Improved Thermal Stability of LiCoO$_2$ by Cyclotriphosphazene Additives in Lithium-ion Batteries

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Fluorinated cyclotriphosphazene is selected as a novel flame-retarding additive in the electrolyte for lithium-ion batteries. The effect of the phosphazenes on the thermal stability of LiCoO$_2$ cathode has been investigated by the thermal analyses on charged LiCoO$_2$ electrodes in the presence of the electrolyte with or without the additives. Possible mechanism for the influence of the additive on the thermal stability of LiCoO$_2$ has been proposed.

In lithium-ion community, more and more attention has been paid to modify the non-aqueous electrolytes by functional additives.[1–6] These additives, despite a very small amount, can play very important roles in lithium-ion batteries, such as triggering SEI (solid electrolyte interface) film formation on the anode surface, protecting overcharge, improving cycle-ability of cathodes, and safety issue, etc. Recently, several groups have explored modification on electrolytes by phosphorous-containing flame-retardants to reduce the fire hazard of lithium-ion batteries.[7–12] Among these flame-retardants, phosphazene-derived compounds are very promising candidates as the nonflammable additives for the electrolytes since the extensive chemistry of phosphazene affords the opportunity for easy structural modification. The phosphazene backbone of alternating nitrogen and phosphorus atoms can be formed in two ways, cyclo- or linear-type, and there are two groups attached to each phosphorus atom in the cyclo-compounds. So the variety in the structure of the groups and the backbone will yield many different chemical and physical properties for the phosphazenes, which can be tailored to satisfy the practical needs in lithium-ion batteries. Hexamethoxycyclotriphosphazene (HMOCPN) has been proposed as an effective flame-retardant additive in lithium-ion batteries,[13] however, it has the shortcomings of high melting point and high viscosity, which lead to lower capacity utilization of the electrode material, lower power, and worse low-temperature performance. In this study, we tried to modify the structure of HMOCPN by fluorine substitution. The details of synthesis can be found in the patent.[14] The effect of this fluorinated cyclotriphosphazene on the thermal stability of LiCoO$_2$ cathode is investigated in the EC (ethylene carbonate)-based electrolyte for lithium-ion batteries.

Two phosphazene-derived flame retardants were added into the base electrolyte of 1 M LiPF$_6$–EC:DMC (1:2 by volume), respectively. The weight portions of the additives account to 5 wt % in the mixed electrolyte. The molecular formulas of both flame-retarding additives are shown in Figure 1. HMOCPN is in a solid state at room temperature. To decrease the melting point, three F groups were attached to the triphosphazene ring. The obtained fluorinated cyclotriphosphazene (FCPN) is in liquid state at room temperature (melting point, lower than −20 °C; boiling point, 170 °C under 1 atm; density, 1.56 g/mL; viscosity, 3.2 mPa·S). The maximum solubility of FCPN in the common electrolytes containing LiPF$_6$ salt can reach 20–25 wt %. If more amount of FCPN was added into the electrolytes, two separated liquid layer could be clearly observed.

R$_1$=R$_2$=OCH$_3$

HMOCPN   FCPN

Figure 1. Molecular formulas of the phosphazene-derived additives.

The effect of the additives on the electrochemical performance of LiCoO$_2$ was tested in CR2032 coin cell. After being charged to desired voltage, the coin cell was disassembled under Ar atmosphere, the LiCoO$_2$ cathode was recovered from the cell and 2 mg cathode material was sealed with 2 mL electrolyte into aluminum pan subject to DSC measurement.

Cyclic voltammetric studies indicate both additives dissolved in the base electrolyte are quite electrochemically stable in the potential range from 2 to 5 V vs. Li/Li$^+$. So it is assumed that there is little decomposition of the additives on LiCoO$_2$ cathode, and thus they can hardly give rise to some detriment influences on the electrochemical performance. Figure 2 shows the initial charge–discharge curves of LiCoO$_2$ at room temperature in the electrolytes with or without the additives, respectively. These three charge–discharge curves are very similar, which may verify the above expectation to some extent. Figure 3 compares the cycling performance of LiCoO$_2$ in the electrolytes with or without the additives. The discharge capacity of LiCoO$_2$ electrode declines against cycles in all these electrolytes. In the case of HMOCPN, the dropdown of the discharge capacity against cycles is the most prominent, while FCPN appears effective in slowing down this
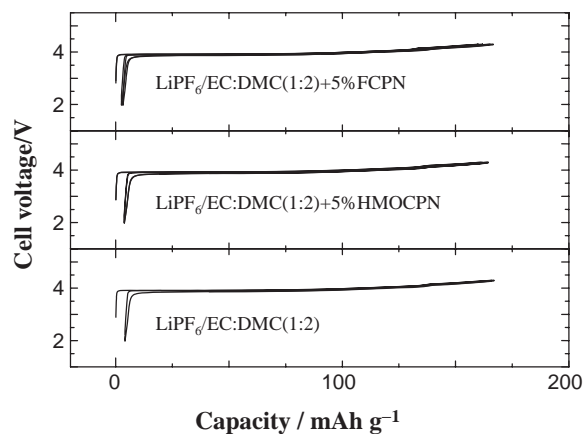

Figure 2. Initial charge–discharge curves of LiCoO$_2$ cathode in the electrolytes with or without additives; the current density was 1 mA/cm^2 and the cutoff voltages were 2 and 4.3 V.
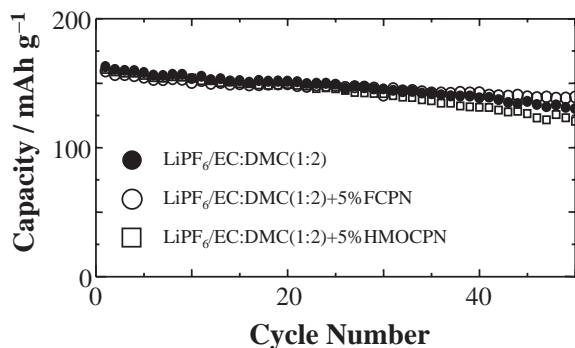
Figure 3. Cycle performance of $LiCoO_2$ in the electrolytes with or without additives.
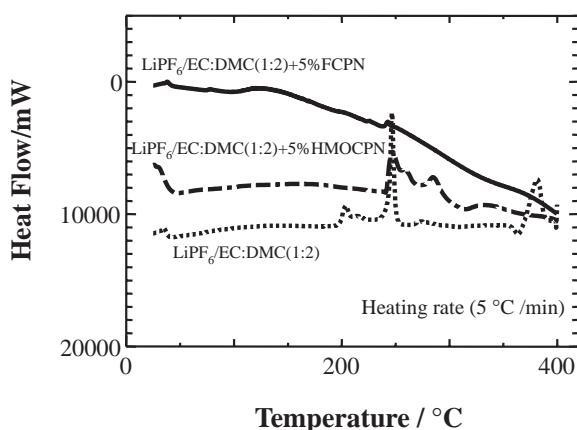

Figure 4. DSC curves of $LiCoO_2$ (2 mg) in the presence of the electrolytes (2 mL) with or without additives.

declining trend as compared with other electrolytes. Thus the superiority of FCPN over the additive HMOCPN could be clearly observed in terms of capacity retention of $LiCoO_2$.

Figure 4 shows the DSC behavior of $LiCoO_2$ charged to 4.3 V with or without the additives. After the addition of the additives, the exothermic peak near 250 °C could be suppressed to some extent as compared with the case for $LiCoO_2$ in the base electrolyte. This exothermic peak originates from the decomposition of $LiCoO_2$ and oxygen release. To investigate the reason for the depression of this heat emission by the additives, we measured the kinetic parameters of this exothermic reaction from DSC tests performed at different ramp rates (°C/min), i.e., the activation energy E_a, the frequency factor A, and the order of the reaction n from Arrehenius's equation:[15]

$$dx/dt = A \cdot \exp(-E_a/RT)(1-x)^n. \quad (1)$$

These kinetic parameters corresponding to the electrolytes with or without the additives are listed in Table 1. Using the kinetic parameters in Table 1, we calculated the heat flow as a function time at a given temperature (700 °C) to compare the effect of the additives on the heat suppression according to the following equation:

$$Q = Q_{TM}(1 - \exp(-kt)). \quad (2)$$

Q_{TM} corresponds to the heat generated from the exothermic reaction at 250 °C, and k equals to $A \cdot \exp(-E_a/RT)$. The temperature of 700 °C was chosen similar to the safety research of lithium ion battery performed by Biensan et al.[16] The result is shown in Figure 5, the heat generation rate becomes very sluggish after the addition of FCPN, so the improvement of thermal stability

Table 1. Kinetic parameters for the exothermic reactions of $LiCoO_2$ cathode (charged to 4.3 V) in the electrolytes with or without additives

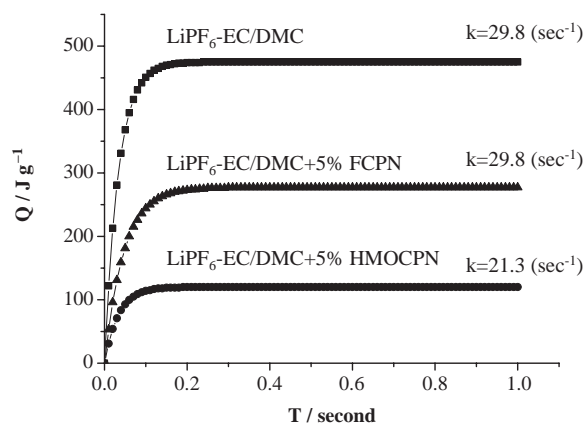| Electrolytes	E_a (kJ/mol)	A (sec^{-1})
1 M $LiPF_6$–EC:DMC(1:2)	100	7×10^6
1 M $LiPF_6$–EC:DMC(1:2)+FCPN	100	7×10^6
1 M $LiPF_6$–EC:DMC(1:2)+HMOCPN	100	5×10^6

Figure 5. Calculated heat generation rates for the $LiCoO_2$ cathode (charged to 4.3 V) in the electrolytes with or without additives.

for the charged $LiCoO_2$ in the presence of FCPN could be clearly seen. The k values for all the three electrolytes are very similar, the influence of the additive could barely been observed on the kinetics, which implies that the additions of HMOCPN or FCPN into the electrolyte don't suppress the decomposition of $LiCoO_2$. Instead, the big difference mainly comes from great contrast in Q_{TM}, as obtained from the exothermic DSC peak near 250 °C. So we believe that the phosphazenes may obstruct the reaction of decomposed products of charged $LiCoO_2$ with the organic solvents, and then the exothermal process was controlled.

In conclusion, the additive of FCPN is very effective in improving the thermal stability of charged $LiCoO_2$ cathode in lithium ion batteries. In the voltage window of $LiCoO_2$ cathode, FCPN is electrochemically stable. Moreover, the addition of FCPN in the electrolyte of 1 M $LiPF_6$–EC:DMC (1:2 by volume) has no detrimental effect on the electrochemical performance of $LiCoO_2$.

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