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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

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 non-flammable 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.

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 ($> 4.5 \text{ V}$, 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 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

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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 economical methods for solving this problem.

Li et al. have reported terthiophene (3THP) and 4-(trifluoromethyl)benzotrionitrile (4-TB) for use 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 the 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. used fluoroethylene carbonate/fluorinated diethyl carbonate (FEC/HFDEC) as an 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 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /Li half-cells [23,24]. Lee et al. found that dopamine in a conventional LiPF_6 /EC+DEC+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 flammability 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 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /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, a 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 non-flammable 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), 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 without PFN, and the discharge capacity of the battery with 5 wt% PFN was 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.

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 first stirred at room temperature and co-precipitated by using a precipitating agent, $\text{NH}_3 \cdot \text{H}_2\text{O}$, at $\text{pH} = 8.0$ for 8 h, and then the precursor was calcined with Li_2CO_3 at 600°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 its 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. In the nuclear magnetic resonance (NMR) spectra shown in Fig. S2 in the Supporting information, the peaks at 4.27–4.23 ppm ($-\text{CH}_2-$ from PFN) and at 1.41–1.38 ppm ($-\text{CH}_3$ from PFN) in the ^1H spectrum are attributable to the saturated hydrogen of the ethyl groups. In the ^{13}C NMR spectrum, the peaks at 65.95 ppm and 15.46 ppm also arise from ethyl groups from PFN. Meanwhile, the peaks at 15.27–15.02 ppm, 9.90 ppm, and 4.15–4.06 ppm in the ^{31}P NMR spectrum represent three different groups, i.e. -PO-, -PF-, and -POF-, respectively. The mass spectrometry (MS) results shown in Fig. S3 in the Supporting information suggests a molecule (M) with the main ion peaks at $m/z = 248$ and $m/z = 230$, the assignment of which is based on the detection of ions with $m/z = 27$ for $[\text{M}-\text{C}_x\text{H}_y]$ and $m/z = 45$ for $[\text{M}-\text{OC}_2\text{H}_5]$. PFN is a colorless and clear liquid at room temperature, and its boiling point and density are 125°C and 2.71 g 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 ($\sim 5 \text{ cm}$ in diameter) were soaked in the electrolytes for several minutes to absorb $\sim 5 \text{ g}$ 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 workstation (USA) with a scan rate of 0.1 mV s^{-1} . The electrochemical impedance spectroscopy (EIS) was also carried out on a Princeton electrochemical workstation in the discharged state over the frequency range from 100 kHz to 0.1 Hz with 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 was around 2 mg/cm^2 .

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