Thermal stability and performance studies of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ with phosphazene additives for Li-ion batteries

Seyoung Ahn · Hyun-Soo Kim · Sunhye Yang · Jung Yun Do · Byung Hwa Kim · Ketack Kim

Abstract Phosphazene derivatives as flame retardant (FR) additives were investigated to evaluate their thermal stability and performance in Li-ion batteries. Hexamethoxy-cyclo-tri-phosphazene (HMTP) and hexaethoxy-cyclo-tri-phosphazene (HETP) were added to the electrolytes of the test cells. Thermal stability and the performance influenced by the additives were evaluated using cathodes prepared with $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$. Concentration dependence on FR properties, rate capabilities, and cycle life was analyzed. The additives formed a surface layer on the cathode. The layer on the cathode reduced electrochemical reaction resistance, which improved the performance of the cells. Optimization studies show that HETP has better FR properties than does HMTP.

Keywords Li-ion batteries · $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ · Flame retardant additives · Electrolytes · Thermal stability · Phosphazenes

S. Ahn · H.-S. Kim · S. Yang · K. Kim (✉)
Battery Research Group,
Korea Electrotechnology Research Institute,
Changwon 641-600, Korea
e-mail: kkim@keri.re.kr

J. Y. Do
Department of Chemistry Education, Pusan National University,
Pusan 609-735, Korea

B. H. Kim
R&D Center, Techno Semichem Company, Ltd.,
Kongju, Chungnam 314-240, Korea

1 Introduction

Safety has become one of the most important concerns in the Li-ion battery industry. In order to resolve safety issues for large batteries, such as the batteries for electric vehicles (EV), hybrid electric vehicles (HEV) [1–3], and uninterrupted power supply (UPS) applications, new materials for Li-ion batteries must be developed and utilized. Electrolytes have been emphasized for safety-related investigations because their main components are flammable solvents. As the demand for high voltage batteries increases, new electrolytes that have wide potential windows must be developed.
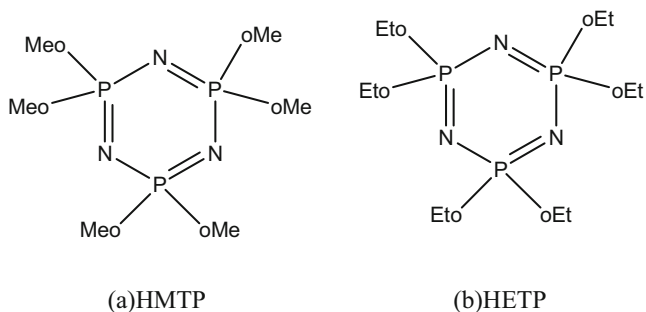
Additives can suppress reactions in batteries, such as exothermic reactions, electrolysis of electrolytes, and gas evolution. However, many additives have negative effects on the performance of batteries. Cyclophosphazenes are very promising as FRs [4–6], because HMTP [5], which has good FR properties, has almost no negative effects on performance.

Compared to $LiCoO_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is relatively stable since oxygen evolution from the compound does not occur until a temperature of almost 250°C is reached, while oxygen evolution from $LiCoO_2$ begins in the temperature range of 190°C to 200°C. Therefore, FR additives combined with $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ can provide improved overall safety compared to those combined with $LiCoO_2$ [7, 8]. Scheme 1 shows the two phosphazene derivatives, HMTP and HETP, used in this study. The HETP molecule has six more carbons than the HMTP molecule. In this paper, the effect of carbon content on the effectiveness of FRs [9] and on the performance of the cells is discussed extensively.

Scheme 1 Phosphazene additives: (a) hexamethoxy-cyclo-tri-phosphazene (HMTP) and (b) hexamethoxy-cyclo-tri-phosphazene (HETP)
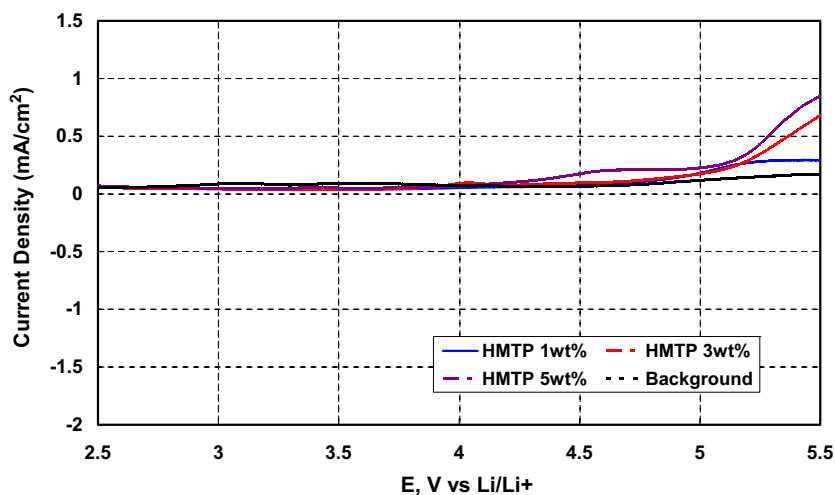
2 Experimental

2.1 Analysis

The electrochemical properties of flame retardant additives in the electrolyte were evaluated by linear sweep voltammetry (LSV) using a model VSP3 potentiostat (Princeton Applied Research). A stainless steel disk was used as the working electrode. A lithium foil serves both as the reference and counter electrodes. The potential was scanned from open circuit potential to 6 V at the rate of 5 mV/s. For comparison purposes, we refer to the electrolyte with no FR additive as 'background'.

The performances of the electrolytes were measured with 2032-type (Hohsen Corp.) coin cells. The active material, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, was well mixed with super p black and polyvinylidene fluoride (PVDF) at a ratio of 86:8:6 in N-Methyl-2 pyrrolidinone (NMP) to make the slurry for the cathode. A lithium foil served as the anode. A 15-μm-thick separator was placed between the two electrodes. All cell preparation was performed in a dry room in which the concentration of water in the air was maintained below 10 ppm.

The cells were cycled between 2.8 and 4.3 V at the rate of $C/5$ ($1C=170$ mAh/g of the active material) for performing two formation cycles. Cell performance was measured using a TOSCAT-2100U (Toyo Systems). Impedance spectra were measured with an IM6 impedance unit (Zahner Electric).

FR properties were evaluated with a differential scanning calorimeter (DSC Q1000, TA) analysis of charged cathode materials. The effects of the additives on oxygen evolution temperatures and heat flow of the cathode material were measured to evaluate the FR properties of the material. The cells were preconditioned by ten cycles at a rate of 0.5°C between 2.8 and 4.3 V. The charged cathode sample was collected for analysis. DSC scans were conducted at a heating rate of 5°C/min from 40°C to 400°C in a nitrogen environment.

2.2 Synthesis of phosphazenes

2.2.1 HMTP

Phosphonitrillic chloride (10.5 ml, 30 mmol) was dissolved in anhydrous benzene (60 ml) and mixed with sodium methoxide (9.92 g, 180 mmol) in methanol (40 ml) at 0°C. The resulting solution was stirred for 20 h at 0°C and 2 h at 15°C. After being concentrated under reduced pressure, the product was vacuum distilled at 0.1 Torr at temperatures of 120°C to 160°C to get methyl cyclotriphosphazene ester as clear liquid (40%). Undistilled residue became viscous resin during the high temperature distillation [10, 11].

2.2.2 HETP

Phosphonitrillic chloride (10.5 ml, 30 mmol) was dissolved in anhydrous benzene (60 ml) and mixed with

Fig. 1 Linear sweep voltammogram on a stainless steel disk in 1.1 M $LiPF_6$ with EC/EMC (4:6 vol.%) containing 1, 3, and 5 wt% HMTP
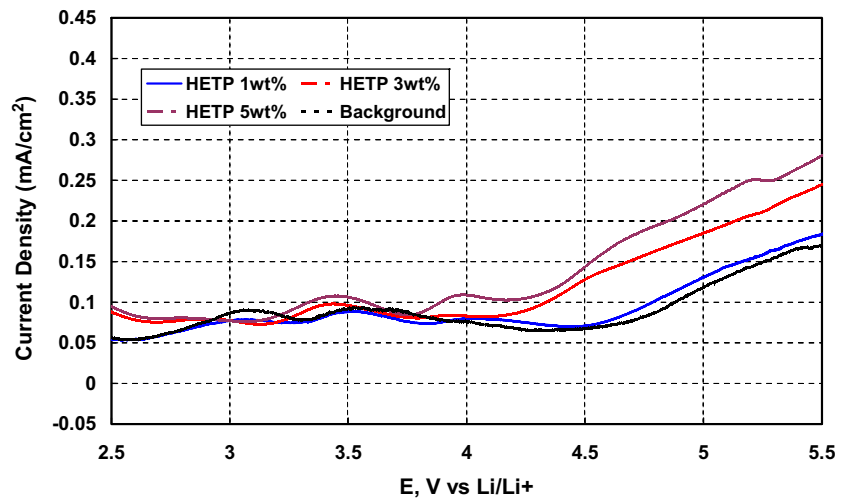
sodium ethoxide (12.76 g, 180 mmol) in ethanol (40 ml)
at 0°C. The resulting solution was stirred for 20 h at 0°C
and 2 h at 15°C. After being concentrated under reduced
pressure, the product was vacuum distilled at 0.1 Torr at
temperatures of 120°C to 160°C to get methyl cyclo-
triphosphazene ester as clear liquid (35%). Undistilled
residue became viscous resin during high temperature
distillation.

Fig. 3 Performance of half cells
with HMTP: (a) rate capability
test and (b) cycle life test. The
cells were charged at a rate of
0.2°C for the rate capability test.
The cycle test was charged and
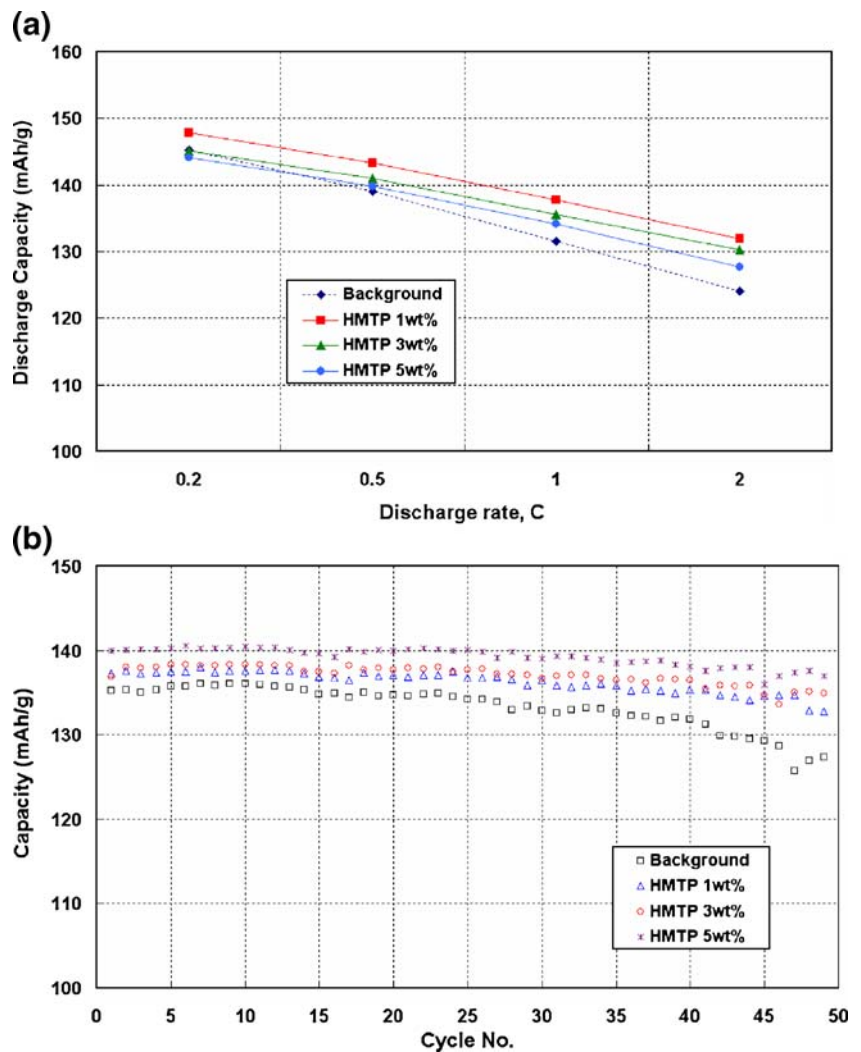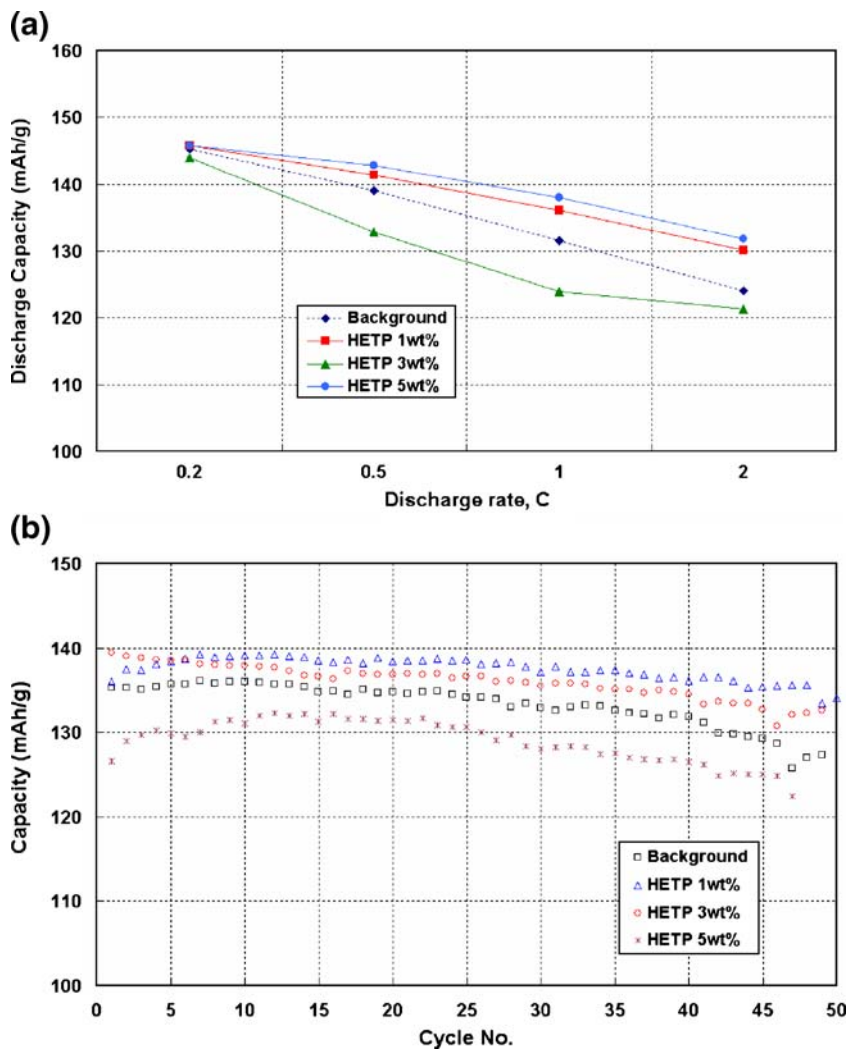discharged at a rate of 0.5°C

Fig. 4 Performance of half cells with HETP: (a) rate capability test and (b) cycle life test. The cells were charged at a rate of 0.2°C for the rate capability test. The cycle test was charged and discharged at a rate of 0.5°C

3 Results and discussion

Electrochemical potential windows were measured by LSV. Both HMTP and HETP give negligible eletrolysis currents

at 1 wt% as shown in Figs. 1 and 2. The currents with the additives are almost the same as the background current. Even though electrolytes with 3 and 5 wt% additives give higher currents than background, the currents are not

Fig. 5 Differential scanning calorimeter (DSC) curves with HMTP. The inset includes background and its rinsed electrode
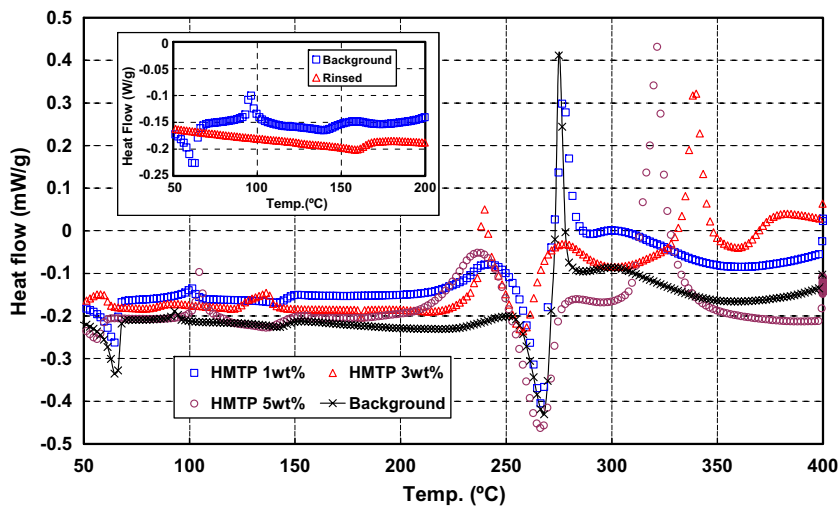
Table 1 Peak temperatures of the oxygen evolution reactions and the heat flow (ΔH) of the peak from Fig. 5.

Additive	Background	HMTP, 1 wt%	HMTP, 3 wt%	HMTP, 5 wt%
Peak temp. (°C)	274.8	276.5	338.3	321.5
ΔH (J/g)	35.8	49.9	44.9	73.1

Table 2 Peak temperatures of the oxygen evolution reactions and the heat flow (ΔH) of the peak from Fig. 6.

Additive	Background	HETP, 1 wt%	HETP, 3 wt%	HETP, 5 wt%
Peak temp. (°C)	274.8	329.9	323.8	329.7
ΔH (J/g)	35.8	45.0	30.7	42.5

significant up to 5 V. Under the charge/discharge condition for the performance test, the electrolysis of the electrolyte is limited. Figure 3 shows capacities at 0.2°C, 0.5°C, 1.0°C, and 2.0°C rates with HMTP. Concentration dependence of the additives on rate capability tests was evaluated by plotting discharge capacity vs. discharge rate, as shown in Fig. 3(a). The Capacity decreases are a trade-off for many additives for electrolytes. HMTP does not have a negative effect on capacities at various discharge conditions. Capacities and rate capabilities were improved at all concentrations compared to background, as shown in Fig. 3(a). Capacity improvement was reported by Lee et al. [5]. Capacities gradually decline as the concentration of the additive increases from 1 to 5 wt%. It is likely that capacity decreases observed at higher concentrations of HMTP were due to the dilution of electrolytes by the additive. In the cycle life tests in Fig. 3(b), improvements in both capacities and charge retention occurred at all HMTP concentrations. As more HMTP was added, the capacity was gradually enhanced. Concentration dependence on performance with HETP (Fig. 4) showed a different trend from the electrolytes with HMTP (Fig. 3). In both Fig. 4(a) and (b), 1 wt% HETP gives better performance than the background in the rate capability and cycle tests. Capacity values with 3 wt% HETP were below the background line, as shown in

Fig. 4(a). In Fig. 4(b) shows, a 5 wt% addition of HETP caused a 7% capacity decrease, compared to the 1 wt% addition. It is believed that the size of HETP is larger than HMTP, which caused the viscosity of the electrolytes to increase as the concentration increased. Because of the rapid increase in viscosity, only 1 wt% HETP provided performance enhancement, whereas enhancements were observed with HMTP at concentrations ranging from 1 to 5 wt%.

Figure 5 shows DSC curves with and without HMTP. Peaks between 90°C and 150°C are thermal decompositions of the surface layers (film) on cathodes [12]. The inset in Fig. 5 shows that the layer peak was formed and detected in the background electrolyte. The peaks can be removed by rinsing the electrodes with fresh background electrolyte. It was observed that the layer formed in background was reinforced by the additive, as evidenced by the broadening of the peak. It is believed that the protection layers play an important role in enhancing rate capability and cycle life. The endothermic reaction near 270°C was due to the evaporation of solvents in the electrolytes. The exothermic peak between 270°C and 350°C resulted from the oxygen evolution reaction from the cathode materials. The addition of 1 wt% HMTP did not provide better thermal stability compared to background. Table 1 shows the peak positions of the exothermic reactions and the heat flows. Three
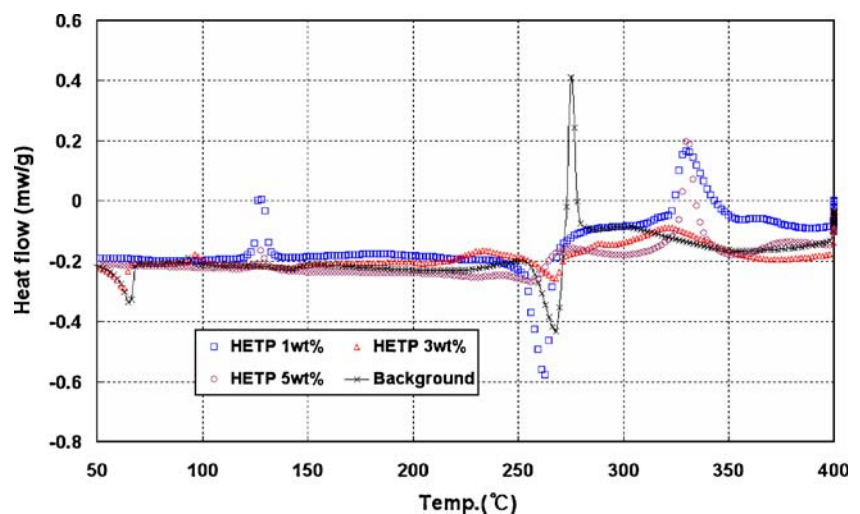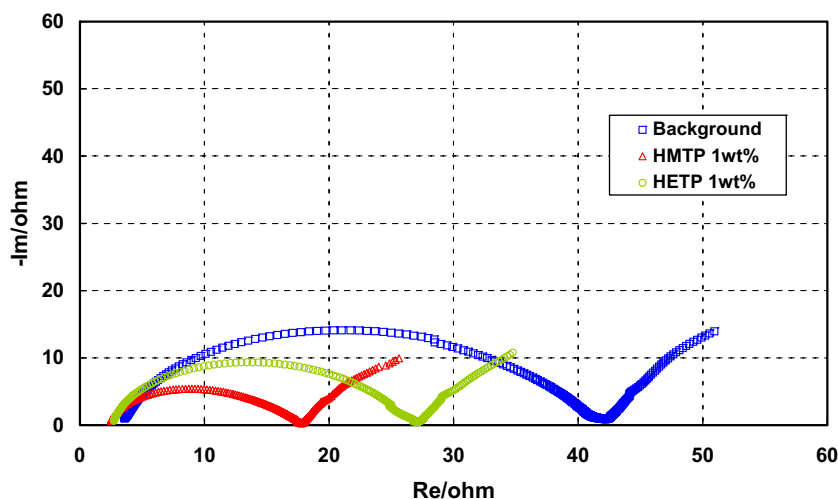
Fig. 6 Differential scanning calorimeter (DSC) curves with HETP

Fig. 7 Impedance spectra of samples with and without the additives

weight percent of HMTP delayed the peak temperature by approximately 64°C compared to the background. The FR properties of HMTP were very effective on the exothermic reaction of the cathode. However, the amount of heat produced by the reaction was not reduced. It was actually increased by the use of the additive. Three weight percent HMTP showed the best FR properties among the tested compositions, as is shown in Fig. 5. Figure 6 is the DSC measurements with HETP, which provided good FR properties with only 1 wt%. The oxygen evolution was delayed with 1 wt% HETP by almost 55°C. As we observed with HMTP, the heat flow given in Table 2 is not concentration dependent for HETP additions. The minimum addition of HETP of 1 wt% showed the maximum enhancement of FR performance.

Figure 7 shows impedance spectra that explain how the performances of the cells can be improved. Cells were cycled five times with 1 wt% additives. The cells remained charged for impedance measurements. By comparing the impedance to the background, the impedances of HMTP and HETP were 39% and 67%, respectively. The layers including the elements of the additives reduced impedance tremendously, which improved the performance of the cells.

In summary, both HMTP and HETP strongly suppress oxygen evolution on cathode materials (metal oxides). The phosphazene derivatives had no negative effects on performance of the cathode materials with 1 wt%. A surface layer was formed on the cathode using background electrolytes. The layer can be reinforced by the additive in a way that protects the electrode for long cycle life and reduces the reaction resistance on the electrode for the rate capability. Studies of surface resistance on the electrodes are underway. Performance decreases were observed at high additive concentrations because the neutral additive molecules hinder electrochemical reactions.

4 Conclusions

Phosphazene derivatives are very effective FR additives for Li-ion batteries. HETP provides RF properties with only 1 wt%, while 3 wt% addition is necessary for HMTP. HETP has better FP properties than HMTP. It is believed the larger HETP molecules, which have six more carbons than HMTP, provide better FR effectiveness [9] and better performance of the cells. Even though the additives are not ionic, they enhance performance of the cathode. Surface layers are formed on the cathode by the electrolysis of the background electrolytes. The elements of additives merged in the layers, which helps to reduce the resistance of the charge transfer in the cells. Low resistance caused by the additive leads to better performance of the cells.

References

1. J.S. Hong, H. Maleki, S. Al Hallaj, L. Reday, J.R. Selman, J. Electrochem. Soc. **145**, 1489 (1998)
2. M.N. Richard, J.R. Dahn, J. Electrochem. Soc. **146**, 2068 (1999)
3. S. Tobishima, J. Yamaki, J. Power Sources. **81–82**, 882 (1999)
4. S.S. Zhang, K. Xu, T.R. Low, J. Power Sources **113**, 116 (2003)
5. C.W. Lee, S.R. Venkatachalapathy, J. Prakach, Electrochem. Solid-State Lett. **3**, 62 (2000)
6. J. Prakash, C.W. Lee, K. Amine, U. S. Patent **6**(455), 200 (2002)
7. H-S Kim, S-I Kim, C-W Lee, S-I Moon, ibid. **17**, 673 (2006)
8. B. Kumar, L.G. Scanlon, ibid **5**, 127 (2000)
9. Y. Ein-Eli, V.R. Koch, J. Electrochem. Soc. **144**, 2968 (1997)
10. B. Dishon, J Amer. Chem. Soc. 2251 (1949)
11. H.R. Allcock, T.J. Fuller, D.P. Mack, K. Matsumura, K.M. Smeltz, Macromolecules **10**, 824 (1977)
12. E.P. Roth, Proceedgins of the Intersociety Energy Conversion Engineering Conference **2**, 962 (2002)