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Fluorinated phosphazene derivative - A promising electrolyte additive for high voltage lithium ion batteries: From electrochemical performance to corrosion mechanism

Abstract

The development of novel electrolytes for next-generation high voltage lithium ion battery is of primary importance. In this work, a fluorinated phosphazene derivative, ethoxy-(pentafluoro)-cyclotriphosphazene (PFN), is proposed as a novel electrolyte additive for improving the electrochemical performance and safety of lithium nickel manganese oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) cathode. With the addition of PFN, the electrolyte can be preferentially oxidized and decomposed, thus producing some linear polymers, multi-ring polymers, LiNO_3 , RONO_2Li (RONO_2 : nitrate ester functional group, with R standing for any organic residue), Li_3PO_4 , and ROPO_3Li (ROPO_3 : monoester phosphate) simultaneously. These as-generated materials form a dense, uniform, and thin protective layer on the surface of the cathode material, which suppresses the decomposition of electrolyte and electrode corrosion, correspondingly protecting the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ from structural destruction. Due to the coverage by the protective film and corrosion suppression, charge and discharge tests demonstrate that PFN is effective for improving the cycling stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The discharge capacity of a battery with 5 wt% PFN is 124.4 mAh g^{-1} and 99.8 mAh g^{-1} after 100 cycles at the current rates of 0.2 C and 1 C, respectively, which is much better than the performance without PFN. Meanwhile, because of the combined structure of the nonflammable cyclophosphazene and fluorine, the PFN creates a highly synergistic flame retardant effect, and a low content of PFN can almost completely extinguish burning electrolyte, leading to excellent safety performance for the lithium ion battery.

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Fluorinated Phosphazene Derivative – a Promising Electrolyte Additive for High Voltage Lithium Ion Batteries: From Electrochemical Performance to Corrosion Mechanism

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Abstract: Development of novel electrolytes for next-generation high voltage lithium ion batteries is of primary importance. In this work, a fluorinated phosphazene derivative ethoxy-(pentafluoro)-cyclotriphosphazene (PFN) is proposed as a novel electrolyte additive for improving the electrochemical performance and safety of lithium nickel manganese oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) cathode. With the addition of PFN, the electrolyte can be more preferentially oxidized and decomposed, thus producing some linear polymers, multi-ring polymers, LiNO_3 , RONO_2Li (RONO_2 : nitrate ester functional group, with R standing for any organic residue), Li_3PO_4 , and ROPO_3Li (ROPO_3 : monoester phosphate) simultaneously. These as-generated materials form a dense, uniform and thin protective layer on the surface of the cathode material, which suppresses the decomposition of electrolyte and electrode corrosion, correspondingly protecting the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ from structural destruction. Due to the coverage of protective film and corrosion suppression, charge and discharge tests demonstrate that PFN is effective for improving the cycling stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The discharge capacity of a battery with 5 wt% PFN is $124.4 \text{ mAh}\cdot\text{g}^{-1}$ and $99.8 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles at the current rates of 0.2 C and 1 C, respectively, which are much better than the performance without PFN. Meanwhile, because of the combined structure of the nonflammable cyclophosphazene and fluorine, the PFN creates a highly synergistic flame retardant effect, and a low content of PFN can almost completely extinguish burning electrolyte, exhibiting excellent safety performance for the lithium ion battery.

Keywords: Electrolyte additive; Fluorinated phosphazene derivative; High voltage

lithium ion battery; High safety lithium ion battery; lithium nickel manganese oxide cathode.

1. Introduction

In recent years, the potential application of lithium ion batteries in electric vehicles (EVs), hybrid EVs (HEVs), and energy storage systems (ESSs) has been widely studied, which has led to higher requirements for lithium ion battery energy density [1-6]. In order to improve the energy density of the lithium ion battery, many studies have proposed high voltage cathode materials, such as LiCoPO_4 , LiCoMnO_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, etc [7-10]. Unfortunately, the oxidative decomposition of the conventional carbonate-based electrolytes (> 4.5 V, vs. Li^+/Li) and the dissolution of the electrode materials have limited their application in commercial high voltage lithium ion batteries. In short, the electrochemical instability of the common organic carbonate solutions has seriously affected the development of high voltage lithium ion batteries [11,12]. Therefore, it is an urgent necessity to develop electrolytes suitable for the high voltage lithium ion battery.

As is well known, a stable solid-electrolyte interphase (SEI) membrane on the anode materials can effectively inhibit the decomposition of electrolyte and improve its electrochemical stability. Some additives, such as vinylene carbonate and ethylene sulfite, can improve the stability of the SEI film, thus suppressing the interface reactions between the anode materials and the electrolyte [13-17]. Similarly, in order to suppress the interface reactions of the cathode materials and the electrolyte, if the

cathode surface can be wrapped in a layer of stable interface membrane, the stability of the electrolyte can be greatly improved in high voltage batteries. In this respect, using different additives in the electrolyte would be one of the most effective and economic methods for solving this problem.

Li et al. have reported terthiophene (3THP) and 4-(trifluoromethyl)-benzonitrile (4-TB) used as novel electrolyte additives for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode in a high voltage lithium ion battery. Charge and discharge tests showed that the cycling stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was significantly improved by using 0.25 wt% 3THP and 0.5 wt% 4-TB as electrolyte additives [18]. Song et al. and Han et al. have proposed tris-(trimethylsilyl)-phosphite (TMSPi) as an effective electrolyte additive to improve the cycling stability and rate capability for high voltage cathode materials ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Mn}_{0.5}\text{Co}_{0.17}\text{O}_2$), mainly due to a relatively high HF scavenging ability that is found among the various phosphite-based compounds [19,20]. Sun et al. have developed lithium bis(2-methyl-2-fluoromalonato)borate (LiBMFMB) as a novel electrolyte salt additive for lithium-ion batteries with voltages greater than 4.7 V. LiBMFMB as an additive for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery exhibits improved efficiency and cycling stability [21]. Zhang et al. have used fluoroethylene carbonate/fluorinated diethyl carbonate (FEC/HFDEC) as electrolyte co-solvent for a high voltage $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ /graphite cell cycled at 4.6 V. Their reported fluorinated co-solvent led to much improved coulombic efficiency and capacity retention when a higher cut-off voltage (4.6 V) was applied [22]. Additionally, many studies have reported that lithium bis(oxalato)borate (LiBOB) additive effectively

improved the performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ half-cells [23,24]. Y. M. Lee et al. found that dopamine in a conventional $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{DMC}$ (EC: ethylene carbonate, DEC: diethyl carbonate, DMC: dimethyl carbonate) electrolyte could act as a novel effective electrolyte additive for high voltage lithium ion batteries at high temperature [25].

Safety is the major concern, however, when using high voltage lithium ion batteries for large-scale application. The flame retardancy of electrolyte is the key problem to be solved [26-28]. Recently Yamada et al. designed a novel electrolyte by mixing a stable lithium salt $\text{LiN}(\text{SO}_2\text{F})_2$ with dimethyl carbonate solvent at extremely high concentrations, which can effectively inhibit the dissolution of both aluminum and transition metals at around 5 V, thus realizing a high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{graphite}$ battery that exhibited excellent cycling stability and enhanced safety [29]. Cao et al. prepared a phosphazenic compound (PNP) by a facile method and characterized it as a flame-retarding electrolyte additive for the lithium ion battery. The half-cells in 10% PNP electrolyte exhibited better capacity, coulombic efficiency, and cycling stability compared to the base electrolyte [30]. Rollins et al. have also proposed unsaturated phosphazenes as co-solvents for improved thermal stability and safety in lithium-ion battery electrolytes [31].

In this work, fluorinated phosphazene derivative is proposed for high voltage lithium ion batteries as a novel type of additive. We have reported a new additive, ethoxy-(pentafluoro)-cyclotriphosphazene ($\text{N}_3\text{P}_3\text{F}_5\text{OCH}_2\text{CH}_3$, PFN), which combines the structure of the nonflammable cyclophosphazene with fluorine to create a highly

synergistic flame retardant effect and good electrochemical compatibility [32-35]. We found that a low content of PFN could extinguish burning electrolyte. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM, before discharge and after discharge with PFN) of high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode were conducted. We found that an amorphous layer was formed on the cathode surface after cycling with PFN. Tests of the electrochemical stability window (ESW) and cycling behavior, and electrochemical impedance spectroscopy (EIS) were conducted with or without PFN. All results, especially for the cycling performance with PFN were much better than that without PFN, and the discharge capacity of the battery with 5 wt% PFN was $124.4 \text{ mAh}\cdot\text{g}^{-1}$ and $99.8 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles at the current rates of 0.2 C and 1 C, respectively.

2. Experimental Section

2.1. Sample preparation

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were synthesized by the co-precipitation method combined with solid phase sintering. $\text{Ni}(\text{Ac})_2\cdot 6\text{H}_2\text{O}$ and MnSO_4 solution were firstly stirred at room temperature and co-precipitated by using a precipitating agent, $\text{NH}_3\cdot\text{H}_2\text{O}$, at pH = 8.0 for 8 h, and then the precursor was calcined with Li_2CO_3 at $600\text{ }^\circ\text{C}$ for 6 h. 1.0 M lithium hexafluorophosphate (LiPF_6) in EC+DEC+DMC (1:1:1 v/v/v) was provided by Hubei Nuobang Technology Co., Ltd of China and used as the standard electrolyte. The novel electrolyte additive, ethoxy-(pentafluoro)-cyclotriphosphazene ($\text{N}_3\text{P}_3\text{F}_5\text{OCH}_2\text{CH}_3$, PFN), was also provided by Hubei Nuobang Technology Co., Ltd

of China. The Fourier transform infrared (FT-IR) spectrum of PFN displays the main peaks at 2918 cm^{-1} from C-H, 1292 cm^{-1} from P-N, 1077 cm^{-1} from P=N and 957 cm^{-1} from P-F respectively, as shown in the Fig. S1 in the Supporting Information. From nuclear magnetic resonance (NMR) spectrum shown in the Fig. S2 in the Supporting Information, the presence of the peaks at 4.27-4.23 ppm (-CH₂- from PFN), 1.41-1.38 ppm (-CH₃ from PFN) in the ¹H spectrum belong to the saturated hydrogen of the ethyl group. In the ¹³C NMR spectrum, the peaks at 65.95 ppm and 15.46 ppm also belong to ethyl group from PFN. Meanwhile the peaks at 15.27-15.02 ppm, 9.90 ppm and 4.15-4.06 ppm in the ³¹P NMR spectrum represent three different groups respectively, i.e. -PO-, -PF- and -POF-. The mass spectrometry (MS) result shown in the Fig. S1 in the Supporting Information suggests a molecule (M) with the main ion scrap peak at $m/z=248$ and $m/z=230$, the assignment of which is based on the detection of the ions with $m/z = 27$ for [M-C_xH_y] and $m/z=45$ for [M-OC₂H₅]. PFN is a colorless and clear liquid at room temperature, and its boiling point and density are 125 °C and $2.71\text{ g}\cdot\text{mL}^{-1}$ (at 25 °C), respectively. The sample was used in the standard electrolyte without any further treatment, and photographs of electrolyte with the additive in different concentrations are shown in Fig. S4 in the Supporting Information. The ionic conductivity of the electrolytes was measured on a Mettler Toledo conductivity device (Germany).

2.2. Combustion tests and characterization

The combustion tests of the electrolytes with or without PFN additive were performed by burning. Round fiberglass sheets (~5 cm in diameter) were soaked into

the electrolytes for several minutes to absorb ~5 g of electrolyte, and then they were ignited to evaluate the flammability of the electrolytes. According to the Clapeyron Clausius equation, the saturated vapor pressures of different electrolyte solutions and PFN were obtained by measuring the boiling point of the liquid under different external pressures.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) was performed on a Princeton electrochemical instrument (USA) with a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$. The electrochemical impedance spectroscopy (EIS) was also carried out on Princeton electrochemical workstation in the discharged state over the frequency range from 100 kHz to 0.1 Hz with a potential amplitude of 5 mV. Swagelok-type cells were manufactured with lithium foil as both the counter and reference electrodes. The working electrodes were prepared by mixing 80 wt. % $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders, 10 wt. % conductive agent (carbon black, Super-P), and 10 wt. % binder (polyvinylidene difluoride, PVDF), with 1.0 M lithium hexafluorophosphate (LiPF_6) in EC+DEC+DMC (1:1:1 v/v/v) as the electrolyte, with and without electrolyte additive, respectively. The galvanostatic charging/discharging measurements were conducted in a voltage window of 2.5–5.0 V using a LAND battery tester. The specific capacity was calculated based on the mass of the cathode materials, and the loading of active material on each electrode is around $2 \text{ mg}/\text{cm}^2$.

2.4. Material characterization

The electrodes after cycles were separated in a glove box and washed in anhydrous DMC to remove the electrolyte on surface, followed by vacuum drying for 24 h at 25

°C. The surface morphology was measured by scanning electron microscopy (SEM, JSM-7100F, Japan) at 30.0 kV with 21.0 mm working distance, and transmission electron microscopy (TEM, FEI Tecnai G20). The Surface compositions of electrodes before and after cycles were characterized using X-ray diffraction (XRD, D8 ADVANCE, BRUKER) with Cu K α radiation (1.54 Å) at a voltage of 40.0 kV, 300 mA and X-ray photoelectron spectroscopy (XPS, Escalab 250Xi Thermo Fisher Scientific by using an Al K α radiation (Ephoton = 1486.6 eV), respectively.

3. Results and Discussion

3.1. Combustion and Conductivity Test

The self-extinguishing time (SET) of the electrolyte with different concentrations of PFN can be seen in Fig. 1a. The SET curve of PFN based electrolyte shows a sharp decrease with the increasing content of PFN, especially from 0 wt% to 1 wt%. When the amount of PFN is 5 wt%, the SET time is 0 s, indicating total non-flammability. The flammability of the electrolytes with or without PFN additive can be visualized in Fig. 1b. The base electrolyte, 1 M LiPF₆/EC+DEC+DMC (1:1:1, v/v/v), shows obviously fierce burning when exposed to fire, while the electrolyte with 5 wt% PFN additive cannot be ignited, indicating excellent flame-retardant efficiency. The conductivity variation with different concentrations of PFN can also be seen in Fig. 1a. It can be observed that the conductivity of the electrolyte decreases as the concentration of PFN increases due to its high viscosity and low dielectric constant. Generally, low conductivity is not beneficial for battery performance. The ionic

conductivity of the electrolyte containing 5 wt% PFN can reach $11.32 \text{ mS}\cdot\text{cm}^{-1}$, however, which is almost equal to the performance of the base electrolyte without additive ($11.82 \text{ mS}\cdot\text{cm}^{-1}$), thus demonstrating that the PFN has almost no influence on the electrochemical performance under general conditions.

In order to study the flame-retardant mechanism of PFN, the saturated vapor pressures of different electrolyte solvents and PFN at different temperatures were first tested by measuring the boiling point of the liquid under different external pressures according to the Clapeyron-Clausius equation. From Fig. S5 in the Supporting Information, the saturated vapor pressure of PFN is less than those of the conventional electrolyte solvents (EC, DEC, DMC, EMC), regardless of whether they are pure or mixed solvents. In general, a higher saturated vapor pressure means that there is more solvent to be evaporated, which indicates that PFN can effectively inhibit the evaporation of solvent in electrolyte and prevent the combustion risk of flammable solvents.

As is well known, the combustion reaction includes free radical generation, and chain reaction initiation and growth. For electrolyte solvents, the combustion reactions of alkyl esters are explained as following equations (1)-(4). With the addition of PFN, free radicals, mainly including $\text{PO}\cdot$, are released when flame retardant additives are heated, and the radicals can capture gaseous hydrogen radicals and oxygen radicals, thereby preventing a chain reaction of hydroxyl radicals. Therefore, the organic electrolyte combustion cannot occur or will be very difficult to

perform [36]. The following interpretation of the mechanism can be observed in Fig. S6 in the Supporting Information in detail.

3.2. Electrochemical Characterization

Fig. 2a shows the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ batteries with no additive or with PFN additive, cycled at 0.2 C between 3.5-4.9 V. It can be obviously observed that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery with 5 wt% PFN additive has better cycling capacity than the one with no additive. The discharge capacity of the battery with 5 wt% PFN is $124.4 \text{ mAh}\cdot\text{g}^{-1}$ after 50 cycles and $122.1 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles, respectively, which appears to show that there is almost no battery capacity attenuation under the discharge condition of 0.2 C. Only $117.7 \text{ mAh}\cdot\text{g}^{-1}$ and $105.8 \text{ mAh}\cdot\text{g}^{-1}$ discharge capacity are respectively obtained, however, from the battery with no additive. Meanwhile the cycling retention of the battery with 5 wt% PFN is 98.1% after 50 cycles and 96.4% after 100 cycles, which is much higher than those of the battery with no additive in the electrolyte (96.5% and 86.1% respectively). Fig. 2b shows that the coulombic efficiency of the battery with additive has always remained always stable at more than 96%, while it is lower than 95% in the first 20 cycles with no additive. This is due to the more rapid formation of the cathode electrolyte interphase

(CEI) film on the surface of the electrode with the additive, thereby preventing the dissolution in electrolyte and consumption of the electrode material, which can effectively promote the intercalation and deintercalation of lithium ions.

In order to discuss the charge and discharge properties at different current densities, Fig. 2d shows the rate performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ batteries with or without PFN-containing electrolyte. In general the battery with 5 wt% PFN demonstrates better rate performance than that with no additive. The specific discharge capacities of the battery with 5 wt% PFN additive at 0.2, 0.5, 1, 2, and 5 C are about 122.3, 120.2, 113.9, 94.8, and 72.9 $\text{mAh}\cdot\text{g}^{-1}$, respectively, while for the battery with no additive, they are only 121.8, 118.7, 110.4, 84.3, and 60.5 $\text{mAh}\cdot\text{g}^{-1}$, respectively. Meanwhile, the reversible capacities at 0.2 C with or without additive are 121.3 and 120.6 $\text{mAh}\cdot\text{g}^{-1}$, respectively. This reveals that the performance of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery with 5 wt% PFN is significantly improved at different current densities, especially at high current densities.

To examine the electrochemical characteristics of the electrolytes, cyclic voltammogram profiles of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in the base and PFN-containing electrolytes are shown in Fig. 3a,b. It must be pointed out that all the CV measurements were performed in 1 M LiPF_6 / EC+DEC+DMC (1:1:1, v/v/v) containing 5 wt% PFN in the potential range from 3.0–5.0 V (vs. Li^+/Li). First, regardless of whether it is the first cycle or the third cycle, we can clearly see a pair of reversible redox peaks in both corresponding to $\text{Ni}^{2+}/\text{Ni}^{4+}$ at around 4.8 V, meanwhile there redox peaks appear in both at around 4.0 V, which is attributed to the oxidation and reduction of $\text{Mn}^{3+}/\text{Mn}^{4+}$.

In the first cycle, a small oxidation current arises at the potential of 3.8 V in the CV results, but only for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in the electrolyte containing 5 wt% PFN, which can be attributed to the electrochemical oxidation of PFN molecules. We can also find that the oxidation potential of PFN is lower than the decomposition potentials of LiPF_6 -based conventional organic electrolytes (around 4.8 V vs. Li^+/Li), indicating that PFN is electrochemically oxidized at a potential lower than that for lithium extraction. Therefore, the PFN molecules are likely to be oxidized on the cathode prior to the decomposition of base electrolyte, which may result in suppression of the electrolyte oxidized decomposition, so as to improve the high voltage performance of the cathode.

Fig. 3c,d presents electrochemical impedance spectra of a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery containing the electrolyte additive before and after long-term cycling. Generally, as in the typical EIS curves of lithium-ion batteries (LIBs), the semicircle in the high-frequency range shows the resistance in the electrochemical reaction and electrolyte interface film of the electrode. For the same electrochemical reaction, the intrinsic impedance of the reaction will not change too much. Therefore, the resistance mainly reflects the electrode surface film resistance. It can be clearly observed that batteries with the PFN additive show lower electrolyte interface film resistance than those without additive after 100 cycles. This indicates that the presence of PFN in the electrolyte changes the cathode surface film, thus improving the cycling performance of the LIBs.

3.3. Material Characterization

The XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes before cycling and after 100 cycles are shown in Fig. S7 in the Supporting Information. It can be observed that the cycled electrode materials, with or without PFN, still exhibit the typical spinel structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and the main characteristic peaks of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ appear. The material structures, however, both show an obvious amorphous transformation after charge and discharge cycling, and the peak intensities of the electrodes cycled in the electrolyte without additive are weaker than those with PFN additive, and some peaks have even completely disappeared for the sample with no additive, indicating that the electrode materials in the electrolyte without additive suffer from more serious structural degradation [37].

To further explore the effects of PFN on the electrode, SEM/TEM images of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode with and without PFN additive after many cycles are presented in Fig. 4. After 50 charge and discharge cycles, the amorphous layers known as the CEI film can be seen on both cathode surfaces, regardless of whether the additive was used or not. The surface of the CEI membrane in the electrolyte with PFN additive is obviously smooth, however, and without any damage, as shown in Fig. 4c. On the contrary, the surface of the CEI without additive appears irregular and even damaged, especially with some cracks on it, as shown in Fig. 4d. Furthermore, after 100 cycles, obvious holes can be observed in Fig. 4f on the surface of the CEI film without additive, while the surface of with the PFN additive appears regular and uniform, and without any damage in Fig. 4e. More SEM images of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode at different resolutions and from different batches are displayed in Fig. S8

and S9 in the Supporting Information. These pictures show the same results, that is, the CEI film with additive appears smooth and uniform, while the CEI film without additive is more or less damaged and uneven [38,39].

In the TEM images, the surface layer formed on the cathode with PFN additive (with a thickness of 3–5 nm, as shown in Fig. 4g) is obviously thinner and more uniform than that without additive (approximately 6–12 nm, as shown in Fig. 4h). Moreover, the surface film with PFN additive appears smooth and regular, while the film without additive appears uneven and has surface damage, which may result in the dissolution of the electrode material and cause degradation of the electrode performance. Fig. 4i illustrates the formation of uniform and damaged CEIs with or without PFN additive, respectively. The thinner and more regular surface film derived from PFN can also shorten the lithium ion diffusion pathways and decrease the interfacial resistance of the electrode, which is beneficial for the performance of the battery.

In order to identify the chemical composition, element content, and valence states of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode surface in the electrolytes with or without additive, XPS measurements were performed after 100 cycles, as shown in Fig. 5. Compared to fresh $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode, the concentrations of C, O, F, Ni, and Mn decrease, while the concentrations of N and P increase for the cycled $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes in electrolyte with PFN additive, indicating that the cathode electrolyte interphase (CEI) is formed on the surfaces of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes through chemical reactions between the electrolyte and cathode.

In the C 1s spectra, four main peaks appear on the electrode in the base electrolyte, corresponding to hydrocarbons (C-H, C-C at 284.8 eV), C-O-C bonds (286-287 eV), C=O bonds (286.5 eV for R-CH₂OCO₂-Li and 288-290 eV for Li₂CO₃), and C-F₂ from PVDF (291 eV), respectively. Notably, the intensities of the two characteristic peaks for C=O bonds appear much lower in the electrolyte with PFN additive than those with no additive. The O 1s spectra in the base electrolyte show three main peaks: O=C (533.7 eV), O-C (532.1 eV), and M-O (529.8 eV, in LiNi_{0.5}Mn_{1.5}O₄). Similarly, the electrode without additives displays slightly stronger C=O peaks from Li₂CO₃. As is well-known, Li₂CO₃ is one of the main decomposition products of carbonate based electrolyte, therefore, the XPS results suggest that the addition of PFN could effectively prevent the decomposition of carbonate-based electrolyte. In the F 1s spectra, three main peaks can be seen in the base electrolyte: C-F₂ from PVDF (688 eV), Li_xPO_yF_z (687 eV), and LiF (685.5 eV). Obviously the peak intensities of Li_xPO_yF_z and LiF are weaker in the electrolyte with additive than in that without additive. As is well known, Li_xPO_yF_z and LiF are the main products of electrolyte decomposition. Once too much Li_xPO_yF_z and LiF are generated, the intercalation and de-intercalation of Li ion during charge and discharge will be seriously affected, mainly because of the poor conductivity and increased interface impedance. These results confirm that the additive inhibits the formation of such by-products and promotes the transport of Li ions in the electrolyte. It can also be concluded that the decomposition of the additive precedes the decomposition of the electrolyte, which is beneficial to the battery [25,38-40].

In the Mn 2p and Ni 2p spectra, strong metal characteristic peaks can be clearly observed in pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes. With the formation of the CEI film, however, a certain amount of surface electrode material needs to be consumed, so that the metal characteristic peaks of the electrode materials are decreased after 100 cycles. In this case, however, the peak intensities for the electrode cycled in the electrolyte without PFN additive are significantly weaker than those in the electrolyte with additive. That is to say, the addition of PFN additive can effectively inhibit the decomposition of electrolyte and prevent further consumption of electrode materials. Note that these results are consistent with the above analysis results.

In the N 1s and P 2p spectra, broad characteristic peaks of N (397-401 eV) and P (132-135 eV) can be observed. Among them, there are two typical peaks in N 1s spectra at 398.1 eV (N=O) and 399.5 eV (C-N), which respectively belong to LiNO_3 and RONO_2Li molecules (RONO_2 : nitrate ester functional group, with R standing for any organic residue). In P 2p spectra, the peaks at 133.3 eV and 134.2 eV derived from P-O and P=O respectively belong to Li_3PO_4 and ROPO_3Li (ROPO_3 : monoester phosphate) molecules. Due to their introduction of large amounts of phosphorus and nitrogen, the PFN additives are involved in the film-forming reaction, suggesting that the surface film is incorporated with PFN, as is confirmed by the more intense peaks of N and P. These results again verify that the SEI film formation is related to the additional PFN.

In order to verify the dissolution of electrode materials during charge and discharge, quantitative determination of the metal elements, including nickel and manganese,

was carried out by inductively coupled plasma – atomic emission spectroscopy (ICP-AES). The cycled $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes were rinsed with dimethylacetamide (DMAC) and dissolved in 5 ml of 3% HNO_3 , and the solution was diluted to 20 mL for analysis. From Fig. S10 in the Supporting Information the results show that the dissolution of nickel and manganese is rather severe in the solution without additive, especially for manganese. On the other hand, in the solution with PFN additive, the dissolution of metals is inhibited, especially manganese, which is consistent with the qualitative detection results of XPS.

3.4. corrosion Mechanism for Electrolyte Interphase Film

Based on the XPS and ICP results and related analysis, the mechanism behind the electrolyte decomposition and changes to the CEI film is first proposed as the “corrosion mechanism”, as is shown in Fig. 6. Under the high voltage, a chemical reaction occurs which opens the hexatomic rings in the PFN molecules, producing chains of phosphrile and octathionitrile due to straight chain polymerization and octatomic ring polymerization, which results in a small peak at around 3.8 V in the CV curves [36], as shown in Fig. 6a, also resulting in the formation of NO_2 , NO_3 , PO_3 , and PO_4 negative groups, as shown in Fig. 6b. Combining with lithium ions in the electrolyte, LiNO_3 , RONO_2Li , Li_3PO_4 , and ROPO_3Li are accordingly generated, as shown in Fig. 6c. In the traditional corrosion mode, as shown in Fig. 6d, the decomposition products of the electrolyte, HF and PF_5 , can be easily reacted with the main components (Li_2CO_3 and ROCO_2Li) of the CEI film, thus producing LiF , ROF_3 ,

RF, etc. Compared with lithium alkyl carbonate (Li_2CO_3 and ROCO_2Li), as shown in Fig. 6e, the decomposition products of PFN (LiNO_3 , RONO_2Li , Li_3PO_4 , and ROPO_3Li) are quite stable, which are almost non-reactive with HF and PF_5 to produce LiF. As is well known, once too much LiF is generated, the intercalation and de-intercalation of Li ions out of/into the electrolyte will be hindered because of the increased interface impedance. Therefore, the diffusion of Li ions through the CEI film in the electrolyte with PFN additive will be enhanced.

Fig. 6f,g further illustrate the working mechanism of the additive on the surface of the electrode, as spherical electrode particles can be seen on the surface from the original distribution, among which the yellow symbols represent the battery adhesive. Initially, a CEI film is formed on the surface of electrode after the first few cycles, whether the additive is added or not. Then, several charge and discharge cycles later, both the electrode material and the adhesive show obvious aggregation and fusion, which is accompanied by increasing thickness of the CEI film, regardless of the presence or absence of the additive. In the absence of additive, the thickness of CEI film increases more, however, along with damage to the CEI and exposed particles in some positions, usually located at the electrode edge or where there is local overheating. On the contrary, the phenomenon of increasing thickness is not obvious with the additive, with almost no film damage and no particles exposed. It should be pointed out that the above interpretation of mechanism can be observed and ascertained from the results of SEM/TEM.

3.5. High Rate Capacity and Cycling Performance of the Full Batteries

In order to confirm the effect of PFN additive on the full battery performance, the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{graphite}$ full cells were assembled and cycled at 1C. Fig. 7 shows the cycling performance and discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{graphite}$ full cell with or without 5 wt% PFN-containing electrolyte at 1 C. It can be seen that the initial discharge capacities of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{graphite}$ battery with or without PFN at 1C are 114.2 and 110.8 $\text{mAh}\cdot\text{g}^{-1}$, respectively, but the reversible discharge capacities after 100 cycles are 99.8 and 79 $\text{mAh}\cdot\text{g}^{-1}$. The capacity retention ratios are 87.3% and 71.2% for the batteries with or without 5 wt% PFN, respectively, demonstrating that PFN has effectively acted as a non-aqueous electrolyte additive that improves the cycling performance of a full lithium ion battery. We believe that PFN is a promising additive in non-aqueous electrolyte for the high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{graphite}$ batteries.

4. Conclusions

Fluorinated phosphazene derivative ethoxy(pentafluoro) cyclotriphosphazene (PFN) as a novel nonaqueous electrolyte additive has been proposed for high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ batteries. Firstly, this additive at mass concentration of 5 wt% shows excellent flame retardancy in flammability testing. Secondly, the electrochemical results demonstrate that the cycling performance and rate capability of batteries with 5 wt% PFN are both much better than those without PFN. Thirdly, the thinner and more regular CEI surface film derived from PFN can shorten the diffusion path for lithium ion, decrease the interfacial resistance of the battery, and suppress the dissolution and

corrosion of the cathode. Accordingly, PFN is an appropriate additive in non-aqueous electrolyte for the high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery.

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Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version.

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Figure Captions

Fig. 1. (a) SET and ionic conductivity of the electrolytes containing different concentrations of PFN; (b) photographs of the flammability testing of the electrolytes: the base electrolyte 1 M $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{DMC}$ (1:1:1, v/v/v) and the same electrolyte with 5 wt% PFN additive.

Fig. 2. (a) Cycling performance and (b) coulombic efficiency of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery with and without PFN additive when cycled at 0.2 C between 3.5-4.9 V; (c) capacity retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery with and without PFN additive; (d) rate performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery with and without PFN additive at different current rates from 0.2 C to 5 C.

Fig. 3. Cyclic voltammograms of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in base and 5 wt% PFN-containing electrolyte: (a) first cycle, (b) third cycle at a sweep rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$; and electrochemical impedance spectra of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in base and 5 wt% PFN-containing electrolyte: (c) before cycling, (d) after 100 cycles.

Fig. 4. SEM and TEM images of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes: (a) fresh and (b) single particle; (c) with PFN additive after 50 cycles; (d) without PFN additive after 50 cycles; (e, g) with PFN additive after 100 cycles; (f, h) without PFN additive after 100 cycles; (i) schematic diagram of uniform and damaged CEIs formed with and without PFN additive respectively, with (j) the inset showing the structure of PFN.

Fig. 5. XPS spectra including C, O, F, N, P, Mn, and Ni in fresh and cycled $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in the electrolytes with or without PFN additive

Fig. 6. (a-e) Illustration of the mechanism of PFN additive decomposition on the surface of the electrode; schematic diagrams of (f) damaged CEI and exposed particles formed due to corrosion

without PFN additive; and (g) uniform CEI formed due to corrosion suppression with PFN additive.

Fig. 7. Charge/discharge curves for selected cycles (a), and specific capacity for those cycles (b); and cycling performance (c) of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery with and without 5 wt% PFN-containing electrolyte at 1 C.

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