# Thermal Synergy Effect between LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> Enhances the Safety of Blended Cathode for Lithium Ion Batteries

Jing Wang,<sup>†</sup> Yangyang Yu,<sup>†</sup> Bing Li,<sup>‡</sup> Peng Zhang,<sup>‡</sup> Jianxin Huang,<sup>†</sup> Feng Wang,<sup>†,§</sup> Shiyong Zhao,<sup>§</sup> Chaolun Gan,<sup>§</sup> and Jinbao Zhao\*<sup>,†,‡</sup>

<sup>†</sup>State Key Lab of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Collaborative Innovation Center of Chemistry for Energy Materials, State-Province Joint Engineering Laboratory of Power Source Technology for New Energy Vehicle, Xiamen University, Xiamen, 361005 Fujian, China

<sup>‡</sup>College of Energy, Xiamen University, Xiamen, 361102 Fujian, China

<sup>§</sup>Zhangjiagang Guotai Huarong Chemical New Material Co., Ltd., Zhangjiagang 215634, Jiangsu, China

ABSTRACT: The layer-structured LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> (L523) with high specific capacity and the spinel  $LiMn_2O_4$ (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 L523 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 L523 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 L523 present, this reaction is eliminated because the H<sup>+</sup> from HF and Li<sup>+</sup> in L523 undergo exchange reaction to prevent further generation of HF. The presence of LMO, however, reduces the total heat generated by L523 reacting with the electrolyte at high temperature. This thermal synergy between LMO and L523 not only improves the thermal safety of the blended cathode but also preserves their structures for better electrochemical performance.

**KEYWORDS:** LiNi<sub>0.5</sub>Co<sub>0.2</sub> $Mn_{0.3}O_2$ , LiMn<sub>2</sub> $O_4$ , 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.<sup>1-6</sup> 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.<sup>7-9</sup> 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.<sup>10–12</sup> 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.<sup>7,13</sup> 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.<sup>14–16</sup>

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,<sup>17-19</sup> surface modification of cathode particles with lithium ion conducting oxides or phosphate materials,<sup>20–22</sup> and morphological control by synthesis design.<sup>23,24</sup> 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.<sup>25</sup> The top two candidate systems are the LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub> and  $LiMn_2O_4$  (LMO).<sup>9,26,27</sup> Thorough studies on the electrochemical and physiochemical properties of the intercalation

```
Received: June 10, 2016
Accepted: July 22, 2016
Published: July 22, 2016
```

Downloaded via XIAMEN UNIV on February 27, 2020 at 00:45:52 (UTC). See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

compounds used as LIB cathode materials revealed that the layer-structured transition metal oxides (especially solid state solution compounds  $\text{LiNi}_{x}\text{Co}_{y}\text{Mn}_{1-x-y}\text{O}_{2}$  and three-dimensional transition metal oxide spinel LiMn<sub>2</sub>O<sub>4</sub> are complementary to each other: rock salt layer-structured Li- $Ni_x Co_y Mn_{1-x-y} O_2$  exhibits high specific capacity, high cycling stability, but low rate capability and low thermal stability at delithiated stage and/or elevated temperature; LiMn<sub>2</sub>O<sub>4</sub> shows moderate specific capacity, high rate capability, and high thermal stability at the delithiated stage, but low structural stability.9 The low thermal stability of the cell with LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub> as cathode is due to its strong oxidation power at delithiated stage toward the organic electrolyte;<sup>28,29</sup> the low structural stability of LMO arises from the reaction between HF in the electrolyte and LMO accompanying with manganese dissolution.<sup>30</sup> Studies have shown that with the increasing nickel content in  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ , the capacity of material is improved. However, the capacity attenuation and resultant thermostability problems are as follows.<sup>31</sup>Among these materials, the cycle stability and capacity of Li-Ni<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> (L523) is acceptably expected to slightly lower thermostability. And another competitive LiMn<sub>2</sub>O<sub>4</sub> 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  $LiMn_2O_4$  as a blended cathode for lithium ion batteries, and results show that this composite material has good thermostability.<sup>27</sup> But the cause of this synergistic effect is still unclear.

In this work, we chose  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  (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<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> 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.**  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  (L523) was purchased from Ningbo Jinhe New Materials Co., Ltd.;  $\text{LiMn}_2\text{O}_4$  (LMO) was purchased from Qingdao LNCM Co., Ltd. The blended materials were obtained by ball milling method (FRITSCH-

Pulverisette 14) from a mixture of L523 and LMO. The mixture of the powders was milled for 20 min at 150 r per minute. L523 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  $\mu$ L 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.** The XRD data were collected on Rigaku miniflex 600 with Cu K $\alpha$  radiation operated at 40 kV and 15 mA scanning from 10° to 90° at 2° min<sup>-1</sup> with a step size of 0.02°. 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<sub>6</sub> 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 L523 (150 mAh· $g^{-1}$ ) and LMO (110 mAh $\cdot$ g<sup>-1</sup>) given by manufactures; while for the composite samples of 7-3, 1-1, and 3-7, the specific capacities were calculated based upon L523 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 $\cdot$ cm<sup>-2</sup>.

# 3. RESULTS AND DISCUSSION

**3.1. Structural Characterization and Electrochemical Performance.** The SEM images of L523 (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 L523 are sphere-like with sizes ranging from 5 to 15  $\mu$ m (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 L523 and LMO are uniformly distributed, as shown in Figure 1d–f, and it is difficult to distinguish between L523 and LMO. To further illustrate the distribution of LMO and L523, EDS spectra of samples were performed, as shown in Figure 2. It is seen that the Ni element distribution which is on behalf of L523 due to the inexistence of Ni in LMO is nearly partly overlapped with that of the left SEM

# **ACS Applied Materials & Interfaces**



Figure 1. SEM images of L523 (a, b), LMO (c), 7-3 (d), 1-1 (e), and 3-7 (f).



Figure 2. SEM plots and corresponding EDS area mappings of 7-3 (a, b), 1-1 (c, d), and 3-7 (e, f).

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 hexagonala-NaFeO<sub>2</sub> structure with a  $R\bar{3}m$  space group with no impurities present,<sup>29</sup> while LMO displays well-defined cubic spinel structures without impur-



Figure 3. XRD plot of samples.

ities.<sup>30</sup> 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  $\alpha$ -NaFeO<sub>2</sub> 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- $Ni_x Co_y Mn_{1-x-y} O_2$ <sup>32</sup> 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. Also 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, 3-7, and LMO are 151.5 mAh g<sup>-1</sup>, 138.2 mAh·g<sup>-1</sup>, 126.2 mAh·g<sup>-1</sup>, 116.1 mAh·g<sup>-1</sup>, and 105.9 mAh·g<sup>-1</sup>, 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 $\cdot$ g<sup>-1</sup>, respectively. After 100 cycles, the discharge capacities decrease gradually to 133.4, 127.3, 117.8, 111.0, and 101.3 mAh·g<sup>-1</sup>, 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 abovementioned 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,



Figure 4. First curves of samples at 0.5 C at 3.0-4.3 V: (a) charge curves and (b) discharge curves.



Figure 5. (a) Cycle performance of samples at 1 C at 3.0-4.3 V and (b) rate capacities of samples.

and 5 C are 147.6 mAh g<sup>-1</sup>, 139.1 mAh·g<sup>-1</sup>, 124.5 mAh g<sup>-1</sup>, and 118.6 mAh g<sup>-1</sup> respectively, and that of LMO are 102.1 mAh·g<sup>-1</sup>, 101.1 mAh·g<sup>-1</sup>, 98.9 mAh·g<sup>-1</sup>, and 95.3 mAh g<sup>-1</sup>, respectively. When the current values are returned back to 0.5 C, reversible discharge capacities of 146.9 and 100.4 mAh g<sup>-1</sup> for L523 and LMO are obtained, which are 97.0% and 98.3% of the initial discharge capacity at the same rate, respectively. The rate capability of L523 is much worse than that of LMO. The discharge capacity of L523 decreases quickly as charge/ discharge rate increases, while LMO shows very little decrease in discharge capacity. It is well documented that lithium ion transport in three-dimensional LMO is much faster than that in two-dimensional L523,<sup>6</sup> thus a much better rate capability for LMO is achieved. 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 intercalationdeintercalation 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<sub>6</sub>, EC/DMC) were investigated by DSC/TG analysis as shown in Figure 6. There are obvious differences among their thermal stabilities. The onset exothermal temperature 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<sup>-1</sup>. While for LMO, the onset



Figure 6. DSC curves of deintercalated samples (4.3 V) with electrolyte.

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  $J \cdot g^{-1}$ , 374  $J \cdot g^{-1}$ lower than that of L523. Moreover, the maximum heat flow of LMO is only 2.4  $W \cdot g^{-1}$ , far lower than 9.8  $W \cdot g^{-1}$  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

electrolyte + samples	onset temp. (°C)	peak temp. (°C)	maximal heat flow $(J \cdot g^{-1})$	reaction heat $(J \cdot g^{-1})$	ca

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

electrolyte + samples	onset temp. (°C)	peak temp. (°C)	maximal heat flow $(J \cdot g^{-1})$	reaction heat $(J \cdot g^{-1})$	calculated value $(J \cdot g^{-1})$
L523	211.4	279.5; 299.5	9.8	1531	1531
7-3	206.8	259.3; 294.1	4.0	1335	1419
1-1	204.7	259.8; 293.6	3.1	1180	1344
3-7	204.0	258.4; 288.1	2.9	1150	1269
LMO	163.1	187.6; 222.0; 236.7; 268.6	2.4	1157	1157



Figure 7. (a) DSC curves of 1 M LiPF<sub>6</sub>/ EC+DMC(1:1 wt %), and deintercalated LMO (4.3 V) with the presence of 2 M LiPF<sub>6</sub>/ EC+DMC (1:1 wt %), 1 M LiPF<sub>6</sub>/ 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 %).

electrolyte around 160-200 °C, disappearing somehow completely in the blend materials. Compared to L523, another interesting phenomenon is also observed that the total heat quantity of each blend sample is largely reduced with increasing LMO quality. The observed heat quantity of the blend samples are even smaller than the calculated values based upon simple percentage addition as shown in Table 1. The heat quantity overall is in the order of L523 < 7-3 < LMO < 1-1, 3-7 at 4.3 V charged state (Table 1). The reducing trend of heat quantity from L523 to 1-1 is distinct, while for 1-1 to 3-7, that almost has no changes. This illustrates that when the LMO addition amount is 50%, it can significantly enough reduce the heat quantity of the L523-LMO system and improve the thermal stability of electrode materials.

DSC results suggest that heat quantities of blended samples are not the simple sum of L523 and LMO monomer, and there are synergy effects between L523 and LMO, so high initial exothermic temperature, low heat quantity, and low heat flow are obtained in the blended samples. This illustrates that LMO addition can significantly enough reduce the heat quantity of L523/LMO system and improve the thermal stability of electrode materials. Considering the thermal stability and electrochemical properties of the material, 1-1 has a relatively better performance than others.

In order to understand how L523 eliminates the exothermic peak of LMO around 160–200  $^\circ\text{C},$  we must figure out what reaction is responsible for this exothermal 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  $LiPF_{6}$  salt), and delithiated LMO electrode in electrolytes with different LiPF<sub>6</sub> concentrations as shown in Figure 7a. The pure electrolyte does not show any exothermal 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<sup>-1</sup>. 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:

$$Mn_2O_4 + 2/5C_3H_4O_3 \rightarrow 2MnO + 6/5CO_2 + 4/5H_2O$$
(1)

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 LiPF<sub>6</sub> 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 position 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 LiPF<sub>6</sub> EC/DMC) case, the heat flow emerges between 160 and 200  $^\circ C$  and the total heat quantity is 1157  $J \cdot g^{-1}$ . When the concentration of LiPF<sub>6</sub> 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  $J \cdot g^{-1}$ . This may be because that the exothermic reaction between 160 and 200  $^\circ C$  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 LiPF<sub>6</sub>, and with the increase of LiPF<sub>6</sub> concentration, the thermal stability of the system worsens. To further consolidate our conclusion that the exothermic onset around 160–200  $^\circ \mathrm{C}$  of the delithiated LMO (4.3 V) in the electrolyte is caused by the LiPF<sub>6</sub>, 1.0 M LiTFSI/ EC + DMC (1:1, wt %) was prepared as electrolyte instead, and the DSC curve of delithiated LMO/(1 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  $\text{LiPF}_6$  electrolyte is caused by the presence of  $\text{LiPF}_6$ .



Figure 8. (a) DSC curve of LiPF<sub>6</sub> in hermetically sealed system, (b) TG-DC curves of LiPF<sub>6</sub> in open system.

The above results show that the exothermic peak of delithiated LMO-electrolyte around 160–200 °C in Figure 7a is associated with LiPF<sub>6</sub>, so thermal stability of LiPF<sub>6</sub> is investigated in a closed system without mass loss during the test process, shown in Figure 8a. Before 160 °C, LiPF<sub>6</sub> does not have apparent thermal behavior; to 165 °C, the LiPF<sub>6</sub> 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<sup>33</sup> that the phase transition of LiPF<sub>6</sub> occurs around 200 °C, so peak at 197 °C in Figure 8a is aroused by the phase transition of LiPF<sub>6</sub>. With the increase of temperature, LiPF<sub>6</sub> continues to show significant endothermic behavior, the endothermic peak at 357 °C is primarily caused by LiPF<sub>6</sub> decomposition as follows:

$$\text{LiPF}_6 \to \text{LiF} + \text{PF}_5(g) \tag{2}$$

Seen from Figure 8b of LiPF<sub>6</sub> TG-DSC curve in a open system, LiPF<sub>6</sub> at about 150 °C has already begun to decompose with quality reduced and PF<sub>5</sub> generated, electrolyte containing trace amounts of water, and PF<sub>5</sub> 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<sub>6</sub> such as PF<sub>5</sub>, LiF, and HF. The LiF is electrochemically inert, so it is possible that PF<sub>5</sub> or HF participates in the reaction between delithiated LMO and electrolyte.

In order to clarify the interaction between delithiated LMO and bare LiPF<sub>6</sub> salt, the thermal behavior of the delithiated LMO with pure LiPF<sub>6</sub> salt was carried out as shown in Figure 9. It only shows a little endothermal peak at 200 °C, which is attributed to the phase transition of LiPF<sub>6</sub>;<sup>33</sup> and a big endothermal peak at 300 °C, which is related to the mutual effect between LMO and PF<sub>5</sub>. This is consisted with the



**Figure 9.** DSC curves of deintercalated LMO (4.3 V) with  $\text{LiPF}_6$  system.

thermal decomposition of LiPF<sub>6</sub> (shown in Figure 8). On the basis of these data, it can be concluded that the reactions between LMO and PF<sub>5</sub> occur at higher temperature (300 °C), thus the exothermal onset at 160 °C must be from some mysterious compounds other than PF<sub>5</sub>, EC, and DMC.

It is well understood that LiPF<sub>6</sub> 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 exothermal onset at 160  $^\circ$ C. To verify this hypothesis, we use Li2CO3 as HF scavenger substituting for L523. The DSC curve of the mixture consisting of delithiated LMO, Li<sub>2</sub>CO<sub>3</sub> and electrolyte with a ratio of 1 mg: 1 mg: 2  $\mu$ L 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<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub>CO<sub>3</sub>. The Li<sub>2</sub>CO<sub>3</sub> + 1 M LiPF<sub>6</sub> EC/DMC also appear an exothermic peak around 130 °C, while for  $Li_2CO_3 + EC/DMC$ , this peak disappears. The only difference between electrolyte and solvent is the existence of LiPF<sub>6</sub> 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<sub>2</sub>CO<sub>3</sub>, and Li<sub>2</sub>CO<sub>3</sub> is good HF-eliminated additives commonly used in lithium ion batteries. This experiment clearly demonstrates that the effect of Li<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub> is reduced to Mn<sub>3</sub>O<sub>4</sub> which deposits on the LMO surface and the organics are oxidized into water and CO2. Meanwhile, the reaction between HF and MnO<sub>2</sub> also generates H<sub>2</sub>O. HF then reacts with Mn<sub>3</sub>O<sub>4</sub> cladded at the surface of delithiated LMO (MnO<sub>2</sub>) to form MnF<sub>2</sub> (dissolved into the electrolyte) and water and expose fresh MnO<sub>2</sub> surface for further oxidation reaction with more heat generated sequentially; and the PF<sub>5</sub> generated by LiPF<sub>6</sub> decomposition will continue react with H2O to produce more HF thus a self-accelerating reaction is triggered. Resultantly the thermal stability is declined after adding LiPF<sub>6</sub> 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



Figure 10. (a) DSC curve of deintercalated LMO (4.3 V) with  $Li_2CO_3$  and electrolyte (1 M LiPF<sub>6</sub>/ EC+DMC(1:1 wt %) and (b) DSC curves of  $Li_2CO_3$  with electrolyte (1 M LiPF<sub>6</sub>/ EC+DMC (1:1 wt %)) or solvent (EC+DMC (1:1 wt %)).

electrolyte coexisting systems present no exothermic reactions around 160–200 °C, which is attributed to H<sup>+</sup>/ Li<sup>+</sup> exchange<sup>34</sup> between HF and L523 that eliminate HF without water produced, reduce the HF content in electrolyte and furthermore avoid self-acceleration reactions caused by HF. The MnF<sub>2</sub> is generated from the reaction between the delithiated LMO and HF, which is proven by XRD results of resulted LMO structural change shown below.

The DSC curve of the mixture contained the delithiated L523,  $Li_2CO_3$ , and electrolyte with a ratio of 1 mg: 1 mg: 2  $\mu$ L coexisting system (L523 +  $Li_2CO_3$  + 1 M LiPF<sub>6</sub> EC/DMC) is displayed in Figure 11. The coexistence system does not appear



Figure 11. DSC curve of deintercalated L523 (4.3 V) with  $\rm Li_2CO_3$  and electrolyte.

exothermic reaction around 100–150 °C, illustrating that the HF content of this system is very low, so the reaction between HF and  $Li_2CO_3$  is very weak. This further indicates that L523 can greatly reduce the HF content in the electrolyte, which proved the accuracy of the above assumptions.

Table 2 shows the concentration of Mn cations of LMO and 1-1 samples dissolved in the electrolyte. The cell was charged to fully delithiated state at 0.2 C, disassembled in an Ar-filled glovebox. The cathode film was soaked in the electrolyte with a ratio of electrode materials to electrolyte was 2 mg to 1 mL electrolyte at 80 °C for 1 day. After acid-treating to remove the

Table 2. Concentration of Mn Ions in the Electrolyte after Storing the Electrodes (Charged to 4.3 V) in the Electrolyte at 80  $^{\circ}$ C for 24 h

sample	Mn ion content $(\mu L \cdot m L^{-1})$
LMO	66.9
1-1	25.4

organics, the storage electrolyte was carried out for metal ion test by ICP instrument. The Mn concentration of delithiated LMO in electrolyte is very high, a clear indication of the delithiated LMO being dissolved into the electrolyte solution. The join of L523 can significantly reduce the amount of Mn dissolved content, and Mn ions dissolved is related to the HF content in electrolyte,<sup>35,36</sup> which further indicates that the L523 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 12a. 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  $^{\circ}$ 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 LiPF<sub>6</sub>. 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 MnF<sub>2</sub> (JCPDS No.01-070-2499). Lin<sup>37</sup> also observed MnF<sub>2</sub> phase formation in studying lithium-rich cathode materials with the electrolyte at high temperature.

The generation of  $MnF_2$  manifests the reduction of delithiated LMO ( $MnO_2$ ), which is reduction products of  $MnO_2$  oxidating electrolyte.  $MnF_2$  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 delibilitated 1-1 samples soaked with the electrolyte at room-



Figure 12. (a) Ex situ XRD results of deintercalated LMO (charged to 4.3 V) at room temperature, deintercalated LMO (charged to 4.3 V) at 200  $^{\circ}$ C, and deintercalated LMO (charged to 4.3 V) with solvent at 200  $^{\circ}$ C and (b) ex situ XRD results of deintercalated LMO (charged to 4.3 V) and deintercalated LMO (charged to 4.3 V) with electrolyte at 200  $^{\circ}$ C or at 200  $^{\circ}$ C holding for 30 min.



**Figure 13.** Ex situ XRD pattern of deintercalated 1-1 sample (charged to 4.3 V) and deintercalated 1-1 sample (charged to 4.3 V) with electrolyte at 200 °C or at 200 °C holding for 30 min.

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 scanvenge HF generated from hydrolysis of LiPF<sub>6</sub> 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  $58^{\circ} \sim 60^{\circ}$  and peaks at  $65^{\circ}$ , 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  $LMO/Li_2CO_3$ /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  $Li_2CO_3$  to terminate LMO/HF reaction by scavenging HF as shown in Figure 14. The mechanism of L523 scavenging HF is



Figure 14. Schematic illustrations of the LS23 effects as a HF scavenging agent by ion exchange reaction  $H^+/Li^+$  between LS23 and HF.

the ion exchange reaction  $H^+/Li^+$  between L523 and HF.<sup>38</sup> 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  $\mathrm{Li^+/}$ H<sup>+</sup> 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

# **ACS Applied Materials & Interfaces**

cathode materials is lowered. The high capacity, excellent rate capability, remarkable heat stability, and low cost are obtained by the L523/LMO blend material, making it a promising cathode material for lithium ion batteries.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: jbzhao@xmu.edu.cn (J.Z.).

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (21321062). The authors also wish to express their thanks to Dr. Dong Sun for his valuable suggestion.

#### REFERENCES

(1) Yang, Y.; Chen, D.; Liu, B.; Zhao, J. Binder-Free Si Nanoparticle Electrode with 3D Porous Structure Prepared by Electrophoretic Deposition for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2015**, *7*, 7497–7504.

(2) Elia, G. A.; Wang, J.; Bresser, D.; Li, J.; Scrosati, B.; Passerini, S.; Hassoun, J. A New, High Energy Sn $-C/\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.4/3}\text{Co}_{0.4/3}\text{Mn}_{1.6/3}]$ -O<sub>2</sub> Lithium-Ion Battery. *ACS Appl. Mater. Interfaces* **2014**, *6*, 12956–12961.

(3) Park, S.-H.; Kim, H. J.; Lee, J.; Jeong, Y. K.; Choi, J. W.; Lee, H. Mussel-Inspired Polydopamine Coating for Enhanced Thermal Stability and Rate Performance of Graphite Anodes in Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 13973–13981.

(4) Jaber-Ansari, L.; Puntambekar, K. P.; Kim, S.; Aykol, M.; Luo, L.; Wu, J.; Myers, B. D.; Iddir, H.; Russell, J. T.; Saldaña, S. J.; Kumar, R.; Thackeray, M. M.; Curtiss, L. A.; Dravid, V. P.; Wolverton, C.; Hersam, M. C. Suppressing Manganese Dissolution from Lithium Manganese Oxide Spinel Cathodes with Single-Layer Graphene. *Adv. Energy Mater.* **2015**, *5*, 1500646–1500655.

(5) Liu, W.; Oh, P.; Liu, X.; Lee, M.-J.; Cho, W.; Chae, S.; Kim, Y.; Cho, J. Nickel-Rich Layered Lithium Transition-Metal Oxide for High-Energy Lithium-Ion Batteries. *Angew. Chem., Int. Ed.* **2015**, *54*, 4440–4457.

(6) Xu, X.; Lee, S.; Jeong, S.; Kim, Y.; Cho, J. Recent Progress on Nanostructured 4 V Cathode Materials for Li-ion Batteries for Mobile Electronics. *Mater. Today* **2013**, *16*, 487–495.

(7) Chen, Z.; Ren, Y.; Lee, E.; Johnson, C.; Qin, Y.; Amine, K. Study of Thermal Decomposition of  $\text{Li}_{1-x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{0.9}\text{O}_2$  Using In-Situ High-Energy X-Ray Diffraction. *Adv. Energy Mater.* **2013**, *3*, 729–736.

(8) Tran, H. Y.; Täubert, C.; Fleischhammer, M.; Axmann, P.; Küppers, L.; Wohlfahrt-Mehrens, M. Li $Mn_2O_4$  Spinel/Li-Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> Blends as Cathode Materials for Lithium-Ion Batteries. J. Electrochem. Soc. **2011**, 158, A556–A561.

(9) Smith, A. J.; Smith, S. R.; Byrne, T.; Burns, J. C.; Dahn, J. R. Synergies in Blended  $LiMn_2O_4$  and  $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$  Positive Electrodes. J. Electrochem. Soc. **2012**, 159, A1696–A1701.

(10) Campion, C. L.; Li, W.; Euler, W. B.; Lucht, B. L.; Ravdel, B.; DiCarlo, J. F.; Gitzendanner, R.; Abraham, K. M. Suppression of Toxic Compounds Produced in the Decomposition of Lithium-Ion Battery Electrolytes. *Electrochem. Solid-State Lett.* **2004**, *7*, A194–A197.

(11) Campion, C. L.; Li, W.; Lucht, B. L. Thermal Decomposition of LiPF<sub>6</sub>-Based Electrolytes for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2005**, *152*, A2327–A2334.

(12) Hammami, A.; Raymond, N.; Armand, M. Lithium-ion batteries: Runaway Risk of Forming Toxic Compounds. *Nature* **2003**, *424*, 635–636.

(13) Maleki, H.; Deng, G.; Kerzhner-Haller, I.; Anani, A.; Howard, J. N. Thermal Stability Studies of Binder Materials in Anodes for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2000**, *147*, 4470–4475.

Research Article

401–414. (15) Wang, Q.; Ping, P.; Zhao, X.; Chu, G.; Sun, J.; Chen, C. Thermal Runaway Caused Fire and Explosion of Lithium Ion Battery. *J. Power Sources* 2012, 208, 210–224.

(16) Kumaresan, K.; Sikha, G.; White, R. E. Thermal Model for a Li-Ion Cell. J. Electrochem. Soc. 2008, 155, A164–A171.

(17) Kiziltas-Yavuz, N.; Bhaskar, A.; Dixon, D.; Yavuz, M.; Nikolowski, K.; Lu, L.; Eichel, R.-A.; Ehrenberg, H. Improving the Rate Capability of High Voltage Lithium-ion Battery Cathode Material  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  by Ruthenium Doping. *J. Power Sources* **2014**, 267, 533–541.

(18) Jang, M.-W.; Jung, H.-G.; Scrosati, B.; Sun, Y.-K. Improved Cosubstituted,  $LiNi_{0.5-x}Co_{2x}Mn_{1.5-x}O_4$  Lithium Ion Battery Cathode Materials. J. Power Sources **2012**, 220, 354–359.

(19) Li, X.; Peng, H.; Wang, M.-S.; Zhao, X.; Huang, P.-X.; Yang, W.; Xu, J.; Wang, Z.-Q.; Qu, M.-Z.; Yu, Z.-L. Enhanced Electrochemical Performance of Zr-Modified Layered LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> Cathode Material for Lithium-Ion Batteries. *ChemElectroChem* **2016**, *3*, 130– 137.

(20) Lu, J.; Peng, Q.; Wang, W.; Nan, C.; Li, L.; Li, Y. Nanoscale Coating of  $LiMO_2$  (M = Ni, Co, Mn) Nanobelts with  $Li^+$ -Conductive  $Li_2TiO_3$ : Toward Better Rate Capabilities for Li-Ion Batteries. *J. Am. Chem. Soc.* **2013**, *135*, 1649–1652.

(21) Zhang, Z.-J.; Chou, S.-L.; Gu, Q.-F.; Liu, H.-K.; Li, H.-J.; Ozawa, K.; Wang, J.-Z. Enhancing the High Rate Capability and Cycling Stability of LiMn<sub>2</sub>O<sub>4</sub> by Coating of Solid-State Electrolyte LiNbO<sub>3</sub>. ACS Appl. Mater. Interfaces **2014**, *6*, 22155–22165.

(22) Chong, J.; Xun, S.; Zhang, J.; Song, X.; Xie, H.; Battaglia, V.; Wang, R. Li<sub>3</sub>PO<sub>4</sub>-Coated LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>: A Stable High-Voltage Cathode Material for Lithium-Ion Batteries. *Chem. - Eur. J.* **2014**, *20*, 7479–7485.

(23) Ryu, W.-H.; Lim, S.-J.; Kim, W.-K.; Kwon, H. 3-D Dumbbelllike LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> Cathode Materials Assembled with Nanobuilding Blocks for Lithium-ion Batteries. *J. Power Sources* **2014**, 257, 186–191.

(24) Lu, Z.; Rui, X.; Tan, H.; Zhang, W.; Hng, H. H.; Yan, Q. Synthesis of Single-Crystalline  $LiMn_2O_4$  and  $LiMn_{1.5}Ni_{0.5}O_4$  Nanocrystals and Their Lithium Storage Properties. *ChemPlusChem* **2013**, 78, 218–221.

(25) Park, O. K.; Cho, Y.; Lee, S.; Yoo, H. C.; Song, H. K.; Cho, J. Who will Drive Electric Vehicles, Olivine or Spinel? *Energy Environ. Sci.* **2011**, *4*, 1621–1633.

(26) Röder, P.; Stiaszny, B.; Ziegler, J. C.; Baba, N.; Lagaly, P.; Wiemhöfer, H.-D. The Impact of Calendar Aging on the Thermal Stability of a LiMn<sub>2</sub>O<sub>4</sub>-Li(Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>)O<sub>2</sub>/graphite Lithium-ion cell. J. Power Sources **2014**, 268, 315–325.

(27) Röder, P.; Baba, N.; Wiemhöfer, H. D. A Detailed Thermal Study of a Li $[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2/LiMn_2O_4$ -based Lithium Ion Cell by Accelerating Rate and Differential Scanning Calorimetry. *J. Power Sources* **2014**, *248*, 978–987.

(28) Zhou, F.; Zhao, X.; van Bommel, A.; Xia, X.; Dahn, J. R. Comparison of Li [ $Li_{1/9}Ni_{1/3}Mn_{5/9}$ ] O<sub>2</sub>, Li [ $Li_{1/5}Ni_{1/5}Mn_{3/5}$ ] O<sub>2</sub>, LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and LiNi<sub>2/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> as High Voltage Positive Electrode Materials. *J. Electrochem. Soc.* **2011**, *158*, A187–A191.

(29) Wang, J.; Yu, Y.; Li, B.; Fu, T.; Xie, D.; Cai, J.; Zhao, J. Improving the Electrochemical Properties of  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  at 4.6 V Cutoff Potential by Surface Coating with  $\text{Li}_2\text{TiO}_3$  for Lithiumion Batteries. *Phys. Chem. Chem. Phys.* **2015**, *17*, 32033–32043.

(30) Lee, M.-J.; Lee, S.; Oh, P.; Kim, Y.; Cho, J. High Performance LiMn<sub>2</sub>O<sub>4</sub> Cathode Materials Grown with Epitaxial Layered Nanostructure for Li-Ion Batteries. *Nano Lett.* **2014**, *14*, 993–999.

(31) Jung, S.-K.; Gwon, H.; Hong, J.; Park, K.-Y.; Seo, D.-H.; Kim, H.; Hyun, J.; Yang, W.; Kang, K. Understanding the Degradation Mechanisms of  $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$  Cathode Material in Lithium Ion Batteries. *Adv. Energy Mater.* **2014**, *4*, 1300787–1300794.

# **ACS Applied Materials & Interfaces**

(32) Jung, H.-G.; Jang, M. W.; Hassoun, J.; Sun, Y.-K.; Scrosati, B. A High-rate Long-life  $Li_4Ti_5O_{12}/Li[Ni_{0.45}Co_{0.1}Mn_{1.45}]O_4$  Lithium-ion Battery. *Nat. Commun.* **2011**, *2*, 516–520.

(33) Jiang, X.; Zuo, X.; Cai, F.; Yang, H. Decomposition Kinetics Research of LiPF<sub>6</sub> at Elevated Temperature. *Chin. J. Power Scource* **2012**, *36*, 467–469.

(34) Numata, T.; Amemiya, C.; Kumeuchi, T.; Shirakata, M.; Yonezawa, M. Advantages of Blending  $LiNi_{0.8}Co_{0.2}O_2$  into  $Li_{1+x}Mn_{2-x}O_4$  Cathodes. *J. Power Sources* **2001**, *97*, 358–360.

(35) Hunter, J. C. Preparation of a New Crystal Form of Manganese Dioxide:  $\lambda$ -MnO<sub>2</sub>. J. Solid State Chem. **1981**, 39, 142–147.

(36) Tran, H. Y.; Täubert, C.; Fleischhammer, M.; Axmann, P.; Küppers, L.; Wohlfahrt-Mehrens, M. Li $Mn_2O_4$  Spinel/Li-Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> 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  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  into  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  Cathodes. J. Power Sources 2001, 97–98, 358–360.