectra of samples were performed, as shown in Figure 2. It is seen that the Ni element distribution which is on behalf of LS23 due to the inexistence of Ni in LMO is nearly partly overlapped with that of the left SEM.
without large blank existed zone, indicating that L523 are distributed evenly around LMO. The XRD patterns of the samples are shown in Figure 3. L523 exhibits a well-defined layer structure based on a hexagonal α-NaFeO2 structure with a R3̅m space group with no impurities present, while LMO displays well-defined cubic spinel structures without impurities. The 7−3, 1−1, and 3−7 are simple blendings of L523 and LMO, thus several pairs of twin peaks at ca. 34.6° and 44.4° are observed. The XRD patterns of all the blended materials can be indexed to a mix-phase of a hexagonal α-NaFeO2 structure and a cubic spinel structure. This indicates that the blended process is the only physical process and the physical mixing of L523 and LMO does not alter their structures. Along with increasing of L523 amount, the intensities of L523 characteristic peaks grow.

The first charge/discharge curves of these samples at 0.5 C are shown in Figure 4. The pure LMO cathode exhibits two characteristic plateaus around 4.1 V; pure L523 cathode shows a characteristic continuous voltage declining phenomenon, which is the characteristic of layer structure for Li-NiCoMn1−x−yO2. While for the voltage−capacity curves of the blended materials, 7−3, 1−1, and 3−7, are the mere addictiveness of L523 and LMO. This is also the reason why the charging and discharging platforms of three blended samples lie in between that of L523 and LMO. Along with the increasing of LMO content, the charging and discharging platforms arise, more like LMO. The first discharge capacities of L523, 7−3, 1−1, and LMO are 151.5 mAh·g−1, 138.2 mAh·g−1, 126.2 mAh·g−1, 116.1 mAh·g−1, and 105.9 mAh·g−1, respectively. With the increasing of LMO weight ratio, the discharge capacities of blended samples decrease, because of lower capacity of LMO.

The cycling discharge profiles of L523, 7−3, 1−1, 3−7, and LMO at 1.0 C charge/discharge rates are shown in Figure 5a. Their first discharge capacities are 147.0, 135.5, 125.1, 117.8, and 104.8 mAh·g−1, respectively. After 100 cycles, the discharge capacities decrease gradually to 133.4, 127.3, 117.8, 111.0, and 101.3 mAh·g−1, which is equal to 90.7%, 93.8%, 94.2%, 94.2% and 96.7% of their initial capacities, respectively. The capacity retention trend indicates that with the increasing of LMO quality, cycling stability enhances. But with the increase of the LMO amount, the circle capacity retention is not a linear increase, that from 0% to 30%, the retention rate significantly increases, and from 30% to 50%, the change is tiny, illustrating that the addition of 30% amount of LMO is enough to well improve the cycle performance of L523 materials. The above-mentioned results indicate that there is a synergetic effect between L523 and LMO, with LMO acting as a cycle stabilization agent to improve cycling stability and L523 boosting the electrical capacities in blended samples.

The biggest improvement in the electrochemical performance of LMO/L523 blends is their rate capability, as shown in Figure 5b. The discharge capacities of L523 at 0.5 C, 1 C, 3 C, 7−3, 1−1, and 3−7 are simple blendings of L523 and LMO, thus several pairs of twin peaks at ca. 34.6° and 44.4° are observed. The XRD patterns of all the blended materials can be indexed to a mix-phase of a hexagonal α-NaFeO2 structure and a cubic spinel structure. This indicates that the blended process is the only physical process and the physical mixing of L523 and LMO does not alter their structures. Along with increasing of L523 amount, the intensities of L523 characteristic peaks grow.
and 5 C are 147.6 mAh g\(^{-1}\), 139.1 mAh g\(^{-1}\), 124.5 mAh g\(^{-1}\),
and 118.6 mAh g\(^{-1}\) respectively, and that of LMO are 102.1
mAh g\(^{-1}\), 101.1 mAh g\(^{-1}\), 98.9 mAh g\(^{-1}\), and 95.3 mAh g\(^{-1}\),
respectively. When the current values are returned back to 0.5
C, reversible discharge capacities of 146.9 and 100.4 mAh g\(^{-1}\)
for L523 and LMO are obtained, which are 97.0% and 98.3% of
the initial discharge capacity at the same rate, respectively. The
discharge capacity of L523 is much worse than that of LMO. The
discharge rate capabilities of the three blend samples are very similar, even though they are not as
good as that of LMO, but a much better capabilities compared
to that of L523, and even better than expected from simple
addition based on ratio calculation. The discharge capacities of
1−1 at 3 and 5 C are even the same as that of 7−3, rather
better than the simple sum results of L523 and LMO, which
means 30% LMO working as three-dimensional lithium ion
transport is favorable enough to the lithium ion intercalation−
deintercalation of L523 in blended samples. LMO improves the
rate capacities of blended samples excellently. On the basis of
these data, we can formulate a blend cathode from high
capacity L523 and high-rate LMO for practical application.

3.2. Thermal Analysis. The thermal behaviors of charged
(delithiated, 4.3 V) L523, 7−3, 1−1, 3−7, and LMO with 301
electrolyte (1 M LiPF\(_6\), EC/DMC) were investigated by DSC/
TG analysis as shown in Figure 6. There are obvious differences
among their thermal stabilities. The onset exothermic tempera-
ture of L523 is 211.4 °C, and two exothermic peak values are
at 279.5 and 299.5 °C. The total heat quantity of L523 among
all samples is the maximum, and the heat quantity per mass of
electrode materials is 1531 J g\(^{-1}\). While for LMO, the onset
exothermal temperature is 163.1 °C, 48.3 °C lower than that of
L523. From this point of view, it seems that the heat stability of
LMO is worse than that of L523, however the heat quantity per
mass of electrode materials for LMO is 1157 J g\(^{-1}\), 374 J g\(^{-1}\)
lower than that of L523. Moreover, the maximum heat flow of
LMO is only 2.4 W g\(^{-1}\), far lower than 9.8 W g\(^{-1}\) of L523,
which will not cause the temperature of the battery to rise
rapidly nor the thermal runaway phenomenon compared with
L523. Thus, it would be misleading based simply upon the
lower onset exothermal point that LMO is responsible for the
thermal stability of the blended material because thermal
runaway is caused by fast heat generation and the total heat
generated. So overall, LMO has better thermal stability than
L523. The DSC curves of the blends 7−3, 1−1, and 3−7 are
very similar to each other and to that of L523, all having two
exothermic peaks with exothermal onset at about 205 °C,
which is significantly higher than that of LMO (163.1 °C) but
slightly lower than that of L523 (211.4 °C). It is obvious that
the low exothermal onset of pure LMO interacted with
Research Article

Delithiated LMO materials is 1263 J·°C, and delithiated LMO electrode in electrolytes with different LiPF6 salt), and delithiated LMO electrode in electrolytes with (charged to 4.3 V) exothermal onset at 209.5 °C. The delithiated LMO in EC/DMC (1:1, wt %) shows an initial exothermal peak of LMO around 160 °C, no heat flow around 160 °C was observable. In the delithiated LMO/1.0 M electrolyte at 187.6 °C, 222.0 °C, 236.7 °C, and 268.6 °C, respectively. The heat flow of each is also worth mentioning. In the case of the delithiated LMO/(EC + DMC), no heat flow around 160 °C-200 °C was observable. In the delithiated LMO/(1.0 M LiPF6 EC/DMC) case, the heat flow emerges between 160 and 200 °C and the total heat quantity is 1157 J·°C. When the concentration of LiPF6 is increased to 2 M, the heat flow between 160 and 200 °C increases with the peak near 260 °C being slightly decreased, and total heat quantity is 1447 J·°C. This may be because that the exothermic reaction between 160 and 200 °C consumes part of the delithiated LMO, leading to heat quantity near 260 °C decrease. These observations strongly suggest that the exothermic peak between delithiated LMO and electrolyte around 160-200 °C, we must figure out what reaction is responsible for this exothermic peak. For this purpose, we carried out DSC analysis on the following: pure electrolyte, delithiated LMO electrode (charged to 4.3 V) immersed in organic solvents made up electrolyte (without LiPF6 salt), and delithiated LMO electrode in electrolytes with different LiPF6 concentrations as shown in Figure 7a. The pure electrolyte does not show any exothermic peak below 270 °C. The delithiated LMO in EC/DMC (1:1, wt %) shows an initial exothermal onset at 209.5 °C with two more exothermic peak around 243.6 and 321.2 °C, and the heat quantity per mass of delithiated LMO materials is 1263 J·g⁻¹. The exothermic reaction between delithiated LMO and solvent is attributed to oxidation of organic solvents by delithiated LMO, a strong oxidant. Taking EC as an example, the reaction is as follows:

\[
\text{Mn}_2\text{O}_3 + 2/5\text{C}_3\text{H}_4\text{O}_3 \rightarrow 2\text{MnO} + 6/5\text{CO}_2 + 4/\text{H}_2\text{O}
\]

However, the exothermal onset of the delithiated LMO/electrolyte is significantly lowered compared to those of pure delithiated LMO/(EC+DMC). It was also observed that as the concentration of LiPF6 increases from 1.0 to 2.0 M, the exothermal onset decreases from 162.4 to 157.6 °C even though the four exothermal peak positions and intensities are different. The peaks of the delithiated LMO/1.0 M electrolyte are at 187.6 °C, 222.0 °C, 236.7 °C, and 268.6 °C, all slightly higher than those of the 2.0 M electrolyte (186.5 °C, 204.5 °C, 232.1 °C, and 260.4 °C, respectively). The heat flow of each is also worth mentioning. In the case of the delithiated LMO/(EC + DMC), no heat flow around 160 °C-200 °C was observable. In the delithiated LMO/(1.0 M LiPF6 EC/DMC) case, the heat flow emerges between 160 and 200 °C and the total heat quantity is 1157 J·°C. When the concentration of LiPF6 is increased to 2 M, the heat flow between 160 and 200 °C increases with the peak near 260 °C being slightly decreased, and total heat quantity is 1447 J·°C. This may be because that the exothermic reaction between 160 and 200 °C consumes part of the delithiated LMO, leading to heat quantity near 260 °C decrease. These observations strongly suggest that the exothermic peak between delithiated LMO and electrolyte around 160-200 °C be associated with LiPF6 and with the increase of LiPF6 concentration, the thermal stability of the system worsens. To further consolidate our conclusion that the exothermic onset around 160-200 °C of the delithiated LMO (4.3 V) in the electrolyte is caused by the LiPF6, 1.0 M LiTFSI/EC+DMC system is displayed in Figure 7b. In this case, no exothermic peak around 160-200 °C is observed, and the heat flow only starts well above 200 °C. Thus, it is unambiguous that the exothermic onset around 160-200 °C of the delithiated LMO in LiPF6 electrolyte is caused by the presence of LiPF6.

### Table 1. Thermodynamic Data of De-Intercalated Samples (4.3 V) with Electrolyte in Figure 6

<table>
<thead>
<tr>
<th>Electrolyte + Samples</th>
<th>Onset temp. (°C)</th>
<th>Peak temp. (°C)</th>
<th>Maximal heat flow (J·g⁻¹)</th>
<th>Reaction heat (J·g⁻¹)</th>
<th>Calculated value (J·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L523</td>
<td>211.4</td>
<td>279.5</td>
<td>9.8</td>
<td>1531</td>
<td>1531</td>
</tr>
<tr>
<td>7−3</td>
<td>206.8</td>
<td>259.3</td>
<td>4.0</td>
<td>1335</td>
<td>1419</td>
</tr>
<tr>
<td>1−1</td>
<td>204.7</td>
<td>259.8</td>
<td>3.1</td>
<td>1180</td>
<td>1344</td>
</tr>
<tr>
<td>3−7</td>
<td>204.0</td>
<td>258.4</td>
<td>2.9</td>
<td>1150</td>
<td>1269</td>
</tr>
<tr>
<td>LMO</td>
<td>163.1</td>
<td>187.6</td>
<td>2.4</td>
<td>1157</td>
<td>1157</td>
</tr>
</tbody>
</table>

**Figure 7.** (a) DSC curves of 1 M LiPF6/ EC+DMC(1:1 wt %), and deintercalated LMO (4.3 V) with the presence of 2 M LiPF6/ EC+DMC (1:1 wt %), 1 M LiPF6/ EC+DMC(1:1 wt %) and EC+DMC (1:1 wt %) and (b) DSC curve of deintercalated LMO (4.3 V) with 1 M LiTFSI/EC+DMC (1:1 wt %).
The above results show that the exothermic peak of delithiated LMO-electrolyte around 160–200 °C in Figure 7a is associated with LiPF$_6$, so thermal stability of LiPF$_6$ is investigated in a closed system without mass loss during the test process, shown in Figure 8a. Before 160 °C, LiPF$_6$ does not have apparent thermal behavior; to 165 °C, the LiPF$_6$ began to show heat absorption, and the endothermic behavior reaches top value at 197 °C (shown as peak). This sharp peak at 197 °C is consistent with other reports$^{33}$ that the phase transition of LiPF$_6$ occurs around 200 °C, so peak at 197 °C in Figure 8a is aroused by the phase transition of LiPF$_6$. With the increase of temperature, LiPF$_6$ continues to show significant endothermic behavior, the endothermic peak at 357 °C is primarily caused by LiPF$_6$ decomposition as follows:

$$\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5 \text{(g)}$$

Seen from Figure 8b of LiPF$_6$ TG-DSC curve in a open system, LiPF$_6$ at about 150 °C has already begun to decompose with quality reduced and PF$_5$ generated, electrolyte containing trace amounts of water, and PF$_5$ will react with water to produce the HF and LiF. The exothermic reaction between LMO and electrolyte around 160–200 °C is likely to be aroused by interaction of LMO and breakdown products of LiPF$_6$ such as PF$_5$, LiF, and HF. The LiF is electrochemically inert, so it is possible that PF$_5$ or HF participates in the reaction between delithiated LMO and electrolyte.

In order to clarify the interaction between delithiated LMO and bare LiPF$_6$ salt, the thermal behavior of the delithiated LMO with pure LiPF$_6$ salt was carried out as shown in Figure 9. It only shows a slight endothermic peak at 200 °C, which is attributed to the phase transition of LiPF$_6$ and a big endothermic peak at 300 °C, which is related to the mutual effect between LMO and PF$_5$. This is consistent with the thermal decomposition of LiPF$_6$ (shown in Figure 8). On the basis of these data, it can be concluded that the reactions between LMO and PF$_5$ occur at higher temperature (300 °C), thus the exothermic onset at 160 °C must be from some mysterious compounds other than PF$_5$, EC, and DMC.

It is well understood that LiPF$_6$ is prone to hydrolysis when water is present to generate HF which is very reactive toward metal oxides. We hypothesize that HF is the mysterious compound responsible for the exothermic onset at 160 °C. To verify this hypothesis, we use Li$_2$CO$_3$ as HF scavenger substituting for LS23. The DSC curve of the mixture consisting of delithiated LMO, Li$_2$CO$_3$ and electrolyte with a ratio of 1 mg: 1 mg: 2 μL is shown in Figure 10a. Three exothermic peaks around 130 °C, 250 °C, and 300 °C were observed, no heat released at 160 °C. Compared to the thermal behaviors of Li$_2$CO$_3$ in the electrolyte and organic solvents shown in Figure 10b, the exothermal peak at 130 °C can be unambiguously assigned to the reaction between HF and Li$_2$CO$_3$. The Li$_2$CO$_3$ + 1 M LiPF$_6$ EC/DMC also appear an exothermic peak around 130 °C, while for Li$_2$CO$_3$ + EC/DMC, this peak disappears.

The only difference between electrolyte and solvent is the existence of LiPF$_6$ in electrolyte, which can react with trace water in the electrolyte to generate HF, thus further prove that the exothermic reaction around 130 °C is the reaction between HF and Li$_2$CO$_3$, and Li$_2$CO$_3$ is good HF-eliminated additives commonly used in lithium ion batteries. This experiment clearly demonstrates that the effect of Li$_2$CO$_3$ is to eliminate HF, and it is HF causing the exothermal onset of the delithiated LMO in the electrolyte at 160 °C.

The exothermic reaction between delithiated LMO (4.3 V) and HF between 160 and 200 °C is self-accelerating. HF first promote the oxidation reaction between the reductant (the organic molecules of the electrolyte) and the superficial oxidant (delithiated LMO, MnO$_2$) by etching solid electrolyte interphase deposited at the surface of delithiated LMO, to release heat into the system. MnO$_2$ is reduced to Mn$_3$O$_4$ which deposits on the LMO surface and the organics are oxidized into water and CO$_2$. Meanwhile, the reaction between HF and MnO$_2$ also generates H$_2$O. HF then reacts with Mn$_3$O$_4$ cladded at the surface of delithiated LMO (MnO$_2$) to form MnF$_2$ (dissolved into the electrolyte) and water and expose fresh MnO$_2$ surface for further oxidation reaction with more heat generated sequentially; and the PF$_5$ generated by LiPF$_6$ decomposition will continue react with H$_2$O to produce more HF thus a self-accelerating reaction is triggered. Resultantly the thermal stability is declined after adding LiPF$_6$ into LMO+EC/DMC (1:1 wt %), and the key factor causing this results lies in the formation of HF. Seen from Figure 6, the blended materials (7–3, 1–1, and 3–7 with...
electrolyte coexisting systems present no exothermic reactions around 160–200 °C, which is attributed to H⁺/Li⁺ exchange between HF and LS23 that eliminate HF without water produced, reduce the HF content in electrolyte and furthermore avoid self-acceleration reactions caused by HF. The MnF₂ is generated from the reaction between the delithiated LMO and HF, which is proven by XRD results of the join of LS23 can significantly reduce the amount of Mn dissolved content, and Mn ions dissolved is related to the HF content in electrolyte, which further indicates that the LS23 can decrease HF content in the electrolyte.

To study the structural changes of the fully delithiated LMO at high temperatures, the delithiated LMO with the electrolyte or organic solvents were first heated to certain temperatures at closed state according to the DSC test methods, then naturally cooled down to room temperature. The delithiated LMO after heat treatment were took out from the sealed crucible in the glovebox and packaged with polyimide tape on glass slides to prevent contact with air and water during test. The XRD results of delithiated LMO at room temperature marking as RT, delithiated LMO at 200 °C denoting as 200 °C, and delithiated LMO with solvent coexisting system at 200 °C labeling as 200 °C + solvent are shown in Figure 7a. All XRD results show no obvious structural change and new phase formation, illustrating that the structures of LMO with and without solvent are stable at 200 °C, which is consistent with the DSC results (Figure 7a). Figure 12b presents XRD results of the fully delithiated LMO with the electrolyte at room-temperature, at 200 °C, and at 200 °C holding for 30 min; which are denoted as RT, 200 °C + electrolyte and 200 °C 30 min + electrolyte, respectively. New diffraction peaks were observed in 200 °C + electrolyte sample, indicating that the system is not stable after the addition of LiPF₆. While holding 200 °C for 30 min, the peaks of 200 °C 30 min + electrolyte samples at 26.0°, 41.2°, and 50.2° are more apparent, which is corresponding to MnF₂ (JCPDS No.01-070-2499). Lin also observed MnF₂ phase formation in studying lithium-rich cathode materials with the electrolyte at high temperature.

The generation of MnF₂ manifests the reduction of delithiated LMO (MnO₂), which is reduction products of MnO₂ oxidating electrolyte. MnF₂ may be generated by the reaction between HF and reduction product on the surface of delithiated LMO materials, that purify the delithiated LMO surface, making the electrolyte continue to be oxidated by internal delithiated LMO, which further proves that HF promote the decomposition of delithiated LMO with electrolyte.

The preservation of LMO structure in the blended cathode (take 1–1 as example) were verified by XRD shown in Figure 13 and ICP analysis (Table 2). The XRD patterns of the delithiated 1–1 samples soaked with the electrolyte at room-

Table 2. Concentration of Mn Ions in the Electrolyte after Storing the Electrodes (Charged to 4.3 V) in the Electrolyte at 80 °C for 24 h

<table>
<thead>
<tr>
<th>sample</th>
<th>Mn ion content (μL/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMO</td>
<td>66.9</td>
</tr>
<tr>
<td>1–1</td>
<td>25.4</td>
</tr>
</tbody>
</table>
temperature, 200 °C, and 200 °C holding for 30 min, which were labeled as RT, 200 °C + electrolyte, and 200 °C 30 min + electrolyte, respectively, showed no structural change after these treatments, thus the blended electrode materials have very good thermal stability at 200 °C and even at 200 °C holding for 30 min, which further proves that L523 stabilizes the LMO structure and inhibits the delithiated LMO to react with HF and organics at high temperature. The ICP results in Table 2 also showed that L523 can significantly reduce the amount of Mn dissolved into the electrolyte, which further indicates that L523 can efficiently scavenge HF generated from hydrolysis of LiPF₆ with water to prevent Mn ions from dissolution into the electrolyte, thus improving the structural stability and cycling performances of LMO/L523 blend cathodes. This is also the reason why the 1−1 and electrolyte coexistence system does not release heat around 150−220 °C as shown in Figure 6. It is worth mentioning that with the delithiated 1−1 electrolyte system, after holding at 200 °C for 30 min, the diffraction peaks of L523 and LMO show a little shift such as peaks around 58°~60° and peaks at 65°, but this does not affect the main body structure of the material and materials at this state is relative stable.

Compared with the thermal behaviors of the systems of LMO/Li₂CO₃/electrolyte (Figure 10a), L523/electrolyte (Figure 6), and LMO/L523/electrolyte (Figure 6), which are very similar and have no peaks at 160 °C, and the ex-XRD result (Figures 11 and 12), it is concluded that L523 plays similar rule as Li₂CO₃ to terminate LMO/HF reaction by scavenging HF as shown in Figure 14. The mechanism of L523 scavenging HF is the ion exchange reaction H⁺/Li⁺ between L523 and HF. The lithium ion in L523 exchange with proton in electrolyte to form LiF which is insoluble in electrolyte. Without HF present as catalyst, the oxidation of organics by delithiated LMO is kinetically impeded, thus initial exothermal onset of delithiated LMO at 160 °C is lifted, and the structure of LMO is preserved.

4. CONCLUSIONS

In summary, we developed a blend cathodes made of LMO and L523 with excellent electrochemical performance and safety performance. More importantly, we thoroughly investigated the thermal synergistic effect between L523 and LMO which enhances the thermal stability of the blend cathodes. We found out that HF is responsible for the low exothermal onset of the delithiated LMO at 160 °C. This exothermal onset can be efficiently eliminated if HF is removed from the system. L523 can act as an HF scavenger in the blend cathode through a Li⁺/H⁺ exchange reaction with HF to preserve LMO structural integrity and improve the electrochemical performances of the blend cathodes, and to avoid the self-acceleration response caused by HF. LMO, however, greatly lowers the heat quantity generated by the blend cathode at elevated temperatures compared to that by L523, and improves the cycle stability and rate performance. Thus, this thermal synergy between L523 and LMO is quite beneficial for high-capacity and high-rate capability lithium ion batteries. In this blended material, shortcomings of monomer are overcome, and comprehensive performance of materials are improved. Also, the cost of
Research Article

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Notes

The authors declare no competing financial interest.

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REFERENCES

(18) Jang, M.-W.; Jung, H.-G.; Scrosati, B.; Sun, Y.-K. Improved Co-substituted, Li[Ni1−xMnx]0.5Mn1.5O4 Lithium Battery Cathode Materials. J. Power Sources 2012, 220, 354–359.
(21) Chang, J.; Sun, S.; Zhang, J.; Song, X.; Xie, H.; Battaglia, V.; Wang, R. Li4PO4 Coated LiNi0.5Mn1.5O4: A Stable High-Voltage Cathode Material for Lithium-Ion Batteries. Chem. – Eur. J. 2014, 20, 7479–7485.
(26) Röder, P.; Baba, N.; Wiemhöfer, H.-D. A Detailed Thermal Study of a Li[Ni0.33Co0.33Mn0.33]O2/LiMn2O4-based Lithium Ion Cell by Accelerating Rate and Differential Scanning Calorimetry. J. Power Sources 2014, 248, 978–987.
(27) Zhou, F.; Zhao, X.; van Bommel, A.; Xia, X.; Dahn, J. R. Comparison of Li[Ni0.5Mn0.5]O2 Li[Ni1/3Mn1/3Co1/3]O2, LiNi0.5Mn1.5O4 and LiNi0.5Mn1.5O4 as High Voltage Positive Electrode Materials. J. Electrochem. Soc. 2011, 158, A187–A191.

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ACS Appl. Mater. Interfaces 2016, 8, 2014–20156
(32) Jung, H.-G.; Jang, M. W.; Hassoun, J.; Sun, Y.-K.; Scrosati, B. A High-rate Long-life Li$_4$Ti$_5$O$_12$/Li[$\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{1.45}$]O$_4$ Lithium-ion Battery. Nat. Commun. 2011, 2, 516–520.
(34) Numata, T.; Amemiya, C.; Kumeuchi, T.; Shirakata, M.; Yonezawa, M. Advantages of Blending LiNi$_{0.45}$Co$_{0.1}$O$_2$ into Li$_{1+x}$Mn$_{2-x}$O$_4$ Cathodes. J. Power Sources 2001, 97, 358–360.
(36) Tran, H. Y.; Täubert, C.; Fleischhammer, M.; Axmann, P.; Küppers, L.; Wohlfahrt-Mehrens, M. LiMn$_2$O$_4$ Spinel/LiNi$_{0.45}$Co$_{0.15}$Al$_{0.05}$O$_2$ Blends as Cathode Materials for Lithium-Ion Batteries. J. Electrochem. Soc. 2011, 158, A556–A561.
(37) Lin, C.-k.; Piao, Y.; Kan, Y.; Bareño, J.; Bloom, I.; Ren, Y.; Amine, K.; Chen, Z. Probing Thermally Induced Decomposition of Delithiated Li$_{1.2-x}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ by in Situ High-Energy X-ray Diffraction. ACS Appl. Mater. Interfaces 2014, 6, 12692–12697.
(38) Numata, T.; Amemiya, C.; Kumeuchi, T.; Shirakata, M.; Yonezawa, M. Advantages of Blending LiNi$_{0.45}$Co$_{0.1}$O$_2$ into Li$_{1+x}$Mn$_{2-x}$O$_4$ Cathodes. J. Power Sources 2001, 97–98, 358–360.