



Tetraethylthiophene-2,5-diylbismethylphosphonate: a novel electrolyte additive for high voltage batteries

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Abstract

In this work, а novel high-voltage electrolyte additive of tetraethylthiophene-2,5-diylbismethylphosphonate (TTD) is synthesized, and the influence of TTD on the electrolyte and its electrochemical performance under different voltages are studied by changing the content of the TTD additive. The results show that the TTD additive significantly improves the capacity, cycle stability and rate capability of batteries when charging/discharging at high voltages. After adding 1% TTD to the basic electrolyte, the capacity retention rate of batteries after 200 cycles at 4.2 V, 4.3 V, 4.4 V and 4.5 V increase by 20.8%, 18.3%, 50%, and 31.9%, respectively. In addition, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) analysis results show that TTD can effectively inhibit the decomposition of the electrolyte and participate in the formation of a uniform, thin and stable cathode electrolyte interface (CEI) film on the electrode surface, thereby effectively inhibiting the side reaction between the electrolyte decomposition product and the CEI membrane, and finally the high voltage performance of the battery is improved. This novel TTD additive used in this work as an

effective strategy to improve the high-voltage performance of the battery, which will provide a cost-effective solution for high-performance high-voltage electrolyte.

Keywords: lithium ion battery; electrolyte; high voltage; CEI film; tetraethylthiophene-2,5-diylbismethylphosphonate (TTD)

Introduction

Lithium-ion batteries have received extensive attention and in-depth research from domestic and foreign research scholars and research institutions due to their advantages of high specific energy, long cycle life, and no memory effect.^[1-4] In recent years, new energy vehicles have been vigorously developed in countries around the world. Under this background, there is no doubt that higher requirements have been put forward on the technology of lithium-ion batteries. Therefore, how to increase the energy density of power batteries and extend the cruising range while ensuring safety and reducing the cost of batteries are the key problems that need to be solved urgently.^[5-9] At present, the electrolyte used in commercial lithium-ion batteries is composed of organic solvent dissolving LiPF₆ electrolyte. Under normal voltage, the electrolyte can effectively guarantee the transport of lithium ions between the two electrodes. However, the commonly used organic carbonate electrolyte will undergo severe oxidation and decomposition when the working voltage exceeds 4.3V, resulting in the increase of the interface impedance between electrode/electrolyte interface, which greatly deteriorates the battery performance.^[10-14] Therefore, in order to solve this problem, the majority of researchers have carried out a series of research work around new high-voltage resistant electrolyte and new electrolyte additives, which provides important ideas for further research.

For example, Zhang^[15] systematically classified electrolyte additives according to different impact mechanisms. Subsequently, researches on additives have gradually increased. In recent years, researchers have further expanded the application range of additives and begin to classify them. Applied to lithium ion batteries with higher specific energy, studies have shown that there are two main technical ways to develop high-voltage electrolytes.^[16] One is to add a small amount of high-voltage additives to the electrolyte to passivate the interface film of positive electrode;^[17-22] the other is to use a new type of anti-oxidation solvent with strong ability to completely or partially replace the existing carbonate solvents with low oxidation resistance.^[23] Dalavi^[24] studied

lithium dioxalate borate (LiBOB) as a high-voltage additive to improve the cycle performance of LiNi_{0.5}Mn_{1.5}O₄ cathodes at high voltages (4.9 V vs Li). The study showed that the addition of LiBOB would improve the cycle performance of LiNi0.5Mn1.5O4 cathodes. Oxidative decomposition and polymerization reaction occur on the surface to form a cathode interface film with low impedance and thin thickness to prevent further oxidation of the solvent in the electrolyte, thereby improving the cycle stability of the high-voltage cathode material. The following years, Hu^[25] et al found that using LiDFOB as an additive can make LiCoPO₄ cathodes show better cycle performance. From the analysis of XPS and FTIR-ATR, LiDFOB helps to form an interphase film and passivate the cathode. Thus, the decomposition of the electrolyte can be suppressed to a certain extent. Compared with LiBOB, LiDFOB helps to form a more stable interfacial film with lower interfacial resistance. The main reason is that one oxalate ion in the LiBOB is replaced by two F atoms, which improves the antioxidant properties of the molecule.^[26] Zhu and coworkers^[27] et al. reported a new type of additive, Diethyl(thiophen-2-ylmethyl)phosphonate (DTYP). Results shown that DTYP can significantly improve the high-voltage cycle stability of LiNi_{0.5}Mn_{1.5}O₄ cathode. At 60 °C, the capacity retention rate of lithium-ion battery is 85% after 280 cycles at 1C (18% without DTYP additive). Similarly, Huang^[28] et al. used 4-(trifluoromethyl)-benzonitrile (4-TB) as a new electrolyte additive, and the results showed that 4-TB can significantly improve the cycle performance of $LiNi_{0.5}Mn_{1.5}O_4$ cathode. And 4-TB can be preferentially oxidized on the surface of the LiNi_{0.5}Mn_{1.5}O₄ cathode to form a low-impedance protective film, thereby preventing the electrolyte from oxidizing and decomposing.

In addition to adding high-voltage additives, researchers have improved the high-voltage performance of lithium-ion batteries by replacing carbonate solvents with new solvents which have strong oxidation resistance. The antioxidant solvents currently studied mainly include dinitriles,^[29] sulfones, ionic liquids and fluorinated reagents, researchers have conducted a lot of in-depth studies on the feasibility of these four types of antioxidant solvents for high-voltage electrolytes. For example, Xiang^[30] and other studies found that the addition of sulfone (tetramethylene sulfone, TMS) will improve the solubility of the lithium salt, and the ionic conductivity is highly compatible with the electrode ionic liquid (PP14-TFSI), and the addition of sulfone will not damage the special performance of the ionic liquid. The results show that the 0.5 M of LiDFOB/(60%) PP14-TFSI/ (40%) TMS mixed electrolyte has better compatibility with the

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cathode of Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ and improves the cycle performance of the battery. However, sulfone is unstable to graphite carbon anodes and has a high viscosity, which is not conducive to the low temperature and high rate performance of LIBs, which limits the widespread use of sulfone. In addition, studies have reported that nitrile solvents can improve electrochemical performance by positively affecting the electrode/electrolyte interface. For example, Wang^[31] et al. found that 3-methoxypropionitrile can improve the charge transfer process at the electrode/electrolyte interface because it can reduce the interface reaction between the solvent and the electrode, and accelerate the desolvation of Li⁺ ions. In addition, adiponitrile (ADN) can form a stable and effective protective film on the surface of the anode and cathode to facilitate capacity retention.^[32-34] In order to meet the needs of high-voltage (5 V) cathode materials, Li^[35] selected the high-voltage electrolyte system of LiDFOB-DEC/EC/ADN, and found that ADN (adiponitrile) can enrich the surface of the cathode material, prevent the electrolyte from further decomposition, and can form a protective passivation film, thereby improving high-voltage performance.

The existing modification work has solved the continuous oxidation decomposition of organic carbonates under high voltage and the solubility of excess metal ions in cathode materials to some extent. However, the problem of organic carbonate electrolytes is that the passivation film formed by the ordinary high-voltage additive on the surface of the positive electrode is unstable, resulting in poor cycle stability of the battery under high voltages. In order to solve this problem, a novel high-voltage electrolyte additive tetraethylthiophene-2,5-diylbismethylphosphonate (TTD) is designed and synthesized in this work, which is used as an electrolyte additive to act on the LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode. A passivation film is formed on the surface of the LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode to stabilize the electrode/electrolyte interface and ultimately improve the high voltage performance of the LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode.

Experimental

Synthesis of TTD

To ensure its purity, TTD was synthesized in the laboratory. 2,5-thiophene dicarboxylic acid (>98%) and triethyl phosphite (>98%) were purchased from Macleans, and LiAlH₄ (97%) was purchased from Aladdin. The synthesis is divided into the following three steps as shown in

Scheme 1: 1) 2,5-thiophene dicarboxylic acid (10 g, 58 mmol) is dissolved in 800 mL of dry tetrahydrofuran, after the mixture is cooled at 0 °C for 20 minutes, the LiAlH₄ (4.4 g, 116 mmol) is added, and then raised to room temperature and the mixture is stirred for 30 minutes. The mixture is heated to 60 °C, and refluxed and stirred for 24 hours. Then the mixture is cooled to 0 °C, and add water to quench the reaction. The mixture is extracted with ethyl acetate (5×200 mL), dried and concentrated with anhydrous sodium sulfate, and the crude product is purified by a silica-gel column with chloroform/ethanol (20:1) as eluent, to obtain the intermediate product of 2,5-dihydroxythiophene. 2) 2,5-dihydroxythiophene (1.44 g, 0.01 mol) is dissolved in 20 mL of dry dichloromethane, then thionyl chloride (3.57 g, 0.03 mol) dropwise is slowly added under the protection of nitrogen, and stirred at room temperature for 10 h, the reaction was processed to obtain 2,5-dichloromeththiophene. 3) 2,5-dichloromethylthiophene is dissolved in N,N-dimethylformamide (DMF), triethyl phosphite is added and stirred at 170 °C for 7 h under nitrogen protection, and the excess DMF was treated with distilled water, then extracted with ethyl acetate, and purified by silica-gel column after rotary evaporation to obtain the final product of tetraethylthiophene-2,5diylbismethylphosphonate (TTD), 2.818g (yield: 73.48%); IR (KBr) (cm⁻¹): 1646 and 1540 (v:C=C), 1480 and 1444 (y:-CH2-), 1393 and 1369 (y:-CH3), 1248 and 1024 (y:P=O), 1164, 718 and 605.5 (y:C-S), 969 and 848 (y:P-O-C), 794.7 (y:P-C), 535.5 (y:C-S-C); 1H NMR (500 MHz, CDCl3) δppm 1.30 (t, J = 7.1 Hz, 12H), 3.27 (d, J = 19.3 Hz, 4H), 4.07 (m, 8H), 6.78 (s, 2H); MS: called for C₁₄H₂₆O₆P₂S: m/z=384, found: m/z=384.12.



Scheme 1. Synthetic routes of tetraethylthiophene-2,5diylbismethylphosphonate (TTD)

Electrode preparation and battery assembly

All the solvents used in this work, such as dimethyl carbonate (DMC), ethyl methyl carbonate

(EMC), ethylene carbonate (EC) and lithium hexafluorophosphate (LiPF₆) are provided by Tianjin Aiweixin Chemical Technology Co, Ltd. The electrolyte is prepared in an argon-filled glove box (Germany MBRAUN), oxygen content < 0.1 ppm, moisture content < 0.1 ppm, 1 M LiPF₆ in DMC/EMC =3:5 (w/w) + PC(4%) is selected as the basic electrolyte and 0.5wt%, 1wt%, 2wt% of TTD as an additive, respectively. The cathode is prepared with a mixture of 90wt% LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) as active material, 5wt% of polyvinylidene fluoride (PVDF) as binder, 5wt% of Super P (SP) as conductive agent, and NMP (N-methyl-pyrrolidone) as a solvent. The mixture is ball-milled to make a uniform slurry and is coated on aluminum foil, and dried at 120 °C for 1 hour. The film is cut into circular pieces with a diameter of 1.2 cm and the area mass loading of the electrode is approximately 3.5 mg cm⁻². The CR2032 NCM/Li button half-cells are assembled with lithium metal as the counter electrode, the electrolyte, and Celgard®3501 (Celgard, Corp., LLC., Charlotte, NC USA) as the separator.

Characterization and electrochemical tests

Linear sweep voltammetry (LSV) test was performed by the CHI660E electrochemical workstation produced by Shanghai Chenhua Company. The linear scan voltammogram was recorded between 2.0 and 6.0 V at a scan rate of 5 mV \cdot s⁻¹. Cyclic voltammetry (CV) and alternating current impedance (EIS) tests of batteries are performed by the Ivium-Stat multi-channel electrochemical workstation produced by Ivium-n-Stat.Xri from Netherlands. The Cyclic voltammograms are recorded at a scan rate of 0.1 mV \cdot s⁻¹ between 2.5 and 4.6 V. Impedance analysis is assessed with frequency range of 100000 ~ 0.01Hz and voltage amplitude of 5 mV. The charge and discharge performance is tested at a current of 0.1 C, and the cycle performance is measured at a current of 0.2 C at room temperature (25 °C), which are performed using the Xinwei battery tester (BTS-5 V/10 mA). The normal voltage range is (2.75~4.2 V), and the high voltage test voltage reaches 4.5 V.

In order to further understand the characteristics of the electrode surface, the battery after cycling is disassembled in an argon glove box, and the cathode electrode piece is rinsed 3 times with DMC to remove the remaining lithium salt and the electrolyte on the electrode surface, and then dried for 12 hours. Electron microscope (SEM) and transmission electron microscope (TEM)

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are observed to analyze the surface morphology of the electrode, and X-ray photoelectron spectroscopy (XPS) is investigated to analyze the surface element composition of the electrode.

Results and discussion

Synthesis and characterization

Under the action of reducing agent LiAlH₄, 2,5-thiophene dicarboxylic acid is reduced into 2,5-dihydroxythiophene. Then the obtained 2,5-dihydroxythiophene is further reacted with SOC1 to form 2,5-dichloromeththiophene. Finally, the nucleophilic substitution reaction of 2,5-dichloromeththiophene with triethyl phosphite is further carried out, and the target compound of tetraethylthiophene-2,5diylbismethylphosphonate (TTD) is obtained. The obtained TTD compound is purified by silica-gel column and then dried any residual impurity under vacuum. The obtained TTD compound is characterized by spectroscopic methods including IR, 1H-NMR and high resolution mass spectrometry (MS) (Figure S1-S3 in supporting information), which are consistent with the proposed structures.

Figure S1 shows the IR spectra of TTD. The peaks at 1646 and 1540 cm⁻¹ can be attributed to the characteristic absorption peak of C=C bond on the thiophene ring. The peaks at 1480 and 1444 cm⁻¹ is the characteristic absorption peak of -CH₂- group, and the peaks at 1393 and 1369 cm⁻¹ is the characteristic absorption peak of -CH₃ group. The peaks at 1248 and 1024 cm⁻¹ can be attributed to the characteristic absorption peak of P=O bond. The peaks corresponding to 1164, 718 and 605.5 cm⁻¹ are the characteristic absorption peak of -C-S bond. The peaks at 969 and 848 cm⁻¹ can be attributed to the characteristic absorption peak of P=O bond. The peaks at 969 and 848 cm⁻¹ can be attributed to the characteristic absorption peak of P-O-C bond, and the peaks corresponding to 794.7 cm⁻¹ and 535.5 cm⁻¹ are the characteristic absorption peak of P-O-C bond, and the peaks corresponding to 794.7 cm⁻¹ and 535.5 cm⁻¹ are the characteristic absorption peak of P-O bond and C-S-C bond, respectively. All the characteristic peaks of the IR spectrum can agree well with the molecular structure of the target compound (TTD). In addition, the data of mass spectrometry (MS) and ¹H NMR spectrum (**supporting information Figure S2-S3**) are completely consistent with the molecular structure of the target compound, which further confirms that the synthesized compound is consistent with the target compound.

Electrochemical performance

Figure 1 shows the linear sweep voltammetry (LSV) curves. The voltage range is 2–6 V (V vs.

Li/Li⁺), and the scanning speed is 5 mV/s. It can be clearly seen that the electrolyte with TTD has a wider electrochemical window than the base electrolyte, indicating that TTD used as an additive can improve the electrochemical stability of the electrolyte. For the pristine electrolyte (0TTD), the current density increases significantly when the scanning voltage is above 4 V. Nevertheless, the current density increases slowly for the electrolyte containing TTD until the decomposition potential is greater than 4.64 V. The starting decomposition voltages of batteries with different electrolyte of 0TTD, 0.5TTD, 1TTD and 2TTD are 3.98, 4.47, 4.29 and 4.64 V, respectively. The results further indicate that TTD can increase the decomposition potential of electrolyte and improve the oxidation stability of electrolyte, and the electrochemical stability window of the battery with 1TTD electrolyte is best.



Figure 1. Linear sweep voltammetry (LSV) curves of batteries with different content of electrolyte

Figure 2 shows the cyclic voltammetry curves of different electrolyte batteries. It can be seen that the cyclic voltammetry curves of the two electrolyte batteries with addition of 0.5 TTD and 1 TTD have higher degree of overlap after the first time, the CV curve of the 2nd, 3rd and 4th times almost completely overlaps. While for the two electrolyte batteries of 0 TTD and 2 TTD, lower overlap in the cyclic voltammetry curves of the next three times was observed. From the overlap of CV curves, it can be predicted that the cycle stability of the 0 TTD and 2 TTD batteries is likely to be relatively worse than the 0.5 TTD and 1 TTD batteries.



Figure 2. Cyclic voltammetry curves of different electrolyte batteries (a) 0TTD; (b) 0.5TTD; (c) 1TTD; (d) 2TTD

The 3rd CV curves and parameters of batteries adding different content of TTD are investigated, as shown in **Figure S4** and **Table 1**, where Φ 1 represents the first pair of oxidation peaks, Φ 2 represents the first pair of reduction peaks, Φ 3 and Φ 4 represent the second pair of oxidation peaks and reduction peaks, respectively. It is generally believed that the smaller the potential difference between the redox peaks, the better the battery stability. It can be seen from **Table 1** that the potential differences of first pair of redox peak for the 0.5TTD and 1TTD batteries are 7 and 5 mV, respectively, and the potential differences of the second pair of redox peak are 66.5 and 65 mV. The potential differences of the first pair of redox peak for the two electrolyte batteries of 0TTD and 2TTD are 35 and 86 mV, respectively. Its obvious that the batteries with 0.5TTD and 1TTD and 1TTD electrolyte have a smaller redox potential difference than those of batteries with 0TTD and 2TTD are stability the batteries with 0.5TTD and 1TTD electrolyte, indicating that the batteries with 0.5TTD and 1TTD electrolyte, the stability of the battery will be improved. However, the addition of excessive TTD may further reduce the stability of the battery.

Electrolyte	$\Phi 1/V$	$\Phi 2/V$	$\Delta \Phi 12/mV$	Φ3/V	$\Phi 4/V$	$\Delta \Phi 34/mV$
0TTD	3.718	3.683	-35	4.2185	4.325	-86
0.5TTD	3.700	3.693	-7	4.2065	4.140	-66.5
1TTD	3.692	3.697	5	4.2070	4.142	-65
2TTD	3.746	3.660	-86	4.229	4.116	-113

Table 1 Redox potential difference of the 3rd CV curves for batteries with different electrolytes

Figure 3 and Figure S5 Shows the initial charge and discharge curves of electrolyte batteries with different TTD additions under different voltages and Table 2 shows the initial coulombic efficiency of different electrolyte batteries. It can be seen that the discharge capacity of electrolyte batteries with different TTD additives is slightly different at the normal voltage of 4.2 V (Figure **3a**). The capacity of 0.5 TTD and 1 TTD cells was increased compared with that of 0TTD battery. After adding 2% of TTD, the capacity of 2TTD battery decreased. The results show that the proper amount of TTD will improve the performance of the battery, but excessive TTD will lead to the decline of the battery performance. With the increase of voltage to 4.3 V, the difference of discharge capacity of batteries with different TTD additives is more obvious (Figure 3b). The capacity of batteries with different TTD of added content shows a similar rule, that is, the capacity of 0.5 TTD and 1 TTD batteries is higher than that of 0TTD battery, while the capacity of excess 2 TTD battery is lower than that of 0TTD battery. With the voltage increasing to 4.4 V and 4.5 V, the capacity of the battery with different TTD is the same (Figure 3c and Figure 3d). No matter at what voltage, the specific discharge capacity of the 0.5TTD and 1TTD batteries are higher than 0TTD battery, but after adding 2TTD, the specific discharge capacity of the battery decreases, which is lower than that of 0TTD battery. A proper amount of TTD significantly improves the high voltage performance of the battery. It can be seen that under the voltage of 4.5V, the specific discharge capacity of the 0TTD electrolyte battery is 226.45 mAh/g when it is formed. When the amount of TTD additives added is 0.5wt%, 1wt%, 2wt%, the specific discharge capacity of the batteries are 233.20 mAh/g, 238.86 mAh/g and 210.94 mAh/g, respectively. The results show that when a small amount of TTD is added, the specific discharge capacity of the battery can be increased, but when excessive TTD is added, the specific discharge capacity of the battery will decrease. Similarly, as can be seen from Figure S5, when a small amount of TTD is added under different voltages, the discharge capacity of the battery also increases, but when an excessive amount of TTD is added, the specific discharge capacity of the battery will decrease. The effect of different TTD additions on the charge-discharge performance of the battery is consistent with that of the CV curves as discussed in **Figure 2**.



Figure 3. The first charge and discharge curves of batteries with different amounts of electrolyte added to TTD

	Table 2. The initial could	ombic efficiency of diff	erent electrolyte batterie	es	
No	Initial coulombic efficiency (%)				
INO.	4.2V	4.3V	4.4V	4.5V	
0TTD	81.9	84.9	90.9	90.1	
0.5TTD	79.0	84.0	87.1	80.4	
1TTD	80.7	86.8	87.5	86.0	
2TTD	82.4	77.0	80.0	75.8	

under different voltages; (a) 4.2V, (b) 4.3V, (c) 4.4V, (d) 4.5V

At the same time, it can be seen from the data in **Table 2** that the first Coulomb efficiency of the battery decreases after adding TTD. The first coulomb efficiency of 0.5% and 1% TTD electrolyte battery was more than 80%, but the first Coulomb efficiency decreased more after adding 2% TTD. At different voltages, the initial Coulomb efficiency of 0TTD electrolyte cell were 81.9%, 84.9%, 90.9% and 90.1% at 4.2, 4.3, 4.4 and 4.5 V, respectively. However, after adding 1TTD, the initial Coulomb efficiency were 80.7%, 86.8%, 87.5% and 86.0% at 4.2, 4.3, 4.4 and 4.5 V, respectively. The results indicate that after adding the TTD, the initial Coulomb efficiency of the battery decreases slightly. It is found from **Table 2**, the initial coulombic

efficiency of 0TTD, 0.5TTD and 1TTD batteries are increased with the increase of voltage from 4.2 V to 4.4 V. Generally, for the ternary cathode material, most of the reaction for forming a CEI film on the surface of electrode sheet is completed before 4 V (usually 3.65 V). The conditions leading to the formation of the CEI electrolyte membrane are not produced at high voltage, but the compact CEI electrolyte film is formed before 3.65 V. Therefore, at different voltages (4.2, 4.3 and 4.4 V), the irreversible capacity consumed by the CEI electrolyte film formed on the electrode surface is substantially less different. However, as we discussed earlier, the capacity contribution generated by the electrodes increases as the charge/discharge voltage increases. As a result, the initial coulombic efficiency of the battery increases with the charge/discharge voltage from 4.2 V to 4.4 V. However, it can also be found from Table 2 that the initial coulombic efficiency of the battery is reduced at a high voltage of 4.5 V compared with 4.4 V, which is due to the decomposition of electrolyte would become more intensive as the voltage reaches above 4.5 V, and at this high voltage, the electrolyte is decomposed so much more that the initial coulombic efficiency is decreased. While when the charge and discharge voltage is below 4.4 V, the electrolyte decomposition is not so serious, making the initial coulombic efficiency of the battery still shows an increasing trend.

As shown in **Figure 4**, the cycling stability of NCM-811 batteries containing different electrolytes under different voltages is studied. At a regular voltage of 4.2 V (**Figure 4a**), the initial discharge specific capacity of the battery without TTD electrolyte is 179.1 mAh/g, while the initial discharge specific capacity of the batteries with 0.5TTD, 1TTD and 2TTD are 188.5, 189.7 and 183.4 mAh/g, respectively. After 200 cycles, the capacity retention rates of 0TTD, 0.5TTD, 1TTD and 2TTD batteries are 63.5%, 74.9%, 84.3% and 67.4%, respectively. Compared with 0TTD, both the initial capacities and the capacity retention rates after 200 cycles of 0.5TTD, 1TTD and 2TTD batteries are improved significantly. Especially for the 1TTD battery, the capacity retention rate is increased by 20.8% compared with the 0TTD battery. As the charge/discharge voltage rises to 4.3 V (**Figure 4b**), the initial discharge specific capacity of the batteries of 57.1%, 70.8%, 75.4% and 58.8% after 200 cycles. As can be seen, the cycle performance of the electrolyte battery after adding TTD additives is obviously improved. In **Figure 4c**, as the charge/discharge voltage continues to increase to 4.4 V,

the capacity retention rate of 0TTD, 0.5TTD, 1TTD and 2TTD batteries are 27.01%, 54.17%, 77.0% and 58.25%, respectively. The results show that the TTD additives can effectively improve the cycle performance of the battery. Especially under high voltage of 4.5 V, the initial discharge specific capacity of the battery without TTD electrolyte is 201.11mAh/g, while the initial discharge specific capacity of batteries with 0.5TTD, 1TTD and 2TTD electrolyte are 217.89, 219.95 and 210.39 mAh/g, respectively. After 200 cycles, the capacity retention rates are 24%, 49.1%, 55.9% and 51.9%, respectively. It can be seen that after adding TTD additives, the cycle performance of the battery is significantly improved. Compared with 0TTD, the capacity retention rate of 1TTD is increased by 31.9%. It can be seen from Figure 4 that, no matter at which voltage, the battery cycle performance with 1TTD electrolyte is the best. That is to say, with the increase of TTD addition, the performance of the battery is improved, and when added content of TTD is 1%, the performance of the battery reaches the optimal value. After that, increasing the amount of TTD, the cycle performance of battery will deteriorate. This is mainly due to the TTD stabilization effect on electrolyte decomposition by-products and the composition, thickness, uniformity and compactness of CEI films are different at different voltages, which will be discussed in detail in subsequent mechanism analysis.



Figure 4. 0.2 C cycle performance graph of batteries with different TTD addition amounts of electrolyte under

different voltages; (a) 4.2 V, (b) 4.3 V, (c) 4.4 V, (d) 4.5 V

Figure 5. Shows the rate cycle curves of batteries with different amounts of TTD in electrolyte under different voltages. It can be seen that the rate performance of the battery is significantly improved after adding right amount of TTD. However, when an excess of TTD is added, the rate performance of battery will deteriorate significantly, especially at high rate of 5 C, the capacity attenuation is more obvious. When the addition of TTD was 0.5% and 1%, the rate performance of 0.5 TTD and 1 TTD batteries are obviously improved compared with 0TTD battery. It can be seen from Figure 5a and Figure 5b that the discharge capacity of batteries with different TTD content at different charge and discharge rate under voltage of 4.2 V and 4.3 V is different, but the difference is not significant. Nevertheless, the discharge capacity difference of the battery with different TTD content at different rate is more obvious at the large charge and discharge voltage of 4.4 V and 4.5 V (Figure 5c and Figure 5d). The discharge capacity of batteries without TTD at different rates varies greatly from that of batteries with 1% of TTD added to the electrolyte, especially at high rate of 5 C. The batteries with 1% of TTD has the best rate performance. Under 4.5 V, its discharge specific capacity at 0.2 C, 0.5 C, 1 C, 2 C, 5 C, and 0.2 C rates are 201.8, 193.5, 183.0, 173.58, 163.3, and 196.0 mAh/g. While for the batteries without TTD, the discharge capacity at different rates of 0.2 C, 0.5 C, 1 C, 2 C, 5 C are 201.5, 185.7, 173.9, 159.7 and 140.50 mAh/g, respectively.

Moreover, an interesting phenomenon has been observed, that is, after 5 C of large rate charge and discharge, and then back to 0.2 C, the battery with TTD shows a higher capacity value than 0TTD battery, indicating that the addition of TTD can also improve the capacity recovery of the battery after large rate charge and discharge. For example, the specific discharge capacities of batteries charge/discharge under 4.5 V at 5 C with 0TTD, 0.5TTD, 1TTD, and 2TTD electrolytes are 140.5, 156.6, 163.3, and 133.5 mAh/g, respectively. And when go back to charge/discharge at low rate of 0.2 C, the specific capacities are 181.7, 200.3, 196.0, and 182.0 mAh/g, respectively. As can be seen from **Figure 5**, the capacity recovery degree of 0 TTD battery is the lowest at different voltages. With the addition of TTD to the electrolyte, the capacity recovery rate of the battery after large rate charge and discharge is obviously improved, in which the capacity recovery rate of 0.5 TTD and 1 TTD is the highest. The results indicates that TTD additives can not only effectively increase the cycle and rate performance of the battery, but also effectively restrain the damage effect of large rate charge and discharge on the battery.



Figure 5. Rate cycle performance of batteries with different content of TTD in electrolyte under different voltages; (a) 4.2 V; (b) 4.3 V; (c) 4.4 V; (d) 4.5 V

Generally, the effect of electrolyte composition on the performance of the battery depends mainly on the CEI film formed on the surface of NCM-811 particles during the charge-discharge process, so that results in the improvement of the stability of the interface between NCM-811 and the electrolyte, which can also be reflected from the change in the interface impedance of the battery after cycling. **Figure 6** reflects the EIS impedance of the electrodes with pristine electrolyte and electrolytes containing different content of TTD. The characteristic concave semicircles at high frequency and the slope line at low frequency are observed. The former semicircles represent the transfer resistance of lithium ions in the electrolyte and the interface issence. As can be seen, the batteries without TTD (0TTD) show the largest semicircle diameter in the high frequency region, indicating that 0TTD batteries have the largest resistance of the lithium ions in the electrolyte. After adding TTD to the electrolyte, the semicircle diameter in the high frequency region of the batteries is reduced, especially for the 1TTD electrolyte battery, the semicircle diameter in the high frequency region is the smallest. The results show that the addition of TTD can effectively reduce the impedance of the electrolyte. However, the EIS impedance of 0 TTD,

0.5TTD and 2 TTD electrolyte cells appear second semicircles in the intermediate frequency region after charge-discharge formation at high voltage of 4.5 V. Generally, the semicircle in the intermediate frequency region is mainly attributed to the interfacial impedance of the CEI film. For the 0TTD battery, a CEI film formed on the electrode surface is thicker and the interface impedance is large. As a result, the semicircle in the intermediate frequency region can be observed. With the addition of TTD, the CEI film is thinner and more uniform, and the composition of the CEI film is more favorable for lithium ion transmission, which makes the interface impedance of the CEI film decrease. When the amount of TTD is 1%, the interface impedance is the smallest, so that the semicircle is not observed in the intermediate frequency region. When the TTD content is too high (2 TTD), the CEI film is more compact, which leads to the increase of the interfacial impedance of the CEI film, and the semicircle can be also observed obviously in the intermediate frequency region. The data of EIS impedance are consistent with the data of previous cycle and rate performance, which further explains the effect of TTD on the formation of CEI film and its effect on impedance and even electrochemical performance.



Figure 6. EIS impedance of batteries with electrolyte adding different content of TTD under different voltage (a)

4.2V, (b) 4.3V, (c) 4.4V, (d) 4.5V.

Mechanism analysis

Different electrolyte components show different electrochemical properties. From the above electrochemical analysis, it can be concluded that the performance of battery with 1% TTD electrolyte is the best, and the performance of battery with 0% TTD electrolyte is the worst. Therefore, in order to further analyze the mechanism of the influence of different electrolytes on the battery performance, the electrodes of the 1TTD battery with the best performance and the 0TTD battery with the worst performance are selected as the following characterization and analysis objects. Figure 7 shows the SEM images of NCM-811 electrode sheet before and after 5 cycles. For the pristine NCM-811 electrode sheet without charge/discharge, the typical particles of NCM-811 ternary cathode materials can be clearly observed, and the surface of NCM-811 particles is smooth and clean without any other deposits or films attached (Figure 7 a-c). While for the NCM-811 electrode sheet with 0TTD electrolyte after charge/discharge at 4.5 V for 5 cycles, a thicker and uneven deposited film can be observed on the surface of NCM811 particles, so that the NCM-811 active particles can not be clearly observed (Figure 7 d-f). After adding 1TTD into the electrolyte, for the NCM-811 electrode sheet with 1TTD electrolyte after charge/discharge at 4.5 V for 5 cycles, the surface of NCM-811 active particles is smooth and can be clearly observed, only a thin and uniform film covering on the surface of NCM-811 positive particles (Figure 7 g-i). The results show that the thickness and uniformity of CEI film formed on the surface of cathode particles after charge-discharge cycle is different for electrolyte with different content of TTD, which will be the key factor affecting battery performance.



Figure 7. SEM images of (a-c) pristine NCM-811 electrode sheet without charge/discharge; (d-f) NCM-811 electrode sheet with 0TTD electrolyte after charge/discharge at 4.5 V for 5 cycles; (g-i) NCM-811 electrode sheet with 1TTD electrolyte after charge/discharge at 4.5 V for 5 cycles

EDS spectra of the cathode sheets from different electrolyte batteries were investigated to further confirm the formation of the CEI film, as shown in **Figure 8** and **Table 3**. For the fresh cathode sheet without charge/discharge, the surface of the cathode particles is smooth, without any deposits attached (**Figure 8a**), and the EDS energy spectrum show that the percentage content of C(wt%), O(wt%), F(wt%) and P(wt%) elements are 8.43%, 33.73%, 1.78%, and 0.04%, respectively (**Figure 8b**). While after 5 cycles, the surface of the cathode particles of the 0 TTD battery is obviously attached to the deposit (**Figure 8c**), and the EDS test results show that the content of C (wt%), O (wt%), F (wt%) and P (wt%) elements are 12.66%, 43.74%, 8.44% and 0.39% respectively (**Figure 8d**). There is no doubt that the element contents on the surface of the cathode surface of the cathode particles is formed on the cathode surface after 5 cycles. However, for the batteries adding 1TTD after 5 cycles, the CEI film is also changed (**Figure 8e**). The EDS spectra show that the content of C and O elements decreases while the the content of F element increases, and a new element S is observed with a content of 0.02%

(Figure 8f). This proves that the composition of RCOOLi and Li₂CO₃ in the CEI layer decreases, while the composition of LiF increases, and the existence of S and P elements further indicates that the TTD additive is effectively involved in the formation of CEI membrane, priority to generate the CEI membranes containing F, S and P elements, which may inhibit the further decomposition of electrolye, and will be further discussed in the following XPS spectra.



Figure 8 SEM and EDS spectra of different electrolyte batteries before and after 5 cycles at room temperature (a,b)

fresh;	(c,d) 0	TTD;	(e,f)	l TTD
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Samples	C(wt%)	O(wt%)	F(wt%)	P(wt%)	S(wt%)	Ni(wt%)	Mn(wt%)	Co(wt%)
Fresh	8.43	33.73	1.78	0.04	0	46.64	2.65	6.72
0 TTD	12.66	43.74	8.44	0.39	0	28.68	1.81	4.28
1 TTD	9.43	37.58	9.73	0.37	0.02	35.01	5.38	2.10

Table 3. EDS spectrum data of different electrolyte batteries before and after 5 cycles

In order to further explore the thickness and uniformity of the CEI film formed on the surface of cathode materials, the TEM images of the NCM-811 electrode sheets before and after cycling are investigated, as shown in Figure 9. For the pristine NCM-811 electrode sheet without

charge/discharge, the outer edge profile of the NCM-811 active particles can be clearly observed, the surface of which is clean and smooth, and no other coverings are found (Figure. 9a-b). After the NCM-811 electrode sheet charge/discharge at 4.5 V for 200 cycles using 0TTD electrolyte, it can be seen that the NCM-811 active particles are surrounded by a film that looks uneven and loose. After analysis and measurement, the thickness of the film is at least 31 nm (Figure 9c-d). However, for the NCM-811 electrode sheet charge/discharge at 4.5 V for 200 cycles using 1TTD electrolyte, a complete, uniform and dense film with thickness of about 20 nm coated on the surface of NCM-811 secondary particles (Figure 9e-f). Compared with the 0TTD electrode sheet, the thickness of CEI film formed on the surface of NCM-811 for the 1TTD electrode sheet is much more uniform, denser and thinner, which is in perfect agreement with the SEM images as discussed in Figure 7. These results further fully demonstrate that the addition of TTD additives will improve the formation of CEI film on the surface of electrode and make the formed CEI film more uniform, dense and thin, which is more conducive to lithium ion transport and more effective protection of electrode materials from electrolyte erosion, which is an important factor that the TTD additives can improve the comprehensive behaviors of lithium ion batteries.



Figure 9. TEM images of NCM811 electrode sheet with different electrolyte batteries, (a, b) original electrode without charge/discharge; (c, d) 0TTD electrolyte after 200 cycles at 4.5V; (e, f) 1TTD electrolyte after 200 cycles

at 4.5V

In order to further analyze the composition and formation mechanism of CEI film on different electrode surfaces, XPS spectra of the cathode sheet before and after cycles was investigated as shown in Figure S6. The characteristic peaks of pristine electrode (fresh) sheet including O 1s peak of LiO- at 531.8 eV, C 1s peak of conductive carbon at 284.5 eV, PVDF at 290.8 eV and 285.9 eV, and F 1s of PVDF at 687.3 eV. These characteristic peaks are also identified in the two electrodes (0TTD and 1TTD) after cycling, but the intensity of the characteristic peaks of the elements changes. For the pristine electrode (fresh), the peaks of C1s and F1s are very strong due to the presence of PVDF, while the peaks of O1s are very weak because of the low content of O elements. After cycling at 4.5 V using 0TTD electrode (base), the characteristic peaks of the F1s and C1s are significantly weakened, while the characteristic peak of the O1s is obviously enhanced, which is due to the fact that the CEI film produced after charge-discharge cycle is covered on the surface of the electrode material, which weakens the peaks of PVDF, and the formed CEI film containing lithium alkyl carboxylic acid enhances the characteristic peak of the O1s. After adding the TTD to the electrolyte, the intensity of O1s and C1s is slightly weakened, while the intensity of F1s is obviously increased, which is due to the change in the composition of the CEI membrane. After adding TTD to the electrolyte, the decomposition products of the electrolyte include C1s of lithium carbonate at 286.5eV and 289.7eV, O1s of lithium carbonate at 531.6 eV, and P2p of $Li_x PF_v$ and $Li_x PO_v F_z$ at 137.3 eV and 133.8 eV, respectively. It can be seen that for the 0TTD electrode after cycling, the peak intensity of C1s and Ols is stronger than that of 1TTD electrode after cycling, and the peak intensity of F1s is weaker than that of 1TTD electrode. In the same P2p spectrum, $Li_x PF_y$ and $Li_x PO_y F_z$ are observed at 137.3eV and 133.8eV, and the intensity is stronger than that of the electrode circulating in 1% TTD electrolyte. This comparison confirms that for the 0TTD electrode after cycling, there is more electrolyte decomposition than the 1TTD electrolyte.

In order to further analyze the components corresponding to different elements, the C1s, O1s, F1s, P2p and S2p XPS spectra corresponding to different electrolyte electrodes were compared and analyzed. Figure 10a-c shows the C1s XPS spectra of different electrolyte battery electrode sheets, for the electrode without charge/discharge process, only two peaks corresponding to PVDF and C-C bond are observed (Figure 10a). After charging and discharging, the peak of PVDF disappeared due to the formation and coverage of the CEI film. For the base electrolyte

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electrode (0TTD), four peaks are observed at 284.5, 286.5, 288.5 and 289.7 eV respectively, corresponding to C-C, C-OR, COOR and MCO₃ (Figure 10b), indicating that the CEI film formed on the basic electrolyte electrode contains Li₂CO₃ and a little mount of alkyl carboxylic acid lithium. While for the 1TTD electrolyte electrode, five peaks corresponding to C-C, C-S, C-P, COOR and MCO₃ at 284.5, 285.6, 286.7, 288.4 and 289.7 eV are observed (Figure 10c), suggesting that CEI membrane contains a new component containing C-S and C-P bonds in addition to the Li₂CO₃ and a small amount of alkyl lithium carboxylic acid. This can be also confirmed from the O1s XPS spectra as shown in Figure 10d-f. In the electrode without charge/discharge process, only the peak corresponding to the surface contaminants such as Li₂CO₃ is observed, which is the reaction product of NCM-811 with moisture and CO_2 in the air (Figure **10d**). However, after the electrode charged and discharged, for the 0TTD electrode sheet, a strong Li-O peak is observed at 531.5 eV, and a weaker COO bond peak is observed at 532.2 eV (Figure **10e**), further confirming the existence of Li₂CO₃ and a small amount of alkyl lithium carboxylate in the CEI membrane. After adding TTD to the electrode (1TTD), the intensity of Li-O and C-O bonds decreased obviously (Figure 10f), indicating that that the content of Li₂CO₃ and lithium alkyl carboxylic acid in the CEI film decreased, which is due to a new component containing P=O bonds appears at 532.1 eV formed in the CEI membrane. In addition, in the F1s XPS spectra, a strong PVDF peak at 688.3 eV is observed for the pristine electrode without charging and discharging process (Figure 10g). However, for the 0TTD electrode after charging and discharging process, a strong LiF peak at 685.1eV and two weak shoulder peaks at 686.1 and 687.5eV correspond to Li_xPF_y and Li_xPO_yF_z can be observed (Figure 10h), indicating that in the CEI film of the basic electrolyte electrode (0TTD), the main components are ROCO₂Li, Li₂CO₃, LiF, Li_xPF_y and Li_xPO_yF_z. While for the 1TTD electrode, the strong LiF peak at 685.1 eV and a weak wide peak at 687.4 eV is observed (Figure 10i), further indicating that the main component of the CEI film in the 1TTD electrolyte electrode is composed of other new components containing novel P-F bonds besides ROCO₂Li, Li₂CO₃ and LiF. In order to further explore the mechanism of CEI membrane formation, P2p XPS spectra were further examined as shown in Figure 10j. Its obvious that there are no P elements in the electrode without charging/discharging process. For the 0TTD electrode after charging/discharging process, a wide weak peak corresponds to $Li_x PF_v$ and $Li_x PO_v F_z$ is observed. However, after adding TTD to the electrolyte, a more stronger peak corresponds to P-F bond is observed, further confirming that a novel component containing P-F bonds is formed in the CEI film of 1TTD electrode. In the F1s spectra (**Figure 10k**), the Li salts mainly contain ROCO₂Li, Li₂CO₃, LiF and a little amount of Li_xPF_y and Li_xPO_yF_z in the 0TTD electrode, while in the 1TTD electrode, the CEI film only contains Li₂CO₃ and LiF, and in addition a little amount of Li₂SO₃ is also contained which can be observed in the S1s spectra as shown in **Figure 10**.



Figure 10. XPS spectra of different electrolyte battery electrode sheets; (a, b, c) C1s spectra; (d, e, f) O1s spectra; (g, h, i) F1s spectra; (j) P2p spectra; (k)) Li1s map; (l) S2p map (where fresh is the original pole piece, base is the electrode piece with 5 cycles of basic electrolyte, and TTD is the electrode piece with 1% TTD electrolyte circulating 5 times, B.E. is the Binding Energy)

Figure 11 shows the infrared spectra of different electrolyte batteries before and after 5 cycles. For the pristine un-cycled fresh electrode sheet, the peaks of 800 cm⁻¹, 1100-1200 cm⁻¹ and 1384 cm⁻¹ are ascribed to the PVDF binder. While for the electrode sheet cycled in the basic electrolyte, in addition to the characteristic peaks of PVDF at 800 cm⁻¹, 1100-1200 cm⁻¹ and 1384 cm⁻¹, some new characteristic peaks are observed, such as the peak of Li_xPF_y at 878.4 cm⁻¹, the peak of Li_xPO_yF_z at 1277.2 cm⁻¹, the peak of Li₂CO₃ at 1438.9 cm⁻¹, as well as the peak of ROCO₂Li at 1638.9 cm⁻¹. This is due to the formation of CEI film after cycling, and the composition of the film is composed of Li_xPF_y, Li_xPO_yF_z, Li₂CO₃ and ROCO₂Li. However, for the electrode sheet cycling with 1TTD electrolyte, the characteristic peaks of PVDF at 800 cm⁻¹, Li₂CO₃ (1438.9 cm⁻¹), ROCO₂Li (1638.9 cm⁻¹) are observed, and a strong new peak of PO3 at 1048.5 cm⁻¹ appears, which indicates that the CEI membrane contains PO3 bond-containing compounds corresponding to the TTD-(PF₃) complex in addition to the lithium salt of LixPFy, LixPOyFz, Li₂CO₃ and ROCO₂Li. The results fully suggest that TTD participates in CEI film formation, which is consistent with the XPS result of **Figure 10**.



Figure 11. IR spectra of battery electrode sheets with different electrolytes before and after 5 cycles

As can be concluded from XPS spectra in **Figure 10** and **Figure 11**, the CEI film formed by the pristine electrolyte (0TTD) battery mainly includes ROCO₂Li, Li₂CO₃, LiF and a little amount of Li_xPF_y and Li_xPO_yF_z. Nevertheless, after adding TTD to the electrolyte, the CEI film formed on the electrode surface of 1TTD electrode contains a new component containing C-S, C-P, P-F and

P-O₃ bonds in addition to the Li salts of LiF, Li₂CO₃. This is mainly due to the different mechanism of CEI film formed by different electrolyte components. When the battery is first charged and discharged, the DMC, EMC and PC solvents in the base electrolyte participate in the formation reaction of the CEI membrane, as shown in the reaction formulas (1) - (4), respectively. As a result, the components in the resulting CEI film contains lithium alkyl carboxylate (ROCO₂Li) and Li₂CO₃. Furthermore, during the charge-discharge process, the LiPF₆ in the electrolyte will decompose under the action of water to produce lithium salts of LiF, Li_xPF_y and Li_xPO_yF_z, as shown in the reaction formulas (5) - (7). Therefore, for the base electrolyte (0TTD), the CEI film mainly contains Li₂CO₃, LiF, ROCOOLi, Li_xPF_y and Li_xPO_yF_z lithium salt components.

$$H_{3}C_{O}C_{O}CH_{3} + e^{-} + Li^{+} \longrightarrow CH_{3} + H_{2}C_{O}C_{O}Li / CH_{3}OLi + H_{3}C_{O}C_{O}C_{O}$$
(1)

DMC

$$C_{2}H_{5} O C_{1}H_{5} O C_{1}H_{3} + e^{z} + Li^{+} \longrightarrow C_{2}H_{5} + H_{2}C O C_{1}H_{5} C_{2}H_{5}OLi + H_{3}C O C_{1}H_{5}OLi + H_{3}OLi + H_{5}OLi + H_{5}OLi + H_{5}OLi + H_{5}OLi + H_{5}OLi$$

$$\begin{array}{cccc} H_{3}C - C & H_{2} \\ 2 & O & O \\ 2 & O & O \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & &$$

trace
$$H_2O + R_0 \stackrel{O}{\leftarrow} Li + Li^+ \longrightarrow Li_2CO_3 \downarrow + R-OH$$
 (4)

$$LiPF_6 + H_2O \longrightarrow LiF_{\downarrow} + 2 HF + PF_3O$$
 (5)

$$PF_{6^{-}} + n e^{-} + n Li^{+} \longrightarrow LiF \checkmark + Li_{x}PF_{y} \checkmark$$
(6)

$$PF_{3}O + ne^{-} + nLi^{+} \longrightarrow LiF \downarrow + Li_{x}PO_{y}F_{z} \downarrow$$
(7)

Scheme 2 Formation reaction of the CEI membrane

Nevertheless, the CEI film formed by the base electrolyte (0TTD) is not stable, and the side reactions such as (9)-(12) will occur under the action of the HF formed by the reaction formula (5) and the decomposition products of the PF_5 formed by the reaction formula (8). This conclusion is in well agreement with the SEM and TEM images. The thickness of the CEI film on the 1TTD electrode surface is much thinner than that on the 0TTD electrode surface. The main reason is that

after adding the TTD additive, the composition of lithium alkyl carboxylic acid and Li₂CO₃ in the CEI film formed on the electrode surface is reduced. This conclusion is completely consistent with the results in the SEM and TEM images (**Figure 7** and **Figure 9**). It can be clearly observed in the SEM and TEM images that the CEI films formed on the surface of the electrolyte electrode are very uneven, which is due to the decomposition reaction of some ROCOOLi and Li₂CO₃ lithium salts.

$$\text{LiPF}_6 \longrightarrow \text{LiF}_{\downarrow} + \text{PF}_5$$
 (8)

$$HF + ROCOOLi \longrightarrow LiF + ROCOOH$$
 (9)

$$HF + Li_2CO_3 \longrightarrow LiF \downarrow + H_2O + CO_2 \uparrow$$
(10)

$$2 \operatorname{ROCOOLi} + \operatorname{PF}_5 + \operatorname{H}_2 O \longrightarrow 2 \operatorname{LiF} + 2 \operatorname{ROCOOH} + \operatorname{PF}_3 O$$
(11)

$$\text{Li}_2\text{CO}_3 + \text{PF}_5 \longrightarrow 2 \text{LiF} + \text{PF}_3\text{O} + \text{CO}_2 \uparrow$$
 (12)



Scheme 3 TTD inhibition of side reactions by decomposition products of the PF₅ and HF

Nevertheless, unlike 0TTD electrolyte electrode, the CEI film formed on the surface of the 1TTD electrolyte electrode is very uniform. This is mainly due to the different CEI membrane reaction mechanisms after the TTD was added to the electrolyte. As shown in the reaction formula (13), after TTD is adding to the electrolyte, the oxygen of phosphate in TTD molecules preferentially participate in the formation of CEI membranes, which will neutralize PF5 derived from the decomposition product of LiPF₆ through acid-base coordination react, and finally generate the compound TTD-(PF₅) complex covering on the surface of the electrode, and quickly forms a stable CEI film which stabilizes the decomposition products PF₅, avoids the subsequent side reactions of (11)-(12). This is why after the addition of TTD, a uniform and thin CEI film is formed on the electrode surface. The main components of the CEI membrane are LiF, TTD-(PF₅) complex and a small amount of Li₂CO₃. For the TTD additive, the oxygen of phosphate in the TTD molecule has the ability to neutralize PF5 through acid-base coordination,^{127-28, 36-371} and to form a stable TTD-(PF₅) complex on the surface of electrode. Compared with the base electrolyte battery (0TTD), the uniform and thin CEI film formed on the surface of 1TTD electrode consumes

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less irreversible lithium and has a smaller interface impedance of the CEI film, which is more favorable for the transport of lithium ions, thus showing better cycling performance, rate performance and high voltage performance. And this is why TTD 1 battery shows better cycling performance, rate capability and high voltage performance than TTD 0 battery.

4 Conclusion

In this work, a novel electrolyte additive, tetraethylthiophene-2,5-diylbismethylphosphonate (TTD), is added to the basic electrolyte in order to improve the high-voltage performance of lithium-ion batteries. As a result, the addition of TTD preferentially participates in the formation reaction of CEI film, avoids the side reactions of LiPF₆ decomposition products HF and PF₅, thus improves the uniformity of CEI film, reduces the thickness of CEI film, and makes the formation of CEI film consume less irreversible lithium. At the same time, the interface impedance of the CEI film is reduced, which is more favorable for ion transport. Finally, the battery with a 1% TTD content shows the best cycle performance, rate performance and high voltage performance. The TTD additives used in this work and the analysis of the improvement mechanism of battery performance would provide new ideas and references for the development of high-performance of high-voltage electrolytes.

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