Ethylene ethyl phosphate as a multifunctional electrolyte additive for lithium-ion batteries

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The effects of ethylene ethyl phosphate (EEP) as a multifunctional electrolyte additive on safety characteristics and electrochemical performance of lithium-ion batteries are investigated. Based on the flammability test, the self-extinguishing time of the electrolyte with 10% EEP is only less than half of the baseline electrolyte, which indicates that EEP is a highly efficient flame retardant for the electrolyte. During overcharging the LiNi0.5Mn1.5O4/Li cells, incorporation of EEP into the electrolyte can postpone the sharp voltage rise. Therefore, EEP is an improver of safety characteristics of lithium-ion batteries, both in terms of flame resistance and overcharge protection. Furthermore, the EEP-containing electrolyte in the half-cells and full-cells both exhibit higher initial coulombic efficiency and cycling stability than the baseline electrolyte. It is concluded that EEP is a good film-formation additive not only for the graphite anode, but also for the LiNi0.5Mn1.5O4 cathode. Therefore, EEP is proposed as a promising multifunctional electrolyte additive for lithium-ion batteries.

Introduction

Lithium-ion batteries (LIBs) have been considered as the most successful secondary battery systems over the past few decades, owing to their contribution on triggering the growth of the consumer electronics market. Now, they are expected to power electric and hybrid electric vehicles, and to store wind and solar energy in smart grids. However, one of the main challenges for the development of lithium ion battery technology comes from the nonaqueous electrolyte. On the one hand, furious reactivity of the electrolyte under some abused conditions, such as overcharge, overheating and short circuit, directly results in safety issues of LIBs.1,4 On the other hand, its poor compatibility with electrode materials can not only restrict the development of high performance electrode materials, but also cause the fading of cell performance. In efforts to develop large-sized LIBs for transportation and grid applications, electrolyte safety and stability have become great challenges.

Introduction of additives into the electrolyte is the economic and efficient strategy to improve the safety characteristics and cell performance in the battery industry. Usually, overcharge protection additives and flame retardant additives are used to improve the safety characteristics of the batteries. The former could postpone the thermal runaway during overcharging the batteries. At present, cyclohexyl benzene (CHB) and biphenyl (BP) are the commonly used overcharge protection additives in commercial electrolytes.5–9 The latter could effectively reduce the harm from thermal runaway and avoid a fire or explosion. The typical representative is organic phosphorous compounds, such as trimethyl phosphate (TMP), dimethyl methylphosphonate (DMMP), etc.10–16 A bifunctional additive with flame resistance and overcharge protection is expected to provide more reliable protection for lithium-ion batteries.17 Film formation additives can tailor interfacial chemistry between the electrolyte and electrode. Many efforts were made in the past to seek improvers to facilitate the formation of a stable solid electrolyte interface (SEI) film on the surface of graphite.18–22 Recently, some cathode film formation additives have been reported to enhance the stability between the electrolyte and cathode, especially for high voltage cathodes (spinel LiNi0.5Mn1.5O4 and Li-rich layered oxide).22–25 Although the integrated electrolyte containing various additives can satisfy cell performance, they definitely increase the complexity and difficulty for the production of the electrolyte. In some commercial electrolytes, dozens of additives are introduced in the electrolyte matrix. Therefore, it is vital to explore multifunctional additives for the electrolyte of LIBs, which will not only simplify the electrolyte system, but also reduce the cost.26–29

Although acyclic phosphate compounds have been widely investigated as flame-retardant additives for the electrolyte of LIBs,10–15 cyclic phosphate compounds are rarely reported. Ota found that ethylene ethyl phosphate (EEP) could improve the compatibility between the trimethyl phosphate (TMP)-based nonflammable electrolyte and graphite anode as a SEI film formation additive.28 In this paper, we explored the feasibility of EEP as a multifunctional additive. The film-formation function

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of EEP was investigated not only on the graphite anode but also on the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 cathode. Additionally, the effects of EEP on the safety characteristics were evaluated in terms of flame resistance and overcharge protection.

**Experimental**

**Materials preparation and cell assembly**

EEP was synthesized as previously described in literature and dried over molecular sieves (4A) before use. It has a melting point below 0 °C, a boiling point above 180 °C and is miscible in the carbonate solvents. An electrolyte of 1 M LiPF_6 in a mixture of 1 : 1 (w/w) ethylene carbonate (EC) and diethyl carbonate (DEC) was selected as a baseline electrolyte. The EEP-containing electrolytes were prepared by adding 10 wt% EEP into the baseline electrolyte in an argon-filled glove box (MBraun).

A positive electrode consisting of LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 (84 wt%), acetylene black (8 wt%) and poly(vinylidene fluoride) (PVDF) (8 wt%) and a negative electrode consisting of graphite (92 wt%) and PVDF (8 wt%) were made on aluminum and copper foils, respectively. The mass loadings of the active materials on the positive electrode and the negative electrode (Φ 14 mm) were about 8 and 4 mg, respectively. CR2032 coin-type cells were assembled in the glove box. A Celgard 2400 microporous polypropylene membrane was used as a separator. An highly pure lithium foil was used as the counter electrode and the reference electrode for the half-cell assembly.

**Measurements on electrochemical properties and safety characteristics**

The electrochemical window of EEP was measured in the stainless steel (SS)/Li coin cells using 1 M LiPF_6/EEP electrolyte by linear sweep voltammetry (LSV) at a scan rate of 0.2 mV s⁻¹. The open circuit voltage (OCV) of the coin cells was 3.35 V. One cell was scanned to 0 V to get the reduction curve and the other to 6.0 V to get the oxidation curve. The cell performance of the EEP-containing electrolyte was evaluated on a multichannel battery cycler (Neware BTS2300). For the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/graphite full-cells and the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/Li half-cells, the charge–discharge tests were carried out between 2.5 and 4.3 V at a current rate of 0.1 C (1 C = 150 mA g⁻¹) during the initial two cycles, followed by a charge–discharge cycling at 1 C. All the graphite/Li half-cells were cycled at the range of 0–3 V at a current density of 15 mA g⁻¹.

To evaluate the effect of EEP on the overcharge protection, LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/Li half-cells containing the electrolyte with/without EEP were overcharged to 6.0 V at 1 C rate on the cycler, after two formation cycles at 0.1 C rate in the potential range of 3.5–4.3 V.

The film-formation property of EEP on the graphite electrodes was measured by cyclic voltammetry (CV) between 0 and 3.0 V at a scan rate of 0.2 mV s⁻¹. Electrochemical impedance spectra (EIS) measurements were performed over the frequency range of 100 kHz to 1 mHz at an amplitude of 10 mV, after the graphite/Li half-cells were cycled for 10 cycles. Both measurements were carried out on a CHI 604D electrochemical workstation. All the electrochemical measurements were performed at room temperature.

The self-extinguishing time (SET) was measured to evaluate the flammability of the electrolytes. Igniting a cotton ball (0.5 g) that has absorbed about 0.2 g electrolyte, we recorded the time it took for the flame to extinguish. Each test was repeated five times and the SET value was obtained by averaging. The detailed procedures are described elsewhere.

**Results and discussion**

The chemical structures of EEP, EC and TMP are shown in Fig. 1. Similar to TMP, EEP was expected to have the flame-retarding property by releasing the radical species containing phosphorus in the flame to scavenge the H⁺ radicals, which are the main active agents of combustion chain branching reactions. EEP with the five-membered ring structure similar to EC, has been validated to be an efficient film formation additive for the TMP-based electrolytes and was capable of preventing the reductive decomposition of TMP on the graphite anode. From the calculation by Gaussian 03 program package (not shown), it is revealed that EEP has higher HOMO energy (−7.87 eV) than EC (−8.23 eV) and DEC (−8.02 eV), which indicates EEP has lower oxidative potential than the carbonate solvents. Previous literature indicated that cyclic phosphate could be polymerized into polyphosphate by cationic and anionic ring-opening mechanisms. Thus, it is expected that EEP could be polymerized to form the cathode–electrolyte interface (CEI) film prior to the oxidative decomposition of EC and DEC, and improve the stability of the electrolyte with the cathode.

As shown in Fig. 2, the electrochemical window of EEP was evacuated in the SS/Li half-cells with the electrolyte of 1 M LiPF_6/EEP by LSV. The SS electrode is proved to be stable to even 6 V in the LiPF_6-based electrolyte, due to a passivating behavior from the LiPF_6 salt. During the negative scan, the reductive peak at 1.25 V reveals that EEP can be decomposed to form a passivating layer on the negative electrode, just like a SEI film formation additive does. During the positive scan, a small anodic peak at 4.6 V is correlated to the CEI film formation because of the ring-opening polymerization of partial EEP, after some radical or ionic species are initiated electrochemically.
whereas the reductive current keeps stable at low potentials. oxidative current sharply increases with the positive scanning, oxidative decomposition of EEP at high potential. Therefore, the electrode does not have the function to completely stop the batteries were investigated, in terms of \( EEP \) successfully, the baseline electrolyte, 1 M LiPF6/EC + DEC (1 : 1, w/w), the electrolyte with and without EEP, as shown in Fig. 3. Obviously, the baseline electrolyte, 1 M LiPF6/EC + DEC (1 : 1, w/w), is very flammable because it has quite a high SET of 140 s g\(^{-1}\). This is just a passivating behavior, after which the oxidative stability can be improved kinetically. Subsequently, a sharp current rise starts at 5.5 V, which is possibly due to the in-depth polymerization and oxidative decomposition of EEP. Here, even though EEP can form the passivating films on both the cathode and the anode, they are still quite different. The SEI film on the negative electrode is an electronic insulation, thus the reductive decompositions of EEP and the other components will be prevented after the compact film is built. However, the CEI film formed on the positive electrode does not have the function to completely stop the oxidative decomposition of EEP at high potential. Therefore, the oxidative current sharply increases with the positive scanning, whereas the reductive current keeps stable at low potentials.

The effects of EEP on the safety characteristics of lithium-ion batteries were investigated, in terms of flame resistance of the electrolyte and overcharge protection of the batteries. Here, the self-extinguishing time was used to evaluate the flammability of the electrolyte with and without EEP, as shown in Fig. 3. Obviously, the baseline electrolyte, 1 M LiPF6/EC + DEC (1 : 1, w/w), is very flammable because it has quite a high SET of 140 s g\(^{-1}\). After 10 wt% EEP was added, the SET value of the EEP-containing electrolyte drops to 65 s g\(^{-1}\), which means that the flammability of the electrolyte has been obviously inhibited. According to previous literature, flame resistance of EEP seems to be weaker than that of DMMP, which can make the electrolyte nonflammable (SET = 0 s g\(^{-1}\)) at the addition of 10%,\(^{14}\) but is comparative with TMP.\(^{12}\) The flame resistance of EEP has also been confirmed by the images of the cotton balls after the flammability testing (inset in Fig. 3). After the flammability testing, the typical cotton ball absorbing the baseline electrolyte is scorched, but the one absorbing the EEP-containing electrolyte is intact. Herein, even though the EEP-containing electrolyte is not completely nonflammable because of the limited content of EEP, the 50% reduction in flammability is still a great advancement compared to previous literature.\(^{17,37,38}\)

In order to evaluate the effect of EEP on the overcharge protection, LiNi1/3Co1/3Mn1/3O2/Li half cells were overcharged to 6.0 V at 1 C rate, after two formation cycles at 0.1 C rate in the potential range of 3.5–4.3 V, as shown in Fig. 4. Before the cells were overcharged to 4.5 V, no significant differences on the voltage profiles were observed. In the potential range of 4.5–5.5 V, the cell using the EEP-containing electrolyte delivers slightly higher capacity than that using the baseline electrolyte. The charge voltage rises up sharply to 6.0 V in the absence of EEP, but quite slowly with appearance of a voltage plateau between 5.5 and 5.8 V in the electrolyte with EEP. Basically, incorporation of 10% EEP to the electrolyte can effectively postpone the voltage rise to 6.0 V for about 10 h. EEP has the tendency to sacrifice polymerize and form a high-resistance passivating layer, which blocks charge transfer in the inner, and thus improves the safety characteristics of the battery. Herein, the 10 h delay for an accident will significantly improve the safety characteristics of the battery system.

Based on the LSV results (Fig. 2), EEP should have the film-formation function on the surface of the graphite anode. Fig. 5 shows the initial CV curves and voltage profiles of the graphite/Li half-cells with two electrolytes. In Fig. 5A, both the cells with the baseline electrolyte and the EEP-containing electrolyte have a couple of typical redox peaks at 0.5–0 V, mainly similar to 1,3-dioxolane.\(^{26}\) This is just a passivating behavior, after which the oxidative stability can be improved kinetically.
corresponding to lithium insertion/extraction in the graphene layers of the graphite crystal. However, it is obvious that the cell with the EEP-containing electrolyte exhibits higher reversibility than the one using the baseline electrolyte. For the baseline electrolyte, a broad peak at about 0.3 V is caused by the reductive decomposition of carbonates. Although EEP helped to build an energetic SEI layer on the surface of graphite, the irreversible reductive decomposition of carbonates was suppressed. As shown in Fig. 5B, the cell using the EEP-containing electrolyte has higher coulombic efficiency (93.6%) compared to the one using the baseline electrolyte (85.6%), which is consistent with the higher reversibility of the EEP-containing electrolyte in Fig. 5A. But, the graphite/Li half-cells with two electrolytes exhibit a comparative discharge capacity (lithium insertion/extraction) in the low current density of 15 mA g\(^{-1}\). The film formation property of EEP is also further supported by the EIS measurements. Fig. 6 shows the Nyquist plots of the graphite/Li half-cells after two formation cycles and the equivalent circuit. Each Nyquist plot is comprised of two semicircles in the high-to-medium frequency range and a straight line in the low frequency range. The high frequency semicircle is related to Li\(^+\) migration through the SEI film, whereas the medium frequency semicircle is attributed to the charge transfer process. The straight line in the low frequency range is related to the Li\(^+\) diffusion in the solid, so-called Warburg diffusion. It is distinct that in the EEP-containing electrolyte, EEP helped to build up a higher conductive SEI film than the one formed in the baseline electrolyte. As shown in Fig. 5A, the cell using the EEP-containing electrolyte has the voltage hysteresis during the initial cycle, which indicates higher polarization than the one using the baseline electrolyte. But, that high polarization existing in the formation cycles is not contradictory to the low SEI impedance after the formation cycles. The former shows the feature for the SEI formation, but the latter reflects the character of the stable SEI film. This result is quite similar to the CEI film formation by trimethyl phosphate in our recent paper.\(^{24}\)

Fig. 7 shows the initial voltage profiles and cycling performance of LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\)/Li half-cells using the baseline electrolyte and the EEP-containing electrolyte. From Fig. 7A, both electrolytes in the LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\)/Li half-cells exhibit comparative discharge capacity. But, the EEP-containing electrolyte exhibited higher coulombic efficiency of 89.23% than the baseline electrolyte (86.16%). As shown in Fig. 7B, the cell using the EEP-containing electrolyte delivers a stable discharge capacity of 140 mA h g\(^{-1}\) after 50 cycles, whereas the cell with the baseline electrolyte experiences the capacity fading to 125 mA h g\(^{-1}\). In addition, the coulombic efficiencies of the cell using the EEP-containing electrolyte are higher. For the baseline electrolyte, the gradual capacity drop was triggered after 18 non-fading cycles. One of the reasons is the surface change of the lithium metal anode during the fast Li deposition/stripping at 1 C, along with the impedance increase.\(^{29}\) However, both the higher coulombic efficiency and the stable cycling performance of the EEP-containing electrolyte are supportive of the fact that EEP can form the CEI film to stabilize LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\), similar as trimethyl phosphate for the Li\(_{1-x}\)Ni\(_{0.15}\)Co\(_{0.15}\)Mn\(_{0.54}\)O\(_2\) cathode.\(^{24}\)
In Fig. 8, the cell performance of the EEP-containing electrolyte in the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$/graphite full-cells is compared with that of the baseline electrolyte. The initial discharge capacity and coulombic efficiency in the full-cells are coincident with the results in the half-cells. That is, the EEP-containing electrolyte has the higher initial coulombic efficiency but slightly lower reversible capacity than the baseline electrolyte in the full-cells, owing to the film-formation function on both the cathode and the anode. Herein, the slightly higher discharge capacities of the full-cells result from the higher charge voltage cutoff ($\sim$4.4 V, calculated from the total sum of 4.3 V and the operating plateau ($\sim$0.1 V) of graphite) for the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ cathode, than the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$/Li half-cells where the voltage cutoff is 4.3 V (4.3 + 0 vs. Li/Li$^+$).

After the two formation cycles, the EEP-containing electrolyte delivers the higher capacity of 152 mA h g$^{-1}$ than the baseline electrolyte does (145 mA h g$^{-1}$) at 1 C. More importantly, the former exhibits the stable cycling performance, whereas the baseline electrolyte has the obvious capacity fading from 145 to 116 mA h g$^{-1}$ during cycling. After 50 cycles, the capacity retentions (compared with the capacity in the 3rd cycle) of the cells with the EEP-containing electrolyte and the baseline electrolyte are 95% and 80%, respectively. During cycling, both the cells have high coulombic efficiencies close to 100% after the 3rd cycle. At last, it should be mentioned that 10 wt% EEP in the electrolyte used in this paper is the optimized content, as a result of a compromise between safety characteristics and cell performance. The flame-retarding ability of EEP depends on the amount added into the electrolyte. A small amount of EEP (e.g., 5% EEP) has a small contribution on the safety characteristics. However, more EEP is not good in terms of the electrochemical stability and the increased cost of the electrolyte. The viscosity of EEP is much higher than those of the common carbonates (DEC, dimethyl carbonate, propylene carbonate, etc.) at room temperature. Higher content of EEP (e.g., 20% EEP) in the electrolyte is proven to result in inferior cell performance, even though the safety characteristics definitely could be improved.

**Conclusions**

EEP has been investigated as a multifunctional electrolyte additive for lithium-ion batteries. After 10 wt% EEP was introduced into the baseline electrolyte, the self-extinguishing time value was decreased to 50% and the voltage rise to 6 V during overcharge was effectively postponed for 10 h. Besides the improvement on the safety characteristics, EEP led to higher initial coulombic efficiency and stable cycling performance either in the half-cells or the full-cells, because of the good film formation function on both the anode and cathode.
concluded that addition of 10 wt% EEP into the common electrolyte can improve not only the safety characteristics, but also the cell performance of the lithium-ion batteries.

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Notes and references

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