Journal of The Electrochemical Society, 2024 **171** 040536

Functional Electrolyte: Highly-Safe LIB Using Branched Carboxylic Acid Ester as Electrolyte Additive

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The electrolyte in current automotive lithium-ion batteries is a mixture of ethylene carbonate (EC), which has a high dielectric constant, and ethyl methyl carbonate or dimethyl carbonate, which have a low viscosity. However, the flash point of these mixed solvents is as low as 25 °C, so safety precautions must be taken. On the other hand, if only EC or propylene carbonate with a high flash point is used, the flash point will be 120 °C or higher. However, the high dielectric constant solvent cannot wet the hydrophobic separator whose material is polyethylene and/or polypropylene. Therefore, there is a problem that the battery does not work. In 1999, we proposed a "functional electrolyte" in which a small amount of an additive with a new function is added to the electrolyte, and many additives have since been commercialized. In recent work, we focused on a low viscosity linear carboxylic acid esters, designed an electrolyte with a flash point above 120 °C that provides wettability to the separator even in an electrolyte with a high dielectric constant solvent.

 [DOI: 10.1149/1945-7111/ad39cb]

Manuscript submitted February 14, 2024; revised manuscript received March 29, 2024. Published April 23, 2024.

Safety is an important issue for LIBs used in large power supplies such as electric vehicles (EVs) and an Energy Storage System (ESS). For this reason, all-solid-state batteries that use flame retardant solid electrolytes have attracted attention, but there are problems with their battery life and low temperature performance, thus, expectations are returning to liquid-based LIBs for a higher safety. These electrolytes have a low viscosity and therefore a high ionic conductivity, but also the disadvantage of a low flash point of about 25 °C. To overcome this disadvantage, many research works have been and still continue regarding flame retardant and nonflammable electrolyte solutions. However, all the investigated compounds, such as phosphate esters,[1–4] halogen-containing compounds,[5–8] ionic liquids,[9–13] and phosphazenes,[14–17] have an insufficient battery performance. Moreover, even if the performance of the nonflammable compounds improves, the incineration of waste liquids is difficult, so the cost of disposal must be significantly increased. Therefore, we aimed to develop a highly-safe electrolyte using a high flash point solvent. With this solution, the battery performance will not rapidly degrade, and incineration of the waste solution will be possible.

In this research work, we decided to use cyclic carbonates, such as EC and PC, which have flash points above 120 °C as a solvent in the highly-safe electrolytes. However, such nonaqueous solvents are highly polar and cannot wet the hydrophobic polyolefin separator, thus making the battery inoperable. Therefore, to make battery working, we need an additive to improve wettability of separator when use EC or PC as a solvent. Trioctyl phosphate (TOP) and tris (2-ethylhexyl) phosphate (TEHP), which are linear and branched structural isomer of phosphate ester, are known as an additive that helps the electrolyte improve its wettability of the separator.[18,19] However, regarding TOP, as reported in a previous work by Shim et al.,[20] adding even 5 wt% of TOP causes a significant decrease in rate and cycling performance, probably due to the increase in cell impedance. In addition, although TEHP has an advantage of the high flash point of 200 °C, TEHP has a very high viscosity of 12 mPa s (Table I), so even a small added amount may have the problem of raising the viscosity of the electrolyte. We also thought that TEHP has a high boiling point of 216 °C/0.53 kPa (estimated to be about 400 °C at normal pressure), making distillation and purification difficult.

Therefore, in this research work, we focused on linear carboxylic acid esters, which have a low viscosity and are easy to modify their structure and purify. In particular, since linear carboxylic acid esters have a viscosity lower than TOP, it is assumed that there is little decrease in conductivity, and thus, the effect on electrochemical cell performance is expected to be very small. For these reasons, we focused on linear carboxylic acid esters, which have a viscosity lower than that of the linear carbonates, and the flash point of the electrolyte was aimed to be 120 °C or higher. If this can improve battery safety, it is expected that such a LIB could be used in new applications such as lead-acid battery substitutes. In this research work, electrolytes with significantly higher flash points were designed by using additives to ensure wettability of the separator by solvents with high flash points.

Experimental

Chemicals.—The electrolytes used, 1 M $LiPF_6$ EC/DMC = 1/2 (v/v), 1 M $LiPF_6$ EC/PC = 7/1(v/v), 1 M $LiPF_6$ EC/PC = 1/1(v/v), 1 M $LiPF_6$ EC/PC = 1/2(v/v), 1 M $LiPF_6$ PC, and 1 M $LiPF_6$ EC/EMC/DMC = 3/3/4(v/v/v) were from the MU Ionic Solutions Corporation. These were controlled at H_2O: <10 ppm, and HF: <30 ppm. The Solid Electrolyte Interphase (SEI) formation additives, vinylene carbonate (VC) and propynyl methane sulfonate (PMS), and the wettability improving additives, n-butyl pivalate (PV-B) and n-hexyl pivalate (PV-H) of battery grade controlled to H_2O: <10 ppm, were also purchased from the MU Ionic Solutions Corporation. Other wettability improving additives, i.e., tris(2-ethylhexyl) phosphate (TEHP), n-butyl acetate (Ac-B), n-butyl propionate (P-B), n-butyl isobutyrate (iB-B), n-hexyl acetate (Ac-H), and methyl undecanoate (MU), were purchased from Tokyo Chemical Industry Co., Ltd. Molecular Sieves 4 A was added to these compounds with H_2O: <10 ppm.

n-Hexyl trifluoroacetate (TF-H), n-heptyl pivalate (PV-Hp), 2-ethylhexyl pivalate (PV-2EH), n-octyl pivalate (PV-O), 2-octyl pivalate (PV-2O), 3-octyl pivalate (PV-3O), and 4-octyl pivalate (PV-4O) were synthesized in our laboratory. As a typical example, to synthesize PV-Hp, 17.0 g (0.165 mol) of pivalic acid and 17.77 g (0.150 mol) of 1-heptanol were added to 1.70 g (0.0165 mol) of 95% sulfuric acid, then refluxed for 3 h under Ar. The product was next distilled under reduced pressure to yield 28.4 g (Yield: 83.3%) of PV-Hp at 114 °C/3.6 kPa. After distillation, these compounds were stored over Molecular Sieves 4 A with H_2O: <10 ppm. The gas chromatograph (GC) purity results of the carboxylic acid esters

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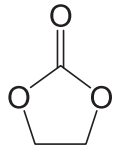
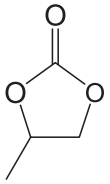
Table I. Boiling point, melting point, flash point, viscosity, and conductivity of the various solvents.

Name		Boiling point (°C)	Melting point (°C)	Flash point (°C)	Viscosity (mPa s)
Cyclic solvent					
EC	Ethylene carbonate	248	36	152	Solid
PC	Propylene carbonate	242	−49	133	2.42
GBL	γ-Butyrolactone	204	−43	100	1.75
Linear solvent					
DEC	Diethyl carbonate	126	−43	33	0.78
EMC	Ethyl methyl carbonate	107	−15	23	0.72
DMC	Dimethyl carbonate	90	3	17	0.61
Phosphate type wetting additive					
TEHP	Tris(2-ethylhexyl) phosphate	$400_{est.}$	N.A.	200	12.4

Cyclic solvent



Ethylene carbonate (EC)



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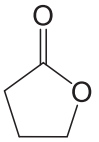
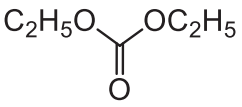
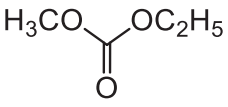


γ-Butyrolactone (GBL)

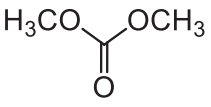
Linear solvent



Diethyl carbonate (DEC)

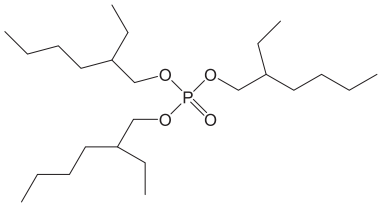


Ethyl methyl carbonate (EMC)



Dimethyl carbonate (DMC)

Phosphate type additive



Tris(2-ethylhexyl) phosphate (TEHP)

synthesized in our laboratory were TF-H (99.6%), PV-Hp (99.9%), PV-2EH (99.7%), PV-O (99.6%), PV-2O (99.4%), PV-3O (99.1%), and PV-4O (97.2%). The mass spectrum (MS/CI) of TF-H was calcd. for $C_8H_{13}F_3O_2$: 198, found $m/z = 199$ ($[M+H]^+$), PV-Hp was calcd. for $C_{12}H_{24}O_2$: 200, found $m/z = 201$ ($[M+H]^+$), and PV-2EH, PV-O, PV-2O, PV-3O, and PV-4O were calcd. for $C_{13}H_{26}O_2$: 214, found $m/z = 215$ ($[M+H]^+$).

Additive solubility test.—Additives must be typically soluble in the electrolyte (Fig. 1a). If the additive is not soluble, a two phase separation will occur (Fig. 1b). In the examples shown in Fig. 1b, the upper phase is the wettability improving additive and the lower phase is the electrolyte. Since only a few percent of the additive is added at this time, it is difficult to visually determine its solubility. Therefore, we sucked up the upper part of the electrolyte using a Pasteur pipette and visually judged it.

Separator wetting test.—The separator used in these experiments was a 20 μm thick 3-layer PP/PE/PP separator (Ube Maxell Co., Ltd.). Figure 1 shows examples for well wetted (Fig. 1c) and completely non-wetted separators (Fig. 1d). Using the contact angle did not result in reliable data, so we visually checked as the color changed from white to gray. The added amount was the minimum amount that exhibited a sufficient wettability within 15 s.

Solvent and electrolyte property evaluation.—The viscosity was measured five times at 25 °C using 0.5 ml of the carboxylic acid esters, solvents or the electrolyte and the average value was used. The instrument used was a Brookfield Viscometer DV-I Prime LV (AMETEK Brookfield).

The conductivity was measured at 25 °C by a CM-42X EC Meter (DKK-TOA Corporation) using 3 ml of the electrolyte (Table II).

The flash point was measured using 55 ml of the carboxylic acid esters, solvents or the electrolyte. The flash point below 90 °C was measured using the TAG Flash Point Tester TAG4 (Anton Paar). The flash point above 90 °C was measured using the Pensky-Martens Flash Point Tester PMA 500 (Anton Paar).

2032-coin cell battery test.—The cathode active material of the 2032-coin cell was $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523), and the anode active material was natural graphite (NG). The cathode sheet was a mixture of NCM523: acetylene black (AB): polyvinylidene difluoride (PVdF) = 92:5:3 and the anode sheet was mixed with NG: styrene-butadiene rubber (SBR): carboxymethyl cellulose (CMC) = 98:1:1 purchased from The Furukawa Battery Co., Ltd In this paper, the positive electrode will be referred to as the cathode and the negative electrode as the anode.

For the NG/Li half-cell, the Ø14 mm, 0.25 mm thick Li metal foil mounted on a Ø15 mm stainless steel grid (100 mesh) was used. The Ø19 mm, 20 μm thick, 3-layer PP/PE/PP separator and Ø16 mm glass fiber filter paper GF/A (Whatman Corporation) were used between the electrodes. The separator was placed so that it faced the NG anode and the glass fiber filter paper faced the thick Li metal foil. Approximately 0.2 cm^3 of electrolyte was added to the coin cell. The base electrolyte was 1 M $LiPF_6$ EC/DMC = 1/2(v/v) along with the addition of the carboxylic acid esters.

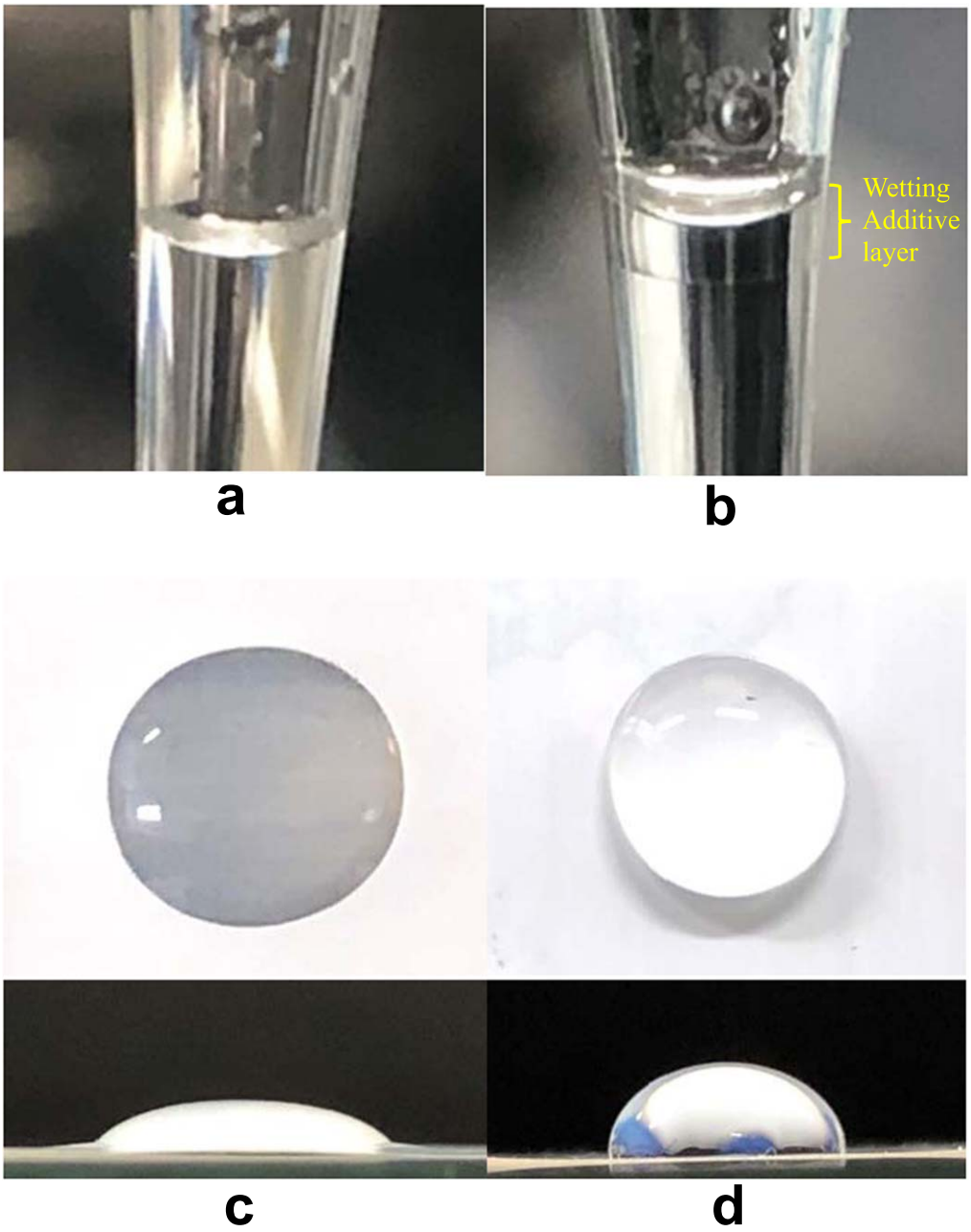


Figure 1. Photograph of separator wetting and electrolyte in Pasteur pipette. (a) single phase, [1 M $LiPF_6$ EC/PC = 1/2(v/v)] + 4 vol%PV-H; (b) two-phase separation, [1 M $LiPF_6$ EC/PC = 1/2(v/v)] + 4 vol%PV-O; (c) well wetting; (d) no wetting.

For the NCM523/NG full cell, the Ø14 mm cathode electrode and Ø15 mm anode electrode were used. The N/P ratio was about 1.34 for all the cells. The N/P ratio of a full cell is defined as the ratio of the initial anode charge capacity to the initial cathode charge capacity. The typical first charge capacity of the NCM523/NG full cell at the 0.5 C rate was 1.58 mAh cm^{-2} and the discharge capacity was 1.20 mAh cm^{-2}. The typical first charge and discharge capacities of the NG/Li half-cell were 2.12 mAh cm^{-2} and 2.00 mAh cm^{-2}, respectively. Thus, the N/P ratio is calculated to be 1.34 (2.12/1.58 = 1.34).

As in the NG/Li half cell, the Ø19 mm, 20 μm thick, 3-layer PP/PE/PP separator and Ø16 mm glass fiber filter paper GF/A were used between the electrodes. The separator was placed so that it faced the NG anode and the glass fiber filter faced the NCM523 cathode. Approximately 0.2 cm^3 of electrolyte was added to the coin cell. Two coin cells were made and the average results of the two were used. The base electrolyte was 1 M $LiPF_6$ EC/PC = 1/2(v/v)+1 wt% VC+1 wt%PMS with a carboxylic acid ester, and 1 M $LiPF_6$ EC/EMC/DMC = 3/3/4(v/v/v)+1 wt%VC+1 wt%PMS was used as the reference.

An ACD-M01A (Aska Denshi Co., Ltd.) instrument was used for the charge/discharge tests. The NG/Li half-cell was charged and discharged between 0.005V-cccv and 2.000V-c.c. at 0.5 C rate. The NCM523/NG full cell was charged and discharged between 4.2V-cccv and 3.0V-cc at 0.5 C or 1 C rate (1 C = 2.3 mA). The measurement temperature was controlled at 25 °C or 60 °C using a temperature-controlled chamber.

Results and Discussion

Determination of base electrolyte composition.—In order to determine the composition of the main solvent of the electrolyte, charge-discharge tests were conducted using electrolytes with different EC/PC volume ratios from 7/1 to 0/1 (Fig. 2). The test

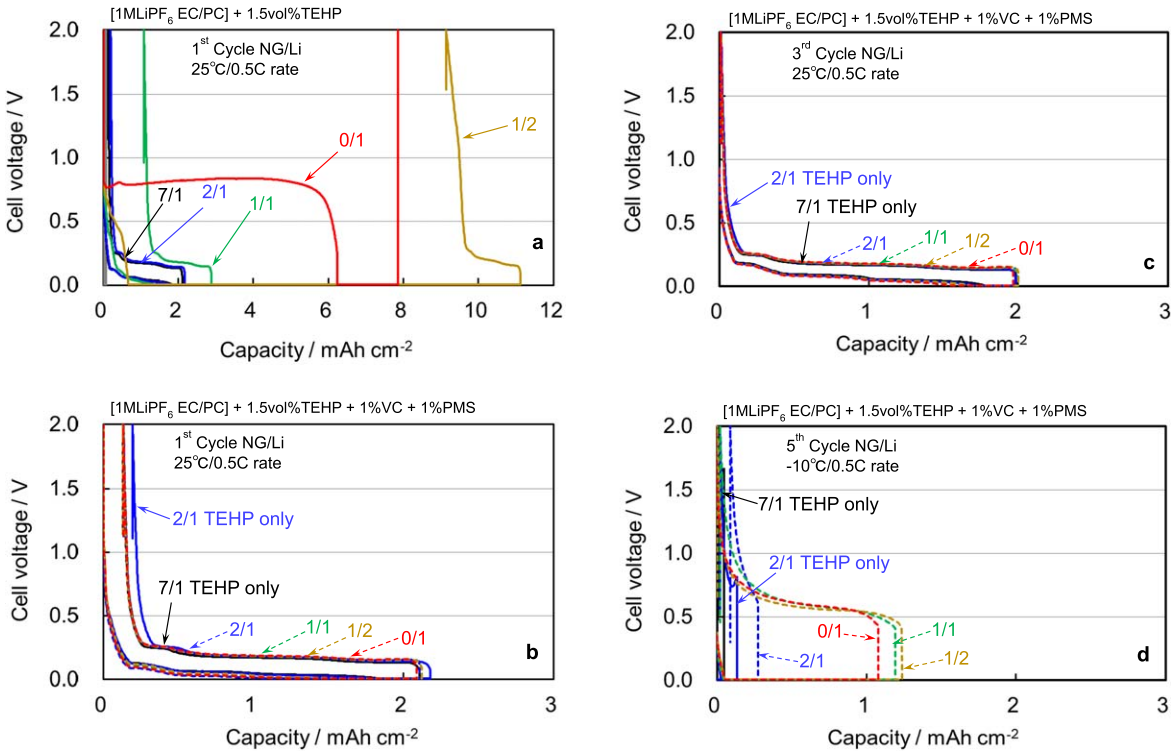


Figure 2. NG/Li half cell charge-discharge curves with various EC/PC volume ratios (shown in the figures) at 25 °C (a-c) and at −10 °C (d). VC and PMS additives are necessary for EC/PC = 1/1 or higher PC content. At −10 °C EC/PC = 1/2 showed highest discharge capacity (d).

Table II. Flash point, viscosity, and conductivity of the various solvents and electrolytes.

	Name	Flash point (°C)	Viscosity (mPa s)	Conductivity (25 °C, mS cm^{-1})
	Electrolyte solvent (v/v/v)			
1	EC/EMC/DMC = 3/3/4	24	1.07	—
2	EC/PC = 1/2	135	2.49	—
	Electrolyte (v/v/v)			
3	1 M LiFSI EC/EMC/DMC = 3/3/4	25	2.66	11.6
4	1 M $LiPF_6$ EC/EMC/DMC = 3/3/4	25	3.18	10.8
5	1 M $LiPF_6$ EC/PC = 1/1	144	7.72	7.0
6	1 M $LiPF_6$ EC/PC = 1/2	142	7.92	6.7
7	1 M $LiPF_6$ PC	130	8.01	6.1

cell used was a half-cell of natural graphite (NG)/Li, and the cycling performance was investigated at 25 °C and 0.5 C rate. We defined C rate using 1st charge capacity of NCM523/NG full cell. The same current was used also in the NG/Li half-cells. Generally, batteries in practical use for electric vehicles are charged and discharged at about 0.5 C, so the 0.5 C rate is used. 1 M $LiPF_6$ EC/PC = 7/1 did not wet the polyolefin separator and neither charged nor discharged. Therefore, we added 1.5 vol% of TEHP, a well-known surfactant, so the polyolefin separator quickly wetted and was able to charge and discharge. The charge and discharge curves for 1 M $LiPF_6$ EC/PC = 7/1 + 1.5 vol%TEHP showed typical, well known curves for Li insertion and deinsertion from graphite (Fig. 2a). The 1st cycle coulombic efficiency for 1 M $LiPF_6$ EC/PC = 7/1 + 1.5 vol%TEHP was 93.4%, which was a typical value (Table III). This indicated that the wettability of the polyolefin separators is important for highly polar solvents such as EC and PC.

Even for 1 M $LiPF_6$ EC/PC = 2/1 + 1.5 vol%TEHP, in which the ratio of PC was increased, the polyolefin separator quickly wetted and charged and discharged. The 1st cycle coulombic efficiency was 91.1%. However, when 1 M $LiPF_6$ EC/PC = 1/1 + 1.5 vol%TEHP was used, it charged but the discharge capacity of the first cycle decreased. The 1st cycle coulombic efficiency was 62.4%, which was much lower than typical value. For the PC solvent (EC/PC = 0/1) no discharge capacity was observed (The 1st cycle coulombic efficiency was 0%). Instead, the well-known PC decomposition plateau at around 0.8 V vs Li/Li^+ was observed during the first charge. Therefore, for 1 M $LiPF_6$ EC/PC = 1/1 + 1.5 vol%TEHP, we added 1 wt%VC + 1 wt%PMS, which are known to form SEI in the graphite anode.[21–23] As a result, a discharge capacity was observed. The 1st cycle coulombic efficiency for 1 M $LiPF_6$ EC/PC = 1/1 + 1.5 vol%TEHP +1 wt%VC+1 wt%PMS was 93.6%, which was a typical value. This was also true for EC/PC = 1/2. Thus, it was found that VC and PMS are necessary to charge/discharge for an electrolyte with the PC content higher than EC/PC = 1/1. The results in Figs. 2b and 2c showed that using the VC and PMS SEI forming additives even when the PC solvent is used (EC/PC = 0/1) almost identical results to the EC/PC = 7/1 charge-discharge curves were obtained.

As all the EC/PC ratios worked at 25 °C, the ionic conductivity of the electrolyte at 25 °C was then investigated. The results showed that the ionic conductivity of the EC/PC-based electrolytes is lower than that of the commonly used EC/EMC/DMC-based electrolytes (Table II; Electrolytes-5,6,7 vs 3,4). Furthermore, the ionic conductivity of EC/PC linearly decreased with the increasing PC content (Fig. 3). It was also found that in electrolytes in which more than

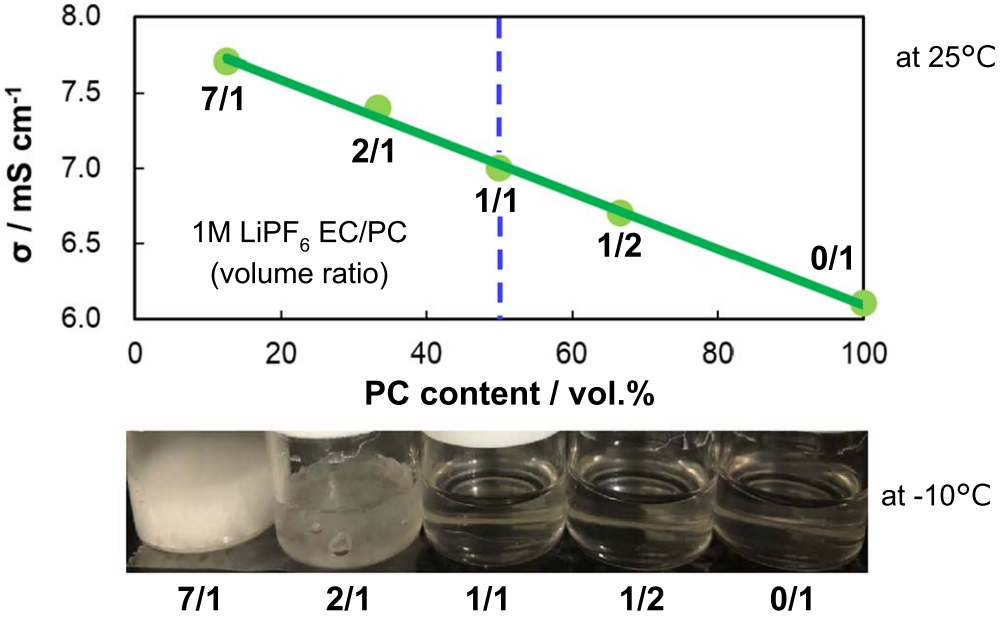


Figure 3. Ionic conductivity of the 1 M $LiPF_6$ EC/PC (volume ratio) at 25 °C and solubility at −10 °C.

Table III. Capacity of half cells in Fig. 2.

	Additives				Discharge capacity (mAh cm^{-2})		
1 M $LiPF_6$	TEHP (vol%)	VC (wt%)	PMS (wt%)	1st Eff. (%)	1st (25 °C)	3rd (25 °C)	5th (−10 °C)
EC/PC = 7/1	0.0	0	0	0.0	0.00	0.00	0.00
EC/PC = 7/1	1.5	0	0	93.8	1.98	1.98	0.04
EC/PC = 2/1	1.5	0	0	91.1	1.98	1.97	0.11
EC/PC = 1/1	1.5	0	0	62.4	1.80	1.95	1.43
EC/PC = 1/2	1.5	0	0	17.8	1.97	1.76	1.01
EC/PC = 0/1	1.5	0	0	0.0	0.00	0.00	0.00
EC/PC = 2/1	1.5	1	1	93.7	1.97	1.98	0.19
EC/PC = 1/1	1.5	1	1	93.6	1.99	1.99	1.17
EC/PC = 1/2	1.5	1	1	93.8	1.99	1.99	1.24
EC/PC = 0/1	1.5	1	1	93.6	1.95	1.96	1.09

half of the EC volume was accounted for, the solidification of EC occurred after 1 h at −10 °C (Fig. 3). This is thought to be due to the fact that the m.p. of EC is 36 °C. In actual use, batteries must be able to operate at temperatures below −10 °C. To find the optimum EC/PC ratio for operating at low temperature, the cells in Fig. 2 were cooled to −10 °C and cycled for 2 more cycles (4th and 5th). The 5th cycle discharge curves in Fig. 2d clearly showed that a low capacity can be obtained for high EC content electrolytes (EC/PC = 7/1, 2/1). The highest capacity was observed for EC/PC = 1/2, so this ratio seems to be optimum for low temperature use. Therefore, in this research, we decided to use a base electrolyte with EC/PC = 1/2(v/v) and 1 wt%VC+1 wt%PMS as the SEI forming additives.

Optimization of the R_1 structure.—The next step was to optimize the structure of R_1 and R_2 of the linear carboxylic acid ester (R_1-COO-R_2), which improves the wettability of the separator. To clarify the reductive degradability of R_1-COO-R_2 on NG, the base electrolyte was the typical 1 M $LiPF_6$ EC/DMC = 1/2 without the need to use SEI forming additives (Fig. 4a). In order to compare all the same amounts of addition, 12 vol% of DMC was added even without additives, thus all the addition amounts were standardized to 12 vol%. R_2 was fixed as the n-C_4H_9 group, and was first evaluated from the structure of R_1. Comparisons were made with n-butyl acetate (Ac-B) with R_1 = CH_3 group, n-butyl propionate (P-B) with R_1 = C_2H_5 group, butyl isobutyrate (iB-B) with R_1 = $(CH_3)_2CH$ group and n-butyl pivalate (PV-B) with R_1 = $(CH_3)_3$ group.

The results showed that the cycling performance decreased as the number of α-hydrogens in R_1 increased, and PV-B with the R_1 = t-C_4H_9 group was found to be the best (Fig. 4a). The reason for the decrease in the cycling performance as the α-hydrogen in R_1 increased may be due to the reductive decomposition of the CH_3 group hydrogen of Ac-B on the graphite anode. To prove this, methyl undecanoate (MU) with two α-hydrogens in R_1 was evaluated. The MU with the R_1 = n-$C_{10}H_{21}$ group also showed an excellent separator wettability, but the cycling performance decreased (Fig. 4b). Based on this result, it is clear that R_1 must be free of the α-hydrogen. Although this is only a matter of speculation, it is presumed that side reactions of the liner carboxylic acid esters having an α-hydrogen(s) gradually occurred as the cycles progressed, and the effects became apparent after about 20 cycles.

The conductivity of 1 M $LiPF_6$ EC/DMC = 1/2 base electrolyte is 12.00 mS cm^{-1}. Also, the conductivities of the electrolyte with 12 vol% additives are 11.21 mS cm^{-1} (Ac-B), 10.20 mS cm^{-1} (PV-B), and 9.96 mS cm^{-1} (MU). As a result, conductivity tends to decrease slightly when wettability improving additives are added. However, there is a difference in conductivity of about 10% between Ac-B (R_1 = CH_3) and PV-B (R_1 = $(CH_3)_3C$), but PV-B with lower

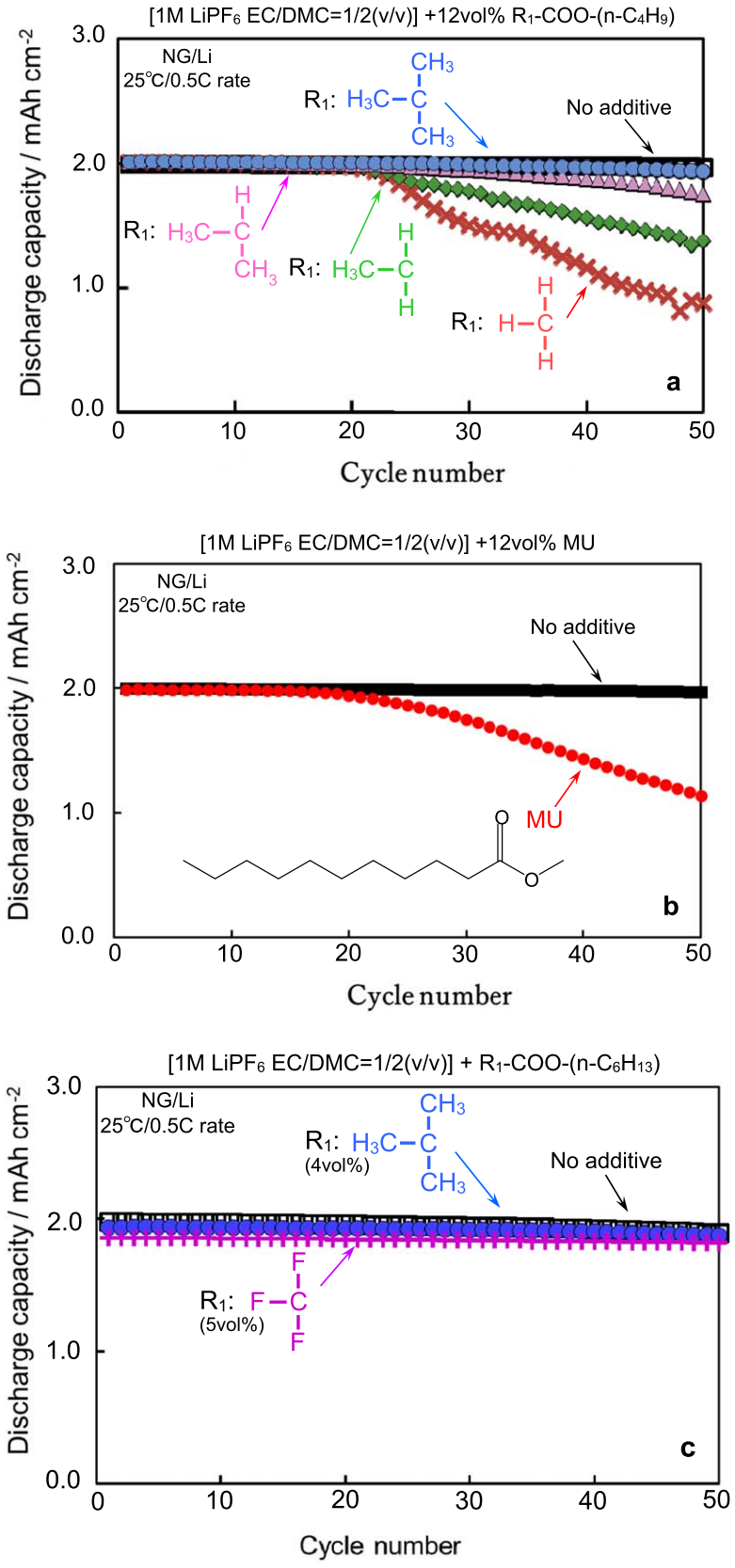


Figure 4. Coin-type half-cell: cycling performances of 1 M $LiPF_6$ EC/DMC = 1/2(v/v) using various carboxylic acid esters as additives.

conductivity has better cycling performance (Fig. 4a). Therefore, in this work, we believe that conductivity does not affect cycling performance. Furthermore, although the difference in conductivity between PV-B and MU is small, the difference in cycling performance is large (Figs. 4a, 4b), so we conclude from this comparison that conductivity does not affect cycling performance.

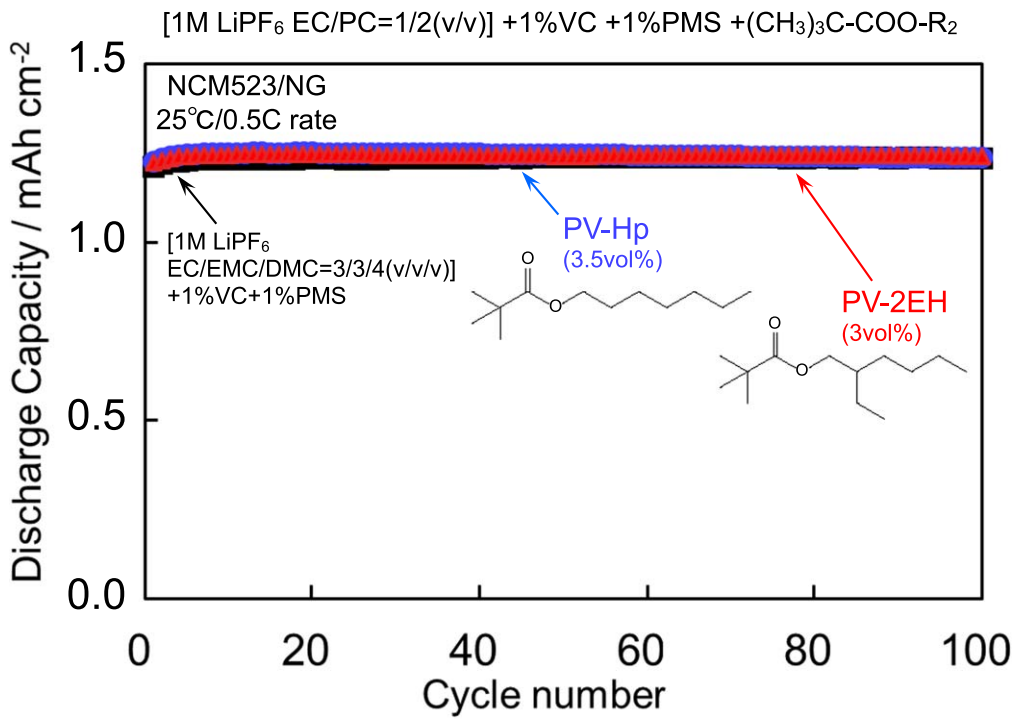


Figure 5. Coin-type full-cell: cycling performances of electrolytes using PV-Hp and PV-2EH as additives.

Next, we focused on the flash point of R_1-COO-R_2. The flash point of PV-B, which had the best performance, was 52 °C (Table IV). If this is added to 1 M $LiPF_6$ EC/PC = 1/2 with a flash point of 142 °C (Table II), it is difficult to achieve 120 °C being reduced by the flash point of PV-B. Therefore, we decided to extend the carbon number of R_2 in order to increase the flash point of R_1-COO-R_2. n-hexyl pivalic acid (PV-H), in which R_2 of PV-B was extended from n-C_4H_9 to n-C_6H_{13}, showed an improved flash point; i.e., PV-B (52 °C) < PV-H (77 °C). The wettability of the separator was also improved to PV-B (5 vol%) > PV-H (4 vol%). However, the viscosity was also found to increase to PV-B (1.13 mPa s) < PV-H (1.68 mPa s). Since the viscosity of EC/PC = 1/2 is 2.49 mPa s, the viscosity of R_1-COO-R_2 must also be less than 2.49 mPa s.

To reduce viscosity, we investigated trifluoroacetic acid n-hexyl (TF-H), in which all the α-hydrogens of the $R_1 = CH_3$ group of n-hexyl acetate (Ac-H) were replaced with fluorine. As a result, the viscosity could be decreased to PV-H (1.68 mPa s) > TF-H (0.99 mPa s). Moreover, the wettability was PV-H (4 vol%) < TH-F (5 vol%), which was close to that of PV-H. Therefore, we decided to add 4 vol%PV-H and 5 vol%TF-H to the typical base electrolyte 1 M $LiPF_6$ EC/DMC = 1/2 (v/v) and investigated the cycling performances of the half cells. The results showed that the cycling performance of TF-H with NG anodes at 25 °C and 0.5 °C rate was comparable to that of PV-H (Fig. 4c). However, TF-H had a significant problem. That is, along with the viscosity, the flash point also significantly decreased from PV-H (77 °C) > TF-H (44 °C).

Based on these results, it is essential that the structure of R_1 in R_1-COO-R_2, which provides the separator wettability, should be free of the α-hydrogen. In addition, it is clear that the structure of R_2 must combine the conflicting properties of a high flash point and low viscosity. Therefore, the third step was to search for a structure of R_2 that combines the conflicting properties of a high flash point and low viscosity.

Optimization of the R_2 structure.—The flash point was found to increase as R_2 was extended to the n-C_4H_9, n-C_6H_{13}, n-C_7H_{15}, and n-C_8H_{17} groups. However, n-octyl pivalic acid (PV-O) with the R_2 = n-C_8H_{17} group was found to separate into two phases when mixed with 1 M $LiPF_6$ EC/PC = 1/2(v/v) as shown in Fig. 1b. This was visually confirmed by aspirating the supernatant of the electrolyte with a Pasteur pipette.

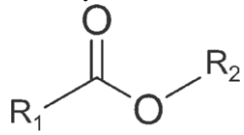
These results indicated that the longest pivalic acid esters that mix in a single phase with 1 M $LiPF_6$ EC/PC = 1/2(v/v) are up to heptyl n-pivalate (PV-Hp) with the R_2 = n-C_7H_{15} group. The flash point of 1 M $LiPF_6$ EC/PC = 1/2(v/v) with PV-Hp, which has a flash point of 90 °C, was 111 °C. (Table IV). Accordingly, in order to achieve a flash point of 120 °C but without separation into two phases, the branching structure of R_2 of the pivalic acid ester was investigated.

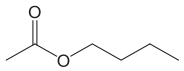
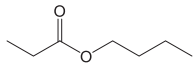
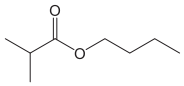
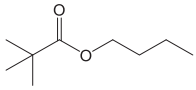
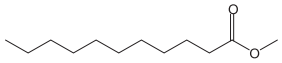
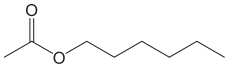
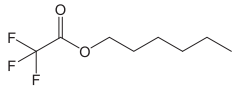
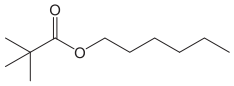
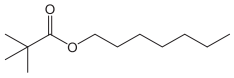
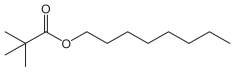
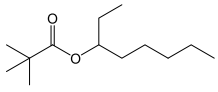
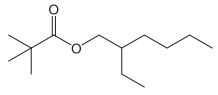
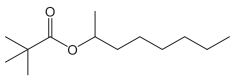
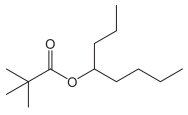
Optimization of the branched R_2 structure.—The branching investigation was based on PV-H, whose main chain is R_2 = n-C_6H_{13}. First, 3-octyl pivalic acid (PV-3O) with an ethyl group in the 1st carbon position and 2-ethylhexyl pivalic acid (PV-2EH) with an ethyl group in the 2nd carbon position were compared to PV-O with R_2 = n-C_8H_{17} having the same molecular weight. As a result, the flash point was PV-H (77 °C) < PV-3O (84 °C) < PV-2EH (94 °C) < PV-O (104 °C), and the flash point of PV-2EH with a C_2H_5 group in the 2nd carbon position was 10 °C higher than that of PV-3O with a C_2H_5 group in the 1st carbon position. The viscosity was PV-H (1.68 mPa s) < PV-3O (2.12 mPa s) ≈ PV-2EH (2.16 mPa s) < PV-O (2.52 mPa s), indicating that branching suppressed the increased viscosity. However, PV-3O with an ethyl group at the 1st carbon position separates into two phases when mixed with 1 M $LiPF_6$ EC/PC = 1/2(v/v), as well as PV-O without branching. Additionally, similar to PV-O and PV-3O, 2-octylpivalate (PV-2O) and 4-octylpivalate (PV-3O) also showed a two-phase separation when added to 1 M $LiPF_6$ EC/PC = 1/2(v/v). Eventually, it was found that only PV-2EH with an ethyl group in the 2nd carbon position did not separate into two phases.

The separator wettability of PV-2EH was PV-2EH (3 vol%) < PV-H (4 vol%), so PV-2EH can wet the separator with a smaller amount than PV-H. Moreover, the flash point of 1 M $LiPF_6$ EC/PC = 1/2(v/v) with PV-2EH achieved 120 °C (Table IV). Thus, among

Table IV. Viscosity, flash point, and wettability (a: single-phase solution, b: two-phase separation, c: well wetting) of some wetting additives.

Carboxylic acid ester



Code	R_1	R_2	Chemical structure	Carboxylic acid ester: Viscosity (mPa s)	Carboxylic acid ester: Flash point (°C)	1 M $LiPF_6$ EC/PC = 1/2(v/v) + carboxylic acid ester: Wettability (vol%)	1 M $LiPF_6$ EC/PC = 1/2(v/v) + carboxylic acid ester: Flash point (°C) (Without $LiPF_6$)
R_1 optimization							
Ac-B	CH_3	n-C_4H_9		0.70	28	a, c: 15	—
P-B	C_2H_5	n-C_4H_9		0.79	42	a, c: 13	—
iB-B	$(CH_3)_2CH$	n-C_4H_9		0.86	35	a, c: 9	—
PV-B	$(CH_3)_3C$	n-C_4H_9		1.13	52	a, c: 5	—
MU	n-$C_{10}H_{21}$	CH_3		2.60	109	a, c: 3	—
Ac-H	CH_3	n-C_6H_{13}		1.12	62	a, c: 7	—
TF-H	CF_3	n-C_6H_{13}		0.99	44	a, c: 5	—
PV-H	$(CH_3)_3C$	n-C_6H_{13}		1.68	77	a, c: 4	101 (101)
R_2 optimization							
PV-Hp	$(CH_3)_3C$	n-C_7H_{15}		2.02	90	a, c: 3.5	111 (109)
PV-O	$(CH_3)_3C$	n-C_8H_{17}		2.52	104	b	—
PV-3O	$(CH_3)_3C$	3-C_8H_{17}		2.12	84	b	—
PV-2EH	$(CH_3)_3C$	$CH_2CH(C_2H_5)C_4H_9$		2.16	94	a, c: 3	120 (115)
PV-2O	$(CH_3)_3C$	2-C_8H_{17}		2.23	90	b	—
PV-4O	$(CH_3)_3C$	4-C_8H_{17}		2.16	85	b	—

the main structural isomers of PV-O, we found that only PV-2EH having a C_2H_5 group at the 2nd carbon position can specifically mix with 1 M $LiPF_6$ EC/PC = 1/2(v/v) resulting in an electrolyte with both a high flash point and low viscosity.

Mechanism of the wetting additives.—Polar solvents with a high dielectric constant are hemispherical due to their high surface tension on the surface of hydrophobic separators such as PE and PP. This is the state in which the separator is not wet (Fig. 1d). However, by adding a "wettability improvement additive" that has a -COO group (hydrophilic group) to be mixed with high dielectric constant solvents and a carbon chain (hydrophobic group) can wet the separator.

In the PP/PE/PP separator, the outer PP is slightly easier to wet than the inner PE, thus it can happen that the PP is wetted but not the PE. Therefore, by fine chopping the amount of the carboxylic acid ester added after wetting the PP, the amount necessary for PE wetting can be measured without error. Coin cells also have the

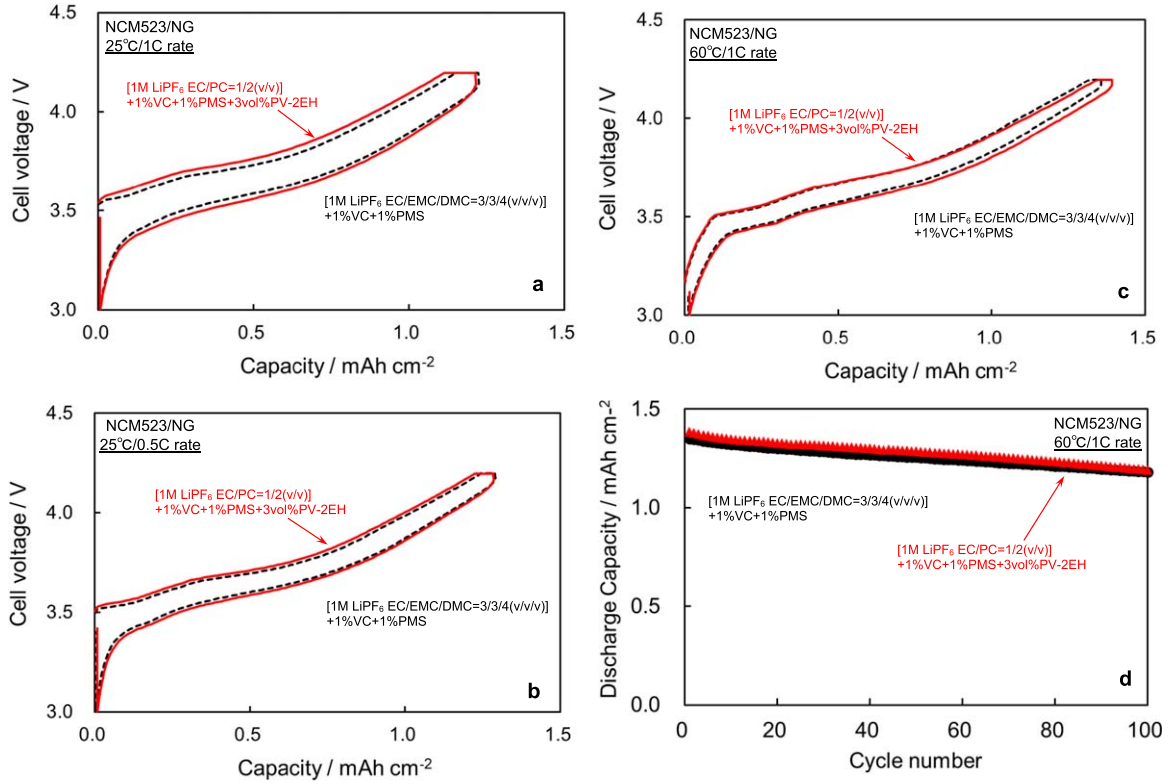


Figure 6. Coin-type full-cell: charge-discharge curves and cycling performances of electrolytes using PV-2EH as an additive. (a: at 25 °C at 1 C rate, b: at 25 °C at 0.5 C rate, c and d: at 60 °C at 1 C rate).

advantage that the wettability of the separator can be visually checked during injection. Pouch cells, which have a larger separator area than coin cells, cannot be visually checked for separator wettability. Thus, it is useful to visually check in advance using coin cells.

The structure of R_1 in R_1-COO-R_2, which gives the separator wettability, was found to require all α-hydrogens to be CH_3 groups to suppress reductive decomposition on the graphite anode. The increased number of carbons in R_1 also improved the wettability of the separator. In this case, in view of the fact that it must have a low viscosity and be homogeneous with the electrolyte, we found that a branched structure is necessary. Considering all of the above facts, it was ultimately clear that PV-2EH, which branches at the 2nd carbon position, was the better choice.

Here should be noted, that even the electrolyte does not burn, it does not mean that the battery will not burn.[24] The reason is that batteries contain flammable graphite anodes and polyolefin separators in addition to the electrolyte. If the viscosity of the electrolyte is increased to the level that polarization is significantly increased, in the battery will be some deposited Li, resulting in poor results in overcharging and nail penetration tests. We conducted this research based on the idea that the important aspect of battery safety is to control the ionic conductivity, viscosity, and solubility of the electrolyte in order to increase the heat resistance of the cathode and anode interfaces.

Coin-type full-cell battery test.—Finally, the cycling performance of the electrolyte was investigated using NCM523 as the cathode, NG as the anode, and PP/PE/PP as the separator. Since the PC ratio is higher than the EC ratio for 1 M $LiPF_6$ EC/PC = 1/2(v/v), 1 wt%VC+1 wt%PMS was added as the SEI forming additive. The results of the 25 °C, 0.5 C rate cycling test in Fig. 5 show that the addition of the linear PV-Hp and branched PV-2EH results in an excellent cycling performance, comparable to the electrolyte using the typical 1 M $LiPF_6$ EC/EMC/DMC = 3/3/4 (v/v/v). Consequently, the next step was to compare the C rate performance.

The charge-discharge curves of the coin cell are shown in Figs. 6a–6c. First, the polarization of EC/PC = 1/2(v/v) at 25 °C and 1 C rate in Fig. 6a is greater than that of EC/EMC/DMC = 3/3/4 (v/v/v). In Fig. 6b, when the rate was changed to 0.5 C, the polarization of EC/PC = 1/2(v/v) was found to be equivalent to EC/EMC/DMC = 3/3/4(v/v/v). In Fig. 6c, the 1 C rate of cells in Fig. 6a remained the same, but the temperature increased to 60 °C. As in Fig. 6b, the polarization of EC/PC = 1/2(v/v) was found to be equivalent to EC/EMC/DMC = 3/3/4(v/v/v). These results clearly indicated that the cause of the higher polarization at 25 °C and 1 C rate in Fig. 6a is not due to irreversible electrode interface degradation, but simply to reversible electrolyte viscosity differences. Even at 60 °C the cycling performance is similar to commonly used electrolyte as can be seen in Fig. 6d. This result clearly presents the opportunity for using this electrolyte in larger, real batteries in future.

Conclusions

At −10 °C, we found that the PC content in [1 M $LiPF_6$ EC/PC] should exceed 50%, and the suitable ratio is EC/PC = 1/2.

We found that the use of branched carboxylic acid esters as separator wetting additives in a high dielectric constant solvent EC/PC = 1/2 produces a safe electrolyte with a flash point of 120 °C or higher. We found that the structure of the R_1 group in R_1-COO-R_2 should be free of α-hydrogens to suppress reductive decomposition on the graphite anode. In addition, for the structure of R_2, it is preferable to have a longer carbon chain to achieve a high flash point. However, we found that it is necessary to have a branched structure at a specific position in order to achieve a low viscosity and homogeneity with the electrolyte. Among these, we found that 2-ethylhexyl pivalic acid (PV-2EH), which has an -C_2H_5 group on the 2nd carbon position of the R_2 = n-C_6H_{13}, is the best for raising the flash point as much as possible. Based on the above research results, it is greatly expected that these electrolytes will be used in automotive cells with high capacities.

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