

Effect of cyclic phosphate additive in non-flammable electrolyte

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Abstract

An additive in the trimethyl phosphate (TMP)-based non-flammable electrolyte was investigated in order to improve the poor reductive stability for the graphite anode. We found that the charge–discharge characteristic of the TMP-based non-flammable electrolyte was improved by adding ethylene ethyl phosphate (EEP) which had function of non-flammability. The solid electrolyte interface (SEI) layers formed on the graphite anode were analyzed with X-ray photoelectron spectroscopy (XPS) and Fourier transformation type infrared spectroscopy (FT-IR). Moreover, evolved gases in the battery were analyzed with gas chromatography/mass spectrometry (GC/MS) to understand the electrochemical reaction in SEI formation. We concluded that the SEI layers including phosphorus created by the EEP additive suppressed the reductive decomposition of TMP.

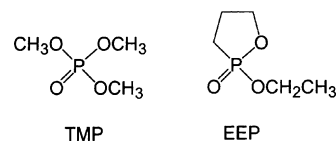
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1. Introduction

The lithium-ion batteries with graphite as the anode have many advantages such as the long cycle life, high energy density and high voltage. Nevertheless, the safety is still an important problem for their commercial application [1–10]. The electrolyte for these batteries typically consists of ethylene carbonate with a high dielectric constant and an alkyl carbonate as a low viscosity solvent containing the LiPF₆ salt. These solvents are flammable. When the internal pressure of the battery increases and the battery is mechanically destroyed, the electrolyte could be led to the dangerous situations such as fire and explosion. These accidents were thought to be related to the flammability of common carbonate-based electrolytes. Therefore, it has been becoming important to find effective method to suppress the flammability of lithium-ion batteries. Some groups reported that the trimethyl phosphate (TMP) solvent undergoes reductive decomposition on graphite anodes and it could not be used as solvent in spite of an excellent self-extinguishing characteristic [11–14]. To improve the reductive characteristic on the graphite anode, several studies on additives have been conducted in recent years [15–20]. In this study, we found that an excellent charge–discharge performance was

obtained by adding ethylene ethyl phosphate (EEP) as an additive.



It has been considered that the solid electrolyte interface (SEI) layer on the graphite anode plays an important role for Li intercalation [21]. We investigated with XPS, FT-IR and evolved gas analysis in order to clarify SEI formation. In addition, the thermal stability of the SEI layer was evaluated by TPD–MS.

2. Experimental

2.1. Evaluation of non-flammable electrolyte

Non-flammability of an electrolyte was evaluated by igniting a glass filter paper containing the electrolyte. The glass filter paper for the evaluation was suspended vertically. A gas burner was used to burn the lower end of the filter paper. The non-flammable electrolyte was defined as that the flame of electrolyte was automatically extinguished within 5 s after removing the burner from the glassy filter.

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2.2. Evaluation charge–discharge test

Lithium metal was used as the counter and reference electrodes. The working electrode was a natural graphite (NG7, Kansai Coke and Chemical. Co.). The electrode sheet was prepared by mixing the material with a solution of poly(vinylidene fluoride) (PVdF) dissolved in *N*-methyl 2-pyrrolidinone (NMP). The content of the binder was 7.5%. The electrode was punched out and to have an area of 1.23 cm². The non-flammable electrolyte used in this study was an ethylene carbonate (EC) + diethyl carbonate (DEC) + trimethyl phosphate (6:2:2 v/v/v) mixture containing 1 mol/dm³ LiPF₆ (Sol-Rite™, Mitsubishi Chemical Cor.). EEP was used the electrolyte additive. The H₂O content was analyzed by the Karl-Fischer titration technique and found to be below 20 ppm. The two-electrode cell was assembled in an Ar-filled grove box. The charge–discharge measurements were performed in the galvanostatic mode using charge–discharge equipment (Nagano, BTS-2004w). The cells were discharged to a potential of 0 V (versus Li/Li⁺) at current density of 0.2 mA/cm². The Li doped graphite was charged at current density of 0.4 mA/cm² to 1.5 V (versus Li/Li⁺).

2.3. Analysis of battery after charge–discharge test

The evolved gas was analyzed with gas chromatography/mass spectrometry (GC/MS, ANELVA AGS-7000). The gases in the cell were collected in a cold trap using liquid nitrogen. After the gas analysis, the cell was disassembled in the Ar glove box. X-ray photoelectron spectroscopy (XPS; ULVAC-PHI5700ci) was used in order to obtain information on the chemical state of the SEI layer. Monochromatic Al K α source (14 kV, 350 W) was used as the X-ray source. Fourier transformation type infrared spectroscopy (FT-IR; Nicolet Magna500) was used to analyze the chemical structure of the surface layer. The measurement was carried out with the ATR method. The thermal stability of the SEI layer was analyzed using temperature programmed desorption or decomposition–mass spectrometry (TPD–MS, ANELVA AGS-7000). The analytical sample was transported using an Ar-filled transfer vessel in order to prevent degeneration of the sample by air exposure.

3. Results and discussion

3.1. Non-flammability (self-extinguishing) evaluation of electrolyte

TMP is known to be a non-flammable solvent. When TMP is added to the carbonate-based electrolyte, it is expected that a better fire resistance of the electrolyte will be obtained. Fig. 1 shows the result of the flammability test. From these results, it is clear that each solvent ratio must be over a 20 vol.% TMP content and under a 20 vol.% DEC content in

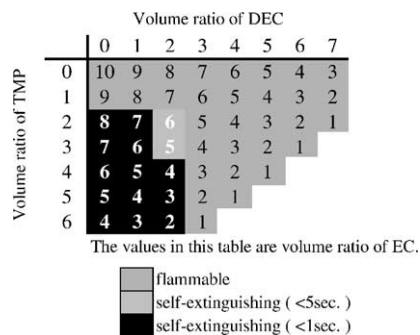


Fig. 1. Compositional range of non-flammability in 1 mol/dm³ LiPF₆/EC + DEC + TMP electrolyte.

order to be self-extinguishing. We think that the self-extinguishing nature of TMP is explained by a flame retarding mechanism involving a radical trap in the gas phase [13].

3.2. Charge–discharge cycling of non-flammable electrolyte

Fig. 2 shows the potential curves using the 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) electrolyte and the based electrolyte containing ethylene ethyl phosphate as an additive. For the non-additive electrolyte, a plateau at 0.4 V (versus Li/Li⁺) was observed in the first cycle. The Li intercalation was smoothly achieved by adding EEP to the TMP-based electrolyte. We confirmed that the EEP-based electrolyte has a self-extinguishing characteristic as does the TMP-based electrolyte. The EEP solvent is not only a non-flammable electrolyte but also an effective additive for the graphite anode.

3.3. The evolved gas analysis after cycle

The evolved gases in a first cycle are very important since evolved gas is closely related to the formation process of SEI layer. Evolved gas analysis was carried out to understand

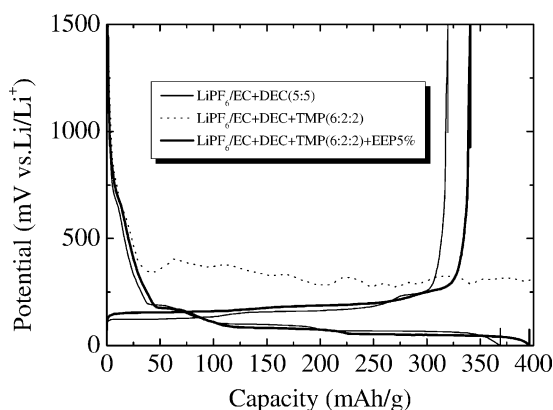
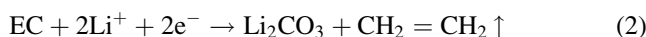
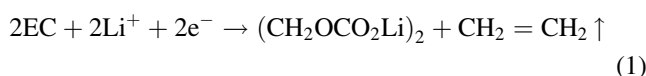


Fig. 2. First discharge and charge curves of 1 mol/dm³ LiPF₆/EC + DEC (5:5), 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) and 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) + EEP 5 wt.% electrolyte.

Table 1
Evolved gas analysis after the first cycle

Li salt	Solvent	Additive	Amount of evolved gas after discharge–charge					
			μl			μl/mg		
			CH ₄	C ₂ H ₄	C ₂ H ₆	CH ₄	C ₂ H ₄	C ₂ H ₆
LiPF ₆	EC + DEC (5:5)	None	<0.1	5.2	0.3	<0.02	0.85	0.05
LiPF ₆	EC + DEC + TMP (6:2:2)	None	58.3	57.3	0.8	9.56	9.39	0.13
LiPF ₆	EC + DEC + TMP (6:2:2)	EEP5%	0.5	6.7	0.6	0.08	1.10	0.10

the electrochemical reaction in the SEI formation. Table 1 shows the results of evolved gas analysis after the first cycle. It was reported that ethylene was formed by the reductive decomposition of EC [22].

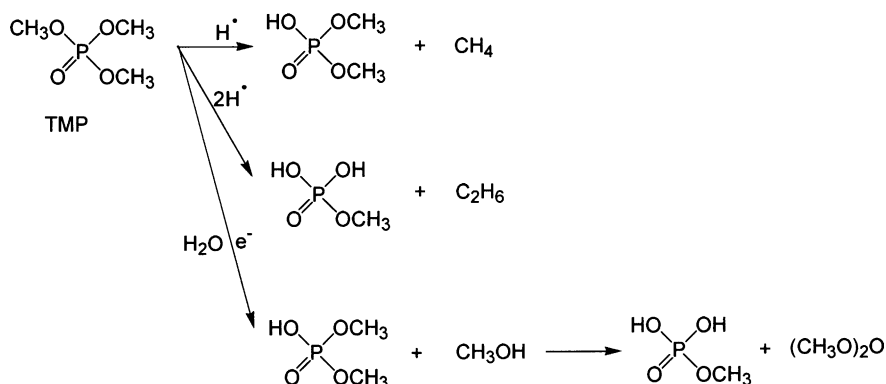


For the TMP system electrolyte (LiPF₆/EC + DEC + MP = 6:2:2), much ethylene and methane were detected. Formation of methane and ethane will be based on the reductive decomposition of TMP as shown in Scheme 1. We consider that H radical generates from reduction of water and solvent. CH₄, C₂H₆ and CH₃OCH₃ were generated from the LiPF₆/TMP electrolyte. However, C₂H₄ was not detected. This clearly shows that the discharging (Li intercalation) process in an electrolyte containing TMP is generated not only by the decomposition of TMP, but also by the decomposition of EC. The evolved gas considerably suppressed by adding EEP to TMP system electrolyte.

3.4. The surface analysis of SEI layer formed on the graphite by XPS

XPS was used in order to analyze the chemical state of the SEI layer formed on the graphite. Fig. 3 and Table 2 show C 1s, O 1s, F 1s, P 2p and Li 1s XPS spectra and surface atomic concentrations of the SEI layer in various electrolytes. In the

P 2p spectrum, a strong peak at 136 eV corresponding to the P–O combination was observed in the EEP additive electrolyte. The P 2p peak from the electrode before charge–discharge of the EEP additive electrolyte was not detected. Therefore, these peaks seem not to be the EEP additive but the SEI component due to the decomposition of EEP. The O 1s peak at 534.3 eV in the EEP additive electrolyte is attributed the P–O component. The peak at 532.8 eV corresponds with CO₃ of the alkyl lithium carbonate species. The C 1s spectrum shows various peaks at 291.5 (CO₃), 290.5 (CF), 288 (ROCOO, P–O–R), 286 (C–O–C) and 284.3 eV (graphite). The EEP additive system has a large peak at 288 eV. The peak at 288 eV is assigned to the alkyl carbon of the alkyl lithium carbonate. The intensity of the carbonate peak at 291.5 V is smaller than the alkyl peak at 288 eV. This 288 eV peak would be assigned alkyl carbon in P–O–R. Li 1s spectrum shows two peaks at 56.5 (LiF) and 55.2 eV (ROCO₂Li). The intensity of the electrolyte with EEP additive was lower than that without EEP. It is considered that the SEI layer of the EEP additive is the organic phosphate component with a small lithium quantity. From the spectrum of F 1s, LiPF₆ (688.2 eV) and PVdF (687.8 eV) and LiF (686 eV) were detected. For the EEP additive electrolyte, the CF component is attributed to the peak of PVdF that was detected. However, the LiPF₆/EC + DEC (5:5) and LiPF₆/EC + DEC + TMP (6:2:2) electrolytes without EEP do not have the CF component. The binder component is covered with the SEI layer formed on the graphite in these electrolytes. The surface contents of P, Li,



Scheme 1. Possible reductive decomposition of TMP.

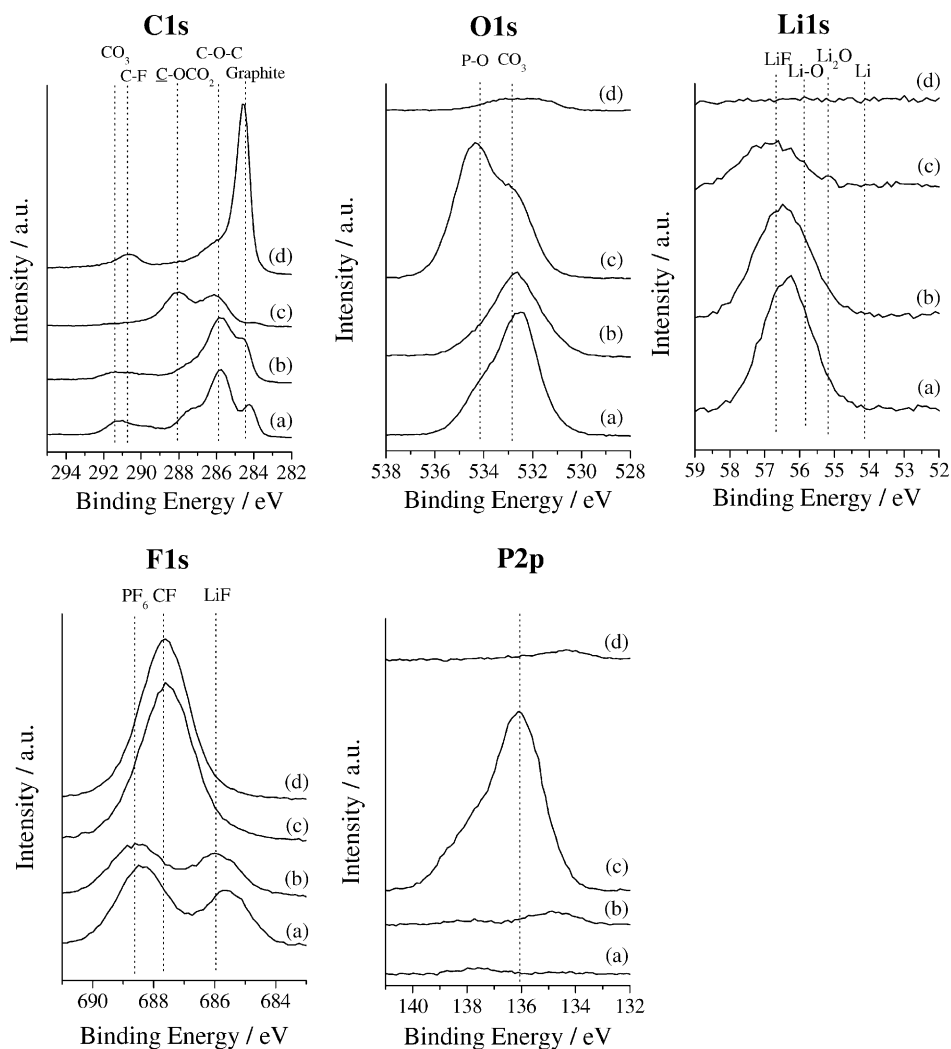


Fig. 3. C 1s, O 1s, F 1s, P 2p and Li 1s XPS spectra of SEI layer formed on the graphite in (a) 1 mol/dm³ LiPF₆/EC + DEC (5:5); (b) 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2); (c) 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) + EEP5%. The (d) is XPS spectra before charging in 1 mol/dm³ LiPF₆/EC + DEC (6:2:2) + EEP5%.

F, O and C in the EEP additive system were 10, 3, 13, 33 and 42% as shown in Table 1. The F 1s peak at 687.8 eV and P 2p peak at 136 eV in the LiPF₆/EC + DEC + TMP (6:2:2) + EEP5% electrolyte could be assigned the LiPO_xF_y species such as LiPO₂F and LiPO₃F₂. The Li content (3 at.%) of the SEI layer in the EEP additive system is lower than the P content (10 at.%). Therefore, it is clear that the P component except for the LiPO_xF_y species exist as the SEI layer component.

3.5. The structure analysis of SEI layer formed on the graphite by FT-IR

FT-IR was used in order to clarify the functional group of the SEI layer. Fig. 4 shows FT-IR spectra of SEI layer formed on the graphite in 1 mol/dm³ LiPF₆/EC + DEC (5:5), 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2), and 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) + EEP2%. The FT-IR spectra of the SEI layers in all electrolytes show

Table 2
XPS atomic concentration table of the SEI layer on the graphite

Solvent	Composition ratio	Additive	Cycling	Atomic concentration (%)				
				Li 1s	C 1s	O 1s	F 1s	P 2p
EC + DEC	5:5		1 cycle	12.5	54.9	23.5	8.9	0.2
EC + DEC + TMP	6:2:2		1 cycle	13.1	60.3	18.6	7.2	0.8
EC + DEC + TMP	6:2:2	EEP5%	1 cycle	5.7	38.8	33.0	12.5	10.0
EC + DEC + TMP	6:2:2	EEP5%	Before	0.0	83.5	3.3	12.6	0.5

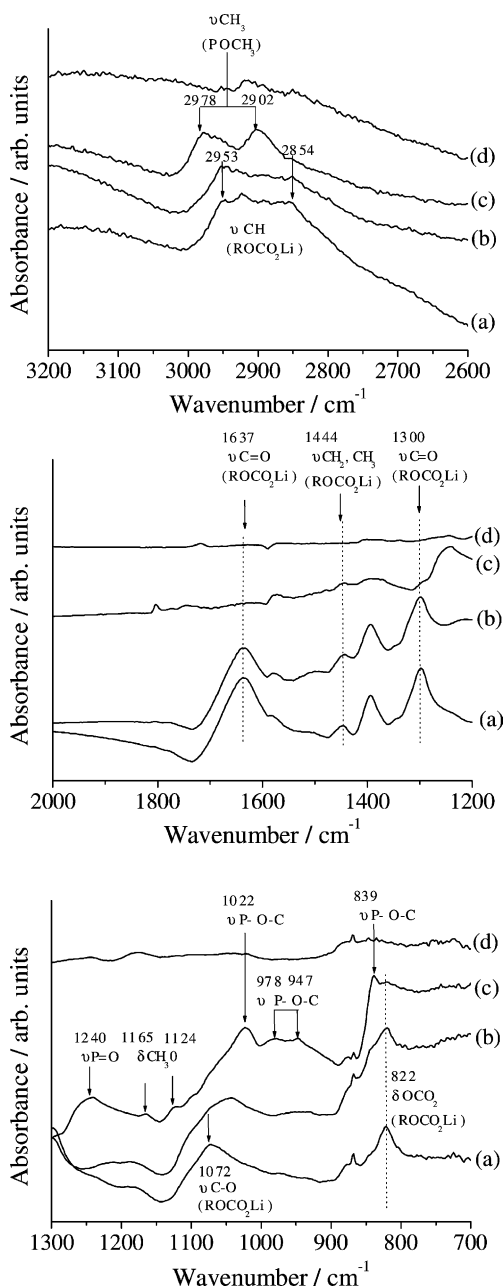


Fig. 4. FT-IR spectra of SEI layer formed on the graphite in (a) 1 mol/dm³ LiPF₆/EC + DEC (5:5); (b) 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2); (c) 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) + EEP5%. The (d) is FT-IR spectrum before charging in 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) + EEP5%.

2953–2854 cm⁻¹ (ν_{CH}), 1637 cm⁻¹ (ν_{asC=O}), 1450 cm⁻¹ (δ_{CH₃,CH₂), 1300 cm⁻¹ (ν_{sC=O}), 1072 cm⁻¹ (ν_{C-O}) and 821 cm⁻¹ (δ_{OCO₂-}). These peaks are attributed to the lithium alkyl carbonate (ROCO₂Li) species [23]. For the SEI layer in the electrolyte containing EEP, peaks at 2978–2902 cm⁻¹ (ν_{CH₃}), 1240 cm⁻¹ (ν_{P=O}), 1022–947 cm⁻¹ (ν_{asP-O-C}) and 839 cm⁻¹ (ν_{sP-O-C}) were detected. These peaks correspond to the P–O–R unit. This was not detected in the graphite-soaked electrolyte, therefore these peaks are not related to EEP. We consider that the ring-opening of EEP occurs on the}

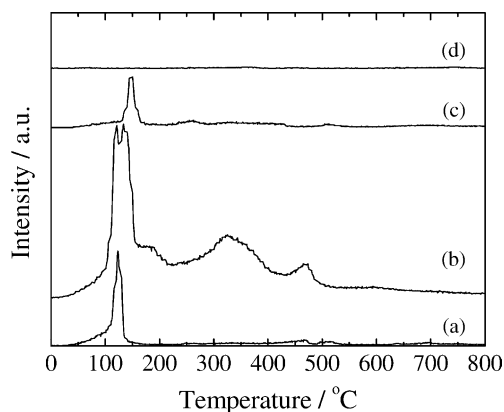


Fig. 5. TPD-MS pattern of graphite after discharge-charge. (a) 1 mol/dm³ LiPF₆/EC + DEC (5:5); (b) 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2); (c) 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) + EEP5%; (d) soak in 1 mol/dm³ LiPF₆/EC + DEC + TMP (6:2:2) + EEP5%.

graphite and the SEI layer containing phosphorus due to reduction of EEP protects from successive decomposition.

3.6. The thermal stability of SEI layer

TPD-MS was used in order to analyze the physical property of the SEI layer formed by the EEP additive. The thermal stability was evaluated by measuring the decomposition gas pattern of CO₂ from the organic carbonate SEI layer. Parent peak of CO₂ is *m/z* 44. This mass peak cannot be used for the evaluation of the thermal stability of the SEI layer as it overlaps with the solvent fragment peak such as EC and DEC. The thermal stability of the SEI layer in various electrolytes was evaluated using the divalent ion (*m/z* 22) of CO₂. The *m/z* 22 ion does not overlap with the fragment-ion of other components. Fig. 5 shows the thermal stability of the SEI layer on the graphite anode. CO₂ was detected by thermal decomposition gas formed from the SEI layer at 130 °C. The graphite anode soaked in the LiPF₆/EC + DEC + TMP (6:2:2) + EEP5% electrolyte dose not provide CO₂ as a thermal decomposition product from the electrolyte. It is known that SEI layers compose of carbonate lithium such as ROCO₂Li and Li₂CO₃. The thermal decomposition of Li₂CO₃ occurred at 700 °C. However, the SEI layer formed on graphite during the first cycle mainly showed decomposition patterns under 200 °C. This peak shows that the SEI layer is organic carbonate type such as ROCO₂Li. The SEI layer in the LiPF₆/EC + DEC + TMP (6:2:2) + EEP5% electrolyte was decomposing at 125 °C. On the other hand, the SEI film in the LiPF₆/EC + DEC (5:5) electrolyte decomposed at 110 °C. From these results, it is found that the thermal stability of the SEI created in EEP is more stable than the SEI without additive. For the LiPF₆/EC + DEC + TMP (6:2:2) electrolyte, a large peak was detected in the temperature region. The charge-discharge characteristic of this electrolyte was very poor, and a large amount of gas was detected. It is considered that thicker layers

form due to the reductive decomposition of the $\text{LiPF}_6/\text{EC} + \text{DEC} + \text{TMP}$ (6:2:2) electrolyte.

4. Conclusion

The $\text{LiPF}_6/\text{EC} + \text{DEC} + \text{TMP}$ electrolyte showed non-flammability (self-extinguishing) for over a 20 vol.% TMP content and under a 20 vol.% DEC content. By adding EEP to the TMP-containing electrolyte, it was found that the reductive decomposition of TMP was suppressed. Based on these results, we can conclude that the SEI component including phosphorus created by the additive EEP suppressed the reductive composition of TMP. It was confirmed that the thermal stability of the SEI layer created by EEP increased compared to the SEI layer of the non-additive electrolyte. We found that EEP solvent had function of additive and non-flammability.

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References

- [1] K. Hasegawa, Y. Arakawa, *J. Power Sources* 44 (1993) 523.
- [2] S.C. Levy, *J. Power Sources* 68 (1997) 75.
- [3] A. Du Pasquier, F. Disma, T. Bowmer, A.S. Gozdz, G. Amatucci, J.-M. Tarascon, *J. Electrochem. Soc.* 145 (1998) 472.
- [4] S. Tobishima, J. Yamaki, *J. Power Sources* 81–82 (1999) 882.
- [5] Ph. Biensan, B. Simon, J.P. Pérès, A. de Guibert, M. Broussely, J.M. Bodet, F. Perton, *J. Power Sources* 81–82 (1999) 906.
- [6] M.N. Richard, J.R. Dahn, *J. Electrochem. Soc.* 146 (1999) 2068.
- [7] M.N. Richard, J.R. Dahn, *J. Electrochem. Soc.* 146 (1999) 2078.
- [8] H. Maleki, S. Al-Hallaj, J.R. Selman, R.B. Dinwiddie, H. Wang, *J. Electrochem. Soc.* 146 (1999) 947.
- [9] S. Tobishima, K. Takei, Y. Sakurai, J. Yamaki, *J. Power Sources* 90 (2000) 188.
- [10] J.P. Pérès, F. Perton, C. Audry, Ph. Biensan, A. de Guibert, G. Blanc, M. Broussely, *J. Power Sources* 97–98 (2001) 702.
- [11] X. Wang, E. Yasukawa, S. Kasuya, Abstract 321, in: Proceedings of the 196th Electrochemical Society Meeting Abstracts, Hawaii, 17–22 October 1999.
- [12] N. Shinoda, J. Ozaki, F. Kita, A. Kawakami, Abstract 335, in: Proceedings of the 196th Electrochemical Society Meeting Abstracts, Hawaii, 17–22 October 1999.
- [13] X. Wang, E. Yasukawa, S. Kasuya, *J. Electrochem. Soc.* 148 (2001) A1058.
- [14] X. Wang, E. Yasukawa, S. Kasuya, *J. Electrochem. Soc.* 148 (2001) A1066.
- [15] Z.X. Shu, R.S. McMillan, J.J. Murray, *J. Electrochem. Soc.* 140 (1993) 922.
- [16] D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai, H. Yamin, *J. Electrochem. Soc.* 141 (1994) 603.
- [17] Z.X. Shu, R.S. McMillan, J.J. Murray, I.J. Davidson, *J. Electrochem. Soc.* 143 (1996) 2230.
- [18] Y. Ein-Eli, S.R. Thomas, V.R. Koch, *J. Electrochem. Soc.* 142 (1997) 1159.
- [19] G.H. Wrodnigg, J.O. Besenhard, M. Winter, *J. Electrochem. Soc.* 146 (1999) 470.
- [20] D.L. Foster, W.K. Behl, J. Wolfenstine, *J. Power Sources* 85 (2000) 299.
- [21] H. Ota, T. Sato, H. Suzuki, T. Usami, *J. Power Sources* 97–98 (2001) 107.
- [22] R. Imhof, P. Novák, *J. Electrochem. Soc.* 145 (1998) 1083.
- [23] D. Aurbach, A. Zaban, A. Schechter, Y. Ein-Eli, E. Zinigrad, B. Markovsky, *J. Electrochem. Soc.* 142 (1998) 2873.