Toward a stable electrochemical interphase with enhanced safety on high-voltage LiCoO₂ cathode: A case of phosphazene additives

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Abstract

(Phenoxy)Pentafluorocyclotriphosphazene N₃P₃(OPh)F₅ (PFPN) is investigated as a bifunctional additive in electrolyte to improve the electrochemical performance and thermal stability of LiCoO₂ simultaneously when the electrodes cycled to high cutoff potentials. The results show that the electrochemical performance of the electrode material with the additive in the electrolyte is enhanced significantly, with a capacity retention of 91% after 300 cycles, which is a great improvement compared with that of only 67% in base electrolyte. More significantly, the thermal stability of LiₓCoO₂ (x < 0.5) in the presence of PFPN or covered with decomposed products of PFPN is also remarkably improved. Our results show that the additive can be oxidized prior to EC and DMC, and the decomposition products of PFPN contribute to the LiCoO₂/electrolyte interphase film (CEI) with more uniform and denser structure. This polymerized CEI processes an excellent electrochemical stability to assist in inhibiting the further decomposition of the electrolyte and reducing the interfacial impedance growth apparently of the cells with a long cycling condition.

Keywords:
(Phenoxy)Pentafluorocyclotriphosphazene Additive LiCoO₂ Cycling performance Thermal stability

1. Introduction

Nowadays, lithium-ion batteries have been required for higher energy density and better safety in the further development of the...
high power electrical equipment. The development of new materials with higher working voltage platform [1,2] or extending the operating voltage of traditional materials [3–5] has increasingly captured researchers’ attention. Meanwhile, much attention has been focused on the safety issue of Lithium-ion battery with high energy density [16].

Layered LiCoO$_2$ is the most widely used cathode material, delivering a specific capacity of 140 mAhg$^{-1}$ in the operating voltage limit of 4.2 V vs. Li$^+$/Li [5]. In an attempt to increase delivered capacity of the LiCoO$_2$, it must be charged to a higher voltage. However, the capacity and power fading will quickly occur and safety issue becomes more serious in such a high voltage condition [7]. Several mechanisms have been proposed for the capacity fading at high voltages: (i) the fairly irreversible phase transition [8]; (ii) the Co dissolution [9]; (iii) severe oxidation of electrolyte [10]; (iv) attack by HF [11]; and (v) impedance growth at the surface [12]. Therefore, researchers have paid intensive efforts to improve the cycling performance of LiCoO$_2$. At present, there are two effective methods to solve these problems. Firstly, cathode surface coating with metal oxides can effectively suppress the electrolyte decomposition and the cobalt dissolution [4,13]. However, surface coatings are often discontinuous deposition and will lead to thermal runaway and ultimately to safety issue becomes more serious in such a high voltage condition [7].

The electrolyte additive, PFPN, was synthesized according to a typical synthetic route as shown in Scheme 1. The electrolyte additive was synthesized by a Nuclear magnetic resonance spectra (NMR) of a Bruker Advance II–400 MHz spectrometer (Bruker) and Fourier transfer infrared (FT-IR) of Nicolet 5700 spectrometer (Nicolet, Madison, WI, USA).

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Chemical characteristics include ¹H NMR (400 MHz, CDCl$_3$): $\delta_{H}$-aromatic 7.3 (d, 2H), $J$ = 8.4 Hz, 7.4 (t, 1H), $J$ = 7.5 Hz, 1.2 Hz; 7.5 (t, 2H), $J$ = 7.8 Hz. $^{13}$C[¹H] NMR (CDCl$_3$): $\delta_{C}$ = 149.7(d), J = 6.8 Hz; $\delta$C$_{2,3}$ 130.9 (s), 127.5 (s); $\delta$C$_{4}$ 121.3 (s). $^{31}$P NMR (CDCl$_3$): $\delta$PF$_{12}$ 10.5, $\delta$PF$_{2}$ = –860 Hz, $\delta$PF$_{1}$ = 10.1 (dm); $\delta$PF$_{3}$ = –910 Hz. $^{19}$F[³¹P]NMR (CDCl$_3$): $\delta$PF$_{2}$ = 69.9 (m); $\delta$PF$_{3}$ = 66.5 (s). IR (cm$^{-1}$): 2926.0 (s), 2855 (m), 1594 (m), 1491 (s), 1457 (m), 1280 (s) (CH str); 1184 (s), 1162 (s) cm$^{-1}$ (PO str); 1014 (m), 993 (m), 957 (s), 952 (s) (PF str); 767 (m), 688 (m).

2. Experimental section

2.1. Preparation of PFPN and characterization

The electrolyte additive, PFPN, was synthesized according to a procedure in the literature [32]. A typical synthetic route is shown in Scheme 1. A typical synthetic route is shown in Scheme 1. Structure and purity of PFPN were checked by Nuclear magnetic resonance spectra (NMR) of a Bruker Advance II–400 MHz spectrometer (Bruker) and Fourier transfer infrared (FT-IR) of Nicolet 5700 spectrometer (Nicolet, Madison, WI, USA).

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For the CR2025 coin half-cell experiments, the cathodes were composed of 80 wt% LiCoO$_2$ (provided by Hunan Shanshan Battery Material Co., Ltd. (China)), 10 wt % polyvinylidenefluoride (PVDF) binder and 10 wt % acetylene black. The average active material loading was about 3.5 mg/cm$^2$. The volume/mass ration of electrolyte vs. active material is approximately 100 $\mu$L of electrolyte per mg of active material. The cycling protocol consists of a constant current/constant voltage (CC/CV) charge-procedure (with 10% cut-off of current) followed by a CC discharge in a voltage range between 4.5 and 3.0 V at a current density of 14 mAg$^{-1}$ for the initial and second cycles and at 140 mAg$^{-1}$ for the following cycles, on an Arbin BT-2000 battery tester at 30 $^\circ$C. The electrochemical impedance spectroscopy (EIS) measurements of 4.2 V charged state electrode were taken from 100 kHz to 10 mHz with an amplitude of 5 mV using a Versa STAT MV Multichannel potentiostat/galvanostat (Princeton Applied Research, USA) at a scan rate of 1 mV/s.

2.2. Electrochemical measurements

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The potential-step test also used CR2025 coin-type cells. The LiCoO$_2$/Li was charged to 4.5 V at a current density of 14 mAg$^{-1}$ and then maintained at 4.5 V, 4.7 V, 4.9 V for 5 h, respectively.

2.3. Material characterization

Scanning electron microscopy (SEM) images were performed on S–4800 (HITACHI, Japan) microscope, operating at 15 kV. Transmission electron microscopy (TEM) were conducted on a Tecnai F30 (Philip FEI, Netherlands) apparatus, operating at 100 kV. For the preparation of TEM samples, acetone was used as dispersing agent. Samples were placed in acetone and ultrasonically treated for 10 min to make sure most of the adhesive (PVDF) was removed. Two drops of the solution were then placed on standard pieces of copper mesh, dried, the brought to the TEM equipment. X-ray photoelectron spectroscopy (XPS) measurement were equipped with a Quantum 2000 ESCA spectrometer (Physical Electronics,
USA) with monochromatic Al Kα radiation (hv = 1486.6 eV), operating at 23.2 W and in a vacuum of <10−8 Torr. The cells were disassembled and stored in a dry glove box under argon, but the cathodes were exposed to air for a short time when they were transferred into the XPS vacuum chamber. The universal contaminant of C-H bond at 284.8 eV was used as a reference for the final adjustment of the energy scale in the spectra. For the differential scanning calorimetry (DSC) measurements of the delithiated LiCoO2 materials, the cells were fully recharged to 4.5 V after 2 cycles and were disassembled in a dry glove box. The cathode materials were rinsed with dimethyl carbonate (DMC) to remove the residual electrolyte and dried under vacuum, then scraped from the current collector. The resulting electrodes (~4 mg) were sealed together with the electrolyte solution (4 μL) in a hermetic stainless steel pan. All DSC measurements and analysis were based on the overall weight of the sample. The DSC experiments were carried out on a STA 409 PC (NETZSCH, Germany) and measurements were performed at a heating rate of 5 °C min⁻¹.

### 2.4. Computational methods

We have employed B3PW91 density functional theory (DFT) method to investigate the oxidation potentials and bond strength of the molecules. The 6-311+G(d,p) basis sets were used, solvation free energies are calculated using the Polarizable Continuum Model (PCM) [33] at these gas-phase optimized geometries. United atom for Hartree-Fock atomic radii and a dielectric constant (ε) of 46.6 (average of the experimental dielectric values 3.4–89.8) were used in all the calculations for additive.

### 3. Results and discussion

Firstly, the electrochemical behavior of PFPN was examined by linear sweep voltammetry (LSV) and the results are presented in Fig. 1a. The curve shows that the base electrolyte is electrochemically stable up to 5.25 V (vs. Li⁺/Li). In comparison, with the addition of the additive, the electrochemical stability of the electrolyte becomes worse with the current sharply increasing at 5.1 V (vs. Li⁺/Li) and the inset magnification figure of the blue frame clearly shows that a small current peak appears at 4.75 V (vs. Li⁺/Li), which is attributed to the oxidation of the additive. After testing, the color of the electrolyte changed from colorless to dark brown. The second approach to investigate the electrochemical stability of the electrolytes is an adaptation of the potential-step technique to the actual operational environment by using LiCoO2 as a working electrode. As shown in Fig. 1b, the leakage currents become larger with the increase of potential. There is a negligible difference in base electrolyte with or without PFPN at 4.5 V and 4.7 V. However, when the potential is raised to 4.9 V, the decomposition of base electrolyte with PFPN becomes significant. This result can reliably reflect the more serious decomposition of PFPN which is catalyzed by the LiCoO2 surface at high voltage. Based on the density functional theory (DFT) calculation of the energy of the highest occupied molecular orbital (HOMO) with the B3PW91/6-311+G(d,p) basis set also shows that the PFPN (−7.44 eV) has a higher HOMO level than EC (−8.73 eV) and DMC (−8.47 eV), expected to a lower oxidation stability [34]. This result is well consistent with the experimental data. Besides, the theoretical calculation indicates that the charged PFPN molecule exhibits some substantial structural changes compared to the pristine molecule. The most significant change of bond length undergoing one-electron oxidation of PFPN is P-O bond which has an elongation of 0.0748 Å, besides, a ~0.0845 Å shrinkage of C-O bonds can also be found. Our calculation indicates that P-O bond will be prone to the most breaking at high voltage to generate corresponding phenoxyl group.

The first charge-discharge profiles and cycling performance of the materials are shown in Fig. 2. It can be seen that the coulombic efficiency at the first cycle decreases from 91.8% to 88.8% after adding additive in the electrolyte, suggesting that the irreversible decomposition of the additive contributes to the lower coulombic efficiency. Fig. 2b displays the cycling performance of LiCoO2/Li cells in the electrolytes with/without additive. After 100 and 200 cycles, the discharge capacity retention of cells in the electrolyte containing 2% PFPN reaches to 98.4% and 95.1% (the ratio to the third cycle discharge capacity), respectively. Even after 300 cycles, the discharge capacity can maintain 169 mAhg⁻¹, corresponding to an excellent capacity retention of 91.4%. In comparison, LiCoO2 material in base electrolyte exhibits quite fast degradation and becomes more serious after 200 cycles. What’s more, the coulombic efficiency is much stable in the electrolytes with additive, remaining above 99.7% after 300 cycles. It demonstrates that cells with PFPN added electrolyte have much more stable cycling performance than that of the additive-free cells.

Electrochemical impedance spectroscopy (EIS) experiments were performed to check the effects of additive on the cycling performance of cells and help understanding the electrochemical process occurring. The measured impedance spectra are presented in Fig. 3a and b. It is discerned that there are two semicircles in the Nyquist plots. The high-frequency semicircle reflects the migration of Li⁺ through the CEI film, while the medium-frequency semicircle is related to the charge-transfer resistance, and the low-frequency tail represents the Li⁺ diffusion process in the solid phase of the electrode [35]. The EIS spectra are fitted with the equivalent circuit (Fig. 3c, inset figure), which is the most widely accepted one by researchers to account for Li⁺ insertion/de-insertion process in the intercalation material [36]. The detailed semi-quantitatively analysis results of Rct and Rce value are summarized and compared in Fig. 3c and d.

In Fig. 3c and d, it demonstrates that, in the electrolyte with additive, the values of Rct and Rce are nearly equal to those of the base electrolyte during the initial film formation, while it displays that the resistances of the CEI is slightly larger than that of the base electrolyte in the subsequent cycling, indicating that oxidation products of PFPN can pile up on cathode surface to increase the
resistance of the Li\(^+\) through the CEI film. It is similar to the phenomenon observed from benzene derivatives additives systems [12,37]. We notice that the individual resistances are in the order of \(R_{CT} > R_{CEI}\), suggesting that the \(R_{cell}\) is dominated by the \(R_{CT}\). This result indicates that reducing \(R_{CT}\) could be the most effective approach to improving the performance of the material [38]. As shown in Fig. 3d, the cell with addition of PFPN shows a lower increasing rate of the charge-transfer resistance than that of the resistance in base electrolyte upon long cycling, indicating that PFPN is helpful to stabilize the electrode/electrolyte interface.

Fig. 4 shows some SEM and TEM images of the electrodes, confirming the formation of the CEI film on the surface of LiCoO\(_2\) electrode after 300 cycles in both electrolytes. Compared to the initial smooth and clear morphology of the pristine electrode (Fig. 4a and a’), it clearly shows the structures of CEI on the cycled cathodes are different. In the base electrolyte (Fig. 4b and b’), the surface of electrode is covered with a relatively rough and loose layer with a large amount of fine particles (approximately 10 nm), which is attributed to the decomposition of carbonate solvent and LiPF\(_6\). After the addition of PFPN (Fig. 4c and c’), we notice that the cathode material surface is completely covered by a smooth and dense layer with a thickness of 10–15 nm, and there is no precipitates can be observed, indicating that the oxidation products of PFPN can help depressing the oxidation of carbonates electrolyte. Combined with the EIS measurement, it can be concluded that the decomposition derived from PFPN could change and optimize the structure and composition of the CEI, e.g. the structural stability, the interphase impedance, which is the key factors to determine the electrochemical cycling performance of the material [39].

The thermal stability of both the electrolyte and the cathode material in charged state is of vital importance to battery safety performance. Differential scanning calorimetry (DSC) was carried out in order to unravel the thermal stability of the electrolyte and electrode material, respectively. Fig. 5a shows the DSC curves of the electrolyte with PFPN (red and blue) and without PFPN (black). It can be clearly seen that the main decomposition peak of the electrolyte shifts toward higher temperature with the more addition of PFPN, indicating that the thermal stability of the electrolyte has
been considerably improved by the additive. Fig. 5b shows the DSC curves of the Li$_x$CoO$_2$ electrode charged in the electrolyte with PFPN and without PFPN. Several peaks can be recognized in Fig. 5b, which are corresponding to the step-by-step decomposition of the charged Li$_x$CoO$_2$ material [40]. The electrolyte decomposition/oxidation at the surface of Li$_x$CoO$_2$ electrode can occur at a lower temperature, which has been identified at around 200 °C [23]. Interestingly, a new peak (indicated by red asterisk) at 206 °C can be observed from the red DSC curve in the presence of 2% PFPN, which is assigned to the thermal-polymerization reaction of PFPN. The first and second major peaks in the red and blue curve shift towards high temperature compared with the corresponding peaks in the black curve. Meanwhile, the intensity of these two peaks decreases significantly. The total heat generation under both testing conditions can be calculated by integrating the various peaks in the DSC curves (Note: the integrating range is between 200 and 300 °C in the present work). The calculation results demonstrate that the total exothermic heat generated from the Li$_x$CoO$_2$ electrode charged in the presence of PFPN (2% PFPN: 36.1% and 5% PFPN: 41.3%) is less than that from the Li$_x$CoO$_2$ electrode charged in the absence of PFPN (black), indicating that the thermal stability of the charged Li$_x$CoO$_2$ electrode is distinctively improved by the addition of electrolyte additive. In order to elucidate the details that how the additive improves the thermal stability of the cathode material, more DSC measurements are carried out under various conditions as shown in Fig. 6 and Fig. 7.

Fig. 6 shows the DSC profile of the LiCoO$_2$ electrode which has been cycled in various PFPN concentrations. The DSC measurements are carried out in the base electrolyte in order to unravel the effect of CEI on the stability for Li$_x$CoO$_2$. The onset of thermal temperature (OET-0, Table 1) becomes higher in the presence of PFPN as can be seen in Table 1. This fact indicates that the PFPN involved polymer film can enhance the temperature of exothermic-reaction between the Li$_x$CoO$_2$ electrode and electrolyte. It is worthwhile to note that the total exothermic heat generation (below 300 °C) can be significantly decreased with the proper content of PFPN (<2%), which indicates that the PFPN involved CEI layer can considerably suppress the thermal decomposition of Li$_x$CoO$_2$, possibly via slowing down the rate of oxygen releasing (see Fig. S3) and electrolyte decomposition. The peak (marked with P0) before the main reactions is attributed to the decomposition of the residual PFPN remained inside the pores of the electrode [23].

Fig. 7 shows the DSC profiles of the LiCoO$_2$ electrode which has been cycled in the base electrolyte while the measurements are carried out in various concentrations of PFPN in order to evaluate the impact of electrolyte component on the thermal stability of the Li$_x$CoO$_2$ electrode. Interestingly, when the measurements are carried out in the presence of PFPN, the OET (OET-0, Table 2) shifts...
toward the high temperature, indicating that the PFPN additive can improve the thermal stability of the electrolyte, which is in line with the results shown in Fig. 5a. The area of the peak before the major reaction (marked with P0) increases with the PFPN concentration due to the thermal polymerization reaction of PFPN. On the contrary, the total exothermic heats decline with the increase of PFPN concentration. In summary, it can be concluded that the thermal stability of the delithiated Li$_x$CoO$_2$ electrode can be greatly improved after adding the PFPN additives into the electrolyte. Massive phosphorus and fluorine radicals generated during the thermal decomposition of PFPN processing will combine with the oxygen radical, and then effectively suppress the combustion reaction of electrolyte [41]. It is worthwhile to note that the exothermic peak (near 280 °C), shows shoulders in 2% and 5% PFPN electrolyte systems. This fact confirms that at higher temperatures the reactions between cathode and electrolyte as well as the combustion of electrolyte have been significantly weakened. However, it needs further study to identify these individual reactions occurred at elevated temperatures. In order to have an in-depth understanding of the role of the PFPN in suppressing the decomposition reactions, more details of the CEI components will be discussed.

In an attempt to obtain information on the CEI composition and properties in different electrolyte systems, XPS measurements were carried out on the material. However, we need to know about the chemical properties of the additive molecule itself firstly.

Fig. 4. SEM images of LiCoO$_2$ electrodes before and after 300 cycles, (a) pristine electrode, (b) Base electrolyte, (c) Base + 2% PFPN. (a’-c’) show the corresponding TEM images.

Fig. 5. DSC curves of (a) base electrolyte with/without PFPN, (b) heat flow profiles of the Li$_x$CoO$_2$ charged to 4.5 V after 2 cycles in the absence and presence of PFPN.
PFPN, and DSC measurement is conducted in the base electrolyte. Absorbed on the electrode to carry out the XPS measurement, the P
binder, sodium alginate (C6H7NaO6) PVdF on the characterization of the additive, we choose a new
set exothermic temperature (OET) of peak 0 and peak 1, the temperature of peak 0
Table 2
The oneset exothermic temperature (OET) of peak 0 and peak 1, the temperature of peak 0–3, respectively, and the total exothermic heat generation below 300 °C.

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<th>OET-0 (°C)</th>
<th>OET-1 (°C)</th>
<th>Peak 0 (°C)</th>
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<th>Peak 3 (°C)</th>
<th>Heat generation (&lt;300 °C) (J/g)</th>
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<td>Base + 0%PFPN 171 205 / 219 247 284 642</td>
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In order to eliminate the interference of P and F from the binder PVdF on the characterization of the additive, we choose a new
set exothermic temperature (OET) of peak 0 and peak 1, the temperature of peak 0
when cycled in base electrolyte, a certain content of LiF component can be detected at the peak 684.5 eV [43] and the P 2p peak (134.2 eV) may correspond to a Li3PF6-type compound, which is a major hydrolysis product of LiPF6 [42]. The two major
peaks in the O 1s spectrum can be attributed to carbonate (C=O: 532.5 eV) and ether oxygen bonds (C–O: 534 eV) [45], which is consistent with the oxidation products of carbonate solvents. The Li 1s spectra peak at 55.5 eV is attributed to lithium salts, e.g. LiF, Li2CO3 [42]. As for Co 2p spectrum, no Co 2p signal can be detected. Thus, a thick interfacial film has been built up over repeated cycling and covers the entire surface. Furthermore, comparing the CEI component between formation process and aging process, it can be ensured that the CEI film becomes thicker during cycling.

When the material is cycled in the electrolyte with additive, in the initial CEI forming stage, a pronounced N 1s spectrum peak near at 399 eV can be detected on the surface of the specimen, which is attributed to the decomposition product of PFPN, ascertaining that the PFPN participates in the CEI formation. Analysis of the F 1s chemical state reveals the presence of two dominant binding energies, the peak intensity at 684.5 eV is stronger than that of 682.5 eV and where there are more covalent Co–O bonds [44]. The Li 1s signal (61.5 eV) is a characteristic of material. The XPS analysis of LiCoO2 after charge-discharge processing shows an obvious CEI film in the electrode surface.

Table 2
The oneset exothermic temperature (OET) of peak 0 and peak 1, the temperature of peak 0–4, respectively, and the total exothermic heat generation below 300 °C.

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<th>OET-0 (°C)</th>
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benzene ring in PFPN molecule structure. Considering stronger intensities of P 2p (134 eV) and F 1s (684 eV), the additive PFPN should be preferential to oxidize on the charged LiCoO₂ surface. Combined with Li 1s (61.5 eV) and Co 2p, the characteristic of LiCoO₂, it demonstrates that a thinner CEI film has formed on the electrode surface. After long cycling, a weak F 1s (684 eV) and a weak Li 1s (56 eV) signals appear, which are corresponding to the degradation of the salt LiPF₆, indicating that the PFPN could help to suppress the hydrolysis of LiPF₆. The strong F 1s peak intensity at 688 eV is assigned to F-P of phosphazene component, accompanied by the formation of electro-polymerization product of additive. The XPS data illustrate clearly that the CEI chemistry can be changed by using additive.

4. Conclusion

A novel phosphazene additive, PFPN, has been proved as an effective bifunctional additive for optimizing the performance of LiCoO₂, e.g. the cycle life characteristics, safety performance of cells. The LiCoO₂ cells exhibit a much better cycling stability and enhance thermal stability in electrolyte with addition of PFPN, e.g. with capacity retention of 91% after 300 cycles, a strong contrast with the 67% measured in base electrolyte. Based on a series of results of electrochemical and spectroscopic characterization experiments, we propose that the decomposition and/or oxidative polymerization of additives are the key formation reactions for new cathode/electrolyte interphase (CEI), i.e., the PFPN will be prior to oxidized on active sites of the electrode surface during the CEI film formation process, and then form a new electro-polymerization film to efficiently suppress the continuous degradation of the electrolyte upon the long cycling process.

The results of thermal analysis of the delithiated Li₄CoO₂ (x < 0.5) electrodes demonstrated that in the presence of PFPN or covered with decomposed products of PFPN can greatly reduce the exothermic heat generated form the corresponding thermal reaction, which is only 64% than that of the base electrolyte did below 300 °C. Therefore, we believe that PFPN will be a promising additive to improve the safety of the high energy density batteries with excellent cycling performance as well.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.05.091.

References
