

Performance of Li-ion cells with new electrolytes conceived for low-temperature applications

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Abstract

In an effort to develop a useful electrolyte for a Li-ion cell applicable in a wide operation temperature, we have studied a number of ternary electrolytes containing a cyclic carbonate (ethylene carbonate (EC)), a linear carbonate (dimethyl carbonate (DMC), diethyl carbonate (DEC), or ethylmethyl carbonate (EMC)), and a low-temperature freezing solvent (methyl acetate, ethyl acetate, isopropyl acetate, isoamyl acetate, or ethyl propionate (EP)). We have studied performance including cycle life of Li-ion cells containing these electrolytes at various temperatures. The performance was various with various electrolyte compositions showing a significant effect of the low-temperature freezing solvents while the effect of the linear carbonates was relatively minor. Cells containing an electrolyte of EC–DMC–MA showed an excellent initial performance at -20°C but it did not give a good cycle life compared with others. Two electrolyte compositions containing EP, EC–DEC–EP and EC–EMC–EP, showed the most attractive overall performance including initial performance at -20°C , cycle life and rate capability at room temperature as well as 50°C . © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lithium-ion cells; Electrolyte; Low-temperature performance; Cycle life

1. Introduction

Many applications of Li-ion cells require a wide range of operation temperature, e.g., -20°C to 60°C . Performance of a Li-ion cell, especially at low temperatures, is often limited by the nature of its electrolyte. Although electrolytes of ethylene carbonate (EC)-containing binary solvent mixtures such as 1 M LiPF_6/EC -dimethyl carbonate (DMC) and 1 M LiPF_6/EC -diethyl carbonate (DEC) have been used for Li-ion cells, their operation temperature range is rather limited to temperatures of approximately above -10°C . These electrolytes freeze or segregate at temperatures of -15°C or above [1]. Electrolytes of many multi-component mixtures have been studied to extend the operation temperature range of the cell. Ternary electrolytes of EC–DEC and methyl acetate (MA), ethyl acetate (EA), methyl propionate (MP) or ethyl propionate

(EP) have been studied in a Li-ion cell [2]. Good capacity at -10°C and good storage characteristics at 60°C were reported with cells containing a 1.5 M LiPF_6/EC –DEC–MP electrolyte although some gas evolution was observed after a 60°C -storage period. Good low-temperature performance of synthetic graphite/lithium cells containing EC–methyl formate (MF) electrolyte was reported by Ein-Eli et al. [3]. A variety of EC-based electrolytes has been studied by Mayer et al. [1] for Li-ion cells. They reported that their cycle life was adversely affected by the addition of MA, EA, MP, EP, and normal propyl acetate (n-PrA) to EC–DEC and EC–DMC electrolytes, although electrolytes containing the ester component showed good performance at low temperatures.

Performance at elevated temperatures, especially cycle life, of Li-ion cells is also important since their application often require operation at elevated temperatures. For example, temperature of the battery compartment of a notebook computer can be as high as 50°C . However, available information on elevated-temperature performance of electrolytes in the cell is rather limited. Behavior of carbon or graphite electrodes is generally sensitive to electrolyte compositions due to their individual chemistry at the electrolyte interface [3,4].

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In this paper, we have studied in cell performance of ternary electrolytes that contain EC, a linear carbonate and a low freezing solvent. Our purpose of the study was to find an electrolyte mixture that is usable at -20°C and gives good cycle life at elevated temperature of 50°C in a Li-ion cell.

2. Experimental

2.1. Chemicals

Following battery grade chemicals, MA, ethylmethyl carbonate (EMC), EC, 1 M $\text{LiPF}_6/\text{EC-DMC}$ (1:1), 1 M $\text{LiPF}_6/\text{EC-DEC}$ (1:1), 1 M $\text{LiPF}_6/\text{EC-EMC}$ (1:1), 1 M LiPF_6/EC , and 1 M LiPF_6/DEC , were obtained from Mitsubishi Chemical, Battery grade solutions of 1 M LiPF_6/EA and 1 M LiPF_6/MA were obtained from Mitsui Petrochemical Industries. Isoamyl acetate (IAA) and isopropyl acetate (IPA), both of 99 + % grade, were obtained from Aldrich. Melting and boiling points of individual electrolyte solvents are shown in Table 1. All solvents were dried using molecular sieves 4A. Ternary electrolytes were prepared by mixing the binary electrolytes, solvents and LiPF_6 salt (Hashimoto Chemical, battery grade) which was used as received.

2.2. Test instruments

Water contents in electrolytes were measured using a Mettler Toledo DL37 KF coulometer. The water contents were in the range of 3–20 ppm. Electrolyte preparation and assembly of coin-type test cell were carried out in an argon-filled glove box made by Vacuum Atmospheres. Assembly of 18650-size test cells was carried out in a dry room. Cycling tests were carried out using a TOSCAT-3000 tester (Toyo System). Low-temperature tests were carried out in a Temperature and Humidity Chamber (Tabai Espec) and tests at 50°C in a 1525 Model Incubator (VWR Scientific).

Table 1
Properties of solvents used in this study

Solvent	Abbreviation	Melting point ($^{\circ}\text{C}$)	Boiling point ($^{\circ}\text{C}$)
Ethylene carbonate $\text{C}_3\text{H}_4\text{O}_3$	EC	36	238
Dimethyl carbonate $(\text{CH}_3\text{O})_2\text{CO}$	DMC	3	90
Ethylmethyl carbonate $\text{CH}_3\text{OCOOC}_2\text{H}_5$	EMC	-15	109
Diethyl carbonate $(\text{C}_2\text{H}_5\text{O})_2\text{CO}$	DEC	-43	127
Isoamyl acetate $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	IAA	-78	142
Isopropyl acetate $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)_2$	IPA	-73	89
Ethyl acetate, $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	EA	-84	77
Methyl acetate, $\text{CH}_3\text{CO}_2\text{CH}_3$	MA	-98	57.5

Table 2

Cycle life of MCF/ LiCoO_2 coin cells (2016-size) containing various 1 M LiPF_6 electrolyte solutions

Electrolyte ID	Solvent mixture	Average cumulative capacity (mAh)	
		At 240 cycle	At 320 cycle
A	EC-DMC-MA	1092	1407
B	EC-DMC-EA	1053	^a
C	EC-DMC-IPA	970	1215
D	EC-DMC-IAA	970	^a
E	EC-DMC-EP	958	^a
F	EC-EMC-EA	1126	1444
G	EC-EMC-EP	1118	^a
H	EC-EMC-MA	1073	1338
I	EC-EMC-IAA	1034	1313
J	EC-EMC-IPA	994	1277
K	EC-DEC-MA	1088	1391
L	EC-DEC-EP	1076	^a
M	EC-DEC-IPA	1075	1391
N	EC-DEC-IAA	1043	1363
O	EC-DEC-EA	996	1271
P	EC-DMC	1114	1459

^aThe test was interrupted due to lab moving.

2.3. Test cells and cycle regimes

All test cells were made of a graphite (MCF) anode and a LiCoO_2 cathode. A coin-type (2016) cell was used for a preliminary electrolyte-screening test to reduce the number of electrolytes from 15 to 6 for the final evaluation in 18650-size cells. Cycle life tests of the coin cells were carried out at room temperature ($22-25^{\circ}\text{C}$) using duplicate test cells for each electrolyte composition. Charge regime for the coin cells consisted of a constant current charging at 3 mA followed by a constant voltage charging with the voltage cutoff limit of 4.1 V. The constant voltage charging was terminated when the current reduced to 0.6 mA. Discharge was carried out under a constant current of 3 mA to a voltage cut-off limit of 2.5 V. An average initial capacity of the coin cell was approximately 5 mAh at discharge rate of 3 mA.

Cycle life test both at room temperature and at 50°C and other performance tests were carried out using 18650-size cells containing the six electrolytes for final evaluation. All tests were carried out using cells from a single production batch to minimize variations from other factors. For capacity test at -20°C , all cells were charged at room temperature at 0.5 C (700 mA) to the voltage cutoff limit of 4.1 V followed by an additional charge at the constant limit voltage to the current limit of 20 mA. Cells, then, were held at -20°C for 3 h prior to discharging.

The cycle life test of 18650 cells was carried out in the following cycle regime. Cells were charged at 1 C rate (1400 mA) to a voltage limit of 4.1 V followed by an additional charge at constant voltage of 4.1 V to the current limit of 20 mA. They were discharged at the same rate to 2.5 V for each cycle. However, at each tenth cycle

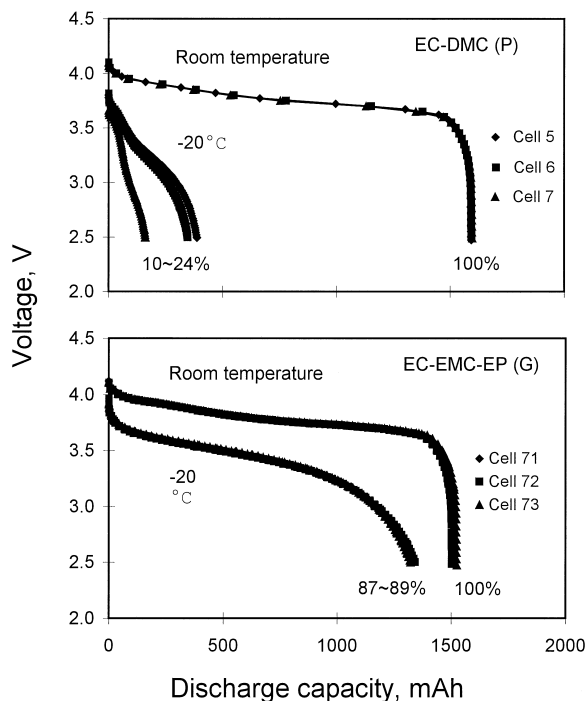


Fig. 1. Capacity of 18650-size lithium-ion cells containing 1 M $\text{LiPF}_6/\text{EC-DMC}$ and 1 M $\text{LiPF}_6/\text{EC-EMC-EP}$ electrolytes at room temperature and -20°C at 0.2 C (280 mA) discharge rate.

both the charge and discharge current was decreased to 0.2 C rate (280 mA) such that the capacity variation at these two rates can be estimated. Test cells were soaked at 50°C for 1 h before start of the elevated temperature cycling test.

3. Results and discussion

3.1. Preliminary selection of electrolytes

Fifteen different electrolytes of ternary mixtures as listed in Table 2 were studied. These electrolytes were made of three main groups of mixtures: (i) mixtures of EC-DMC with a third component in volume ratio of 30:30:40, (ii) mixtures of EC-DEC with the third component (30:35:35), and (iii) mixtures of EC-EMC with the third component (30:30:40). The third component was

chosen from a group of low-freezing-point solvents: MA, EA, IAA, IPA and EP. An electrolyte of 1 M $\text{LiPF}_6/\text{EC-DMC}$ (50:50 by volume) was used for comparison standard (control mixture) for performance.

Results of a low-temperature soaking test showed that all ternary electrolytes used in this study did not freeze or segregate after 1 day of storage at -20°C whereas the EC-DMC control mixture (P) showed a clear visual sign of segregation at this temperature. A cumulative discharge capacity of the coin cell has been calculated by adding capacity values of individual cycles in order to estimate relative cycle life of the cells. Cumulative capacity values of the cells containing various electrolytes are shown in Table 2. Each value is an average of duplicate cells.

Six best electrolytes (A, F, G, K, L, M) and the control electrolyte (P) were chosen for further evaluation in 18650-size cells. The choice was based on the cumulative capacities of the coin cell at 240th cycle since the results at 320th cycle were available only for a part of the cells.

3.2. Low-temperature performance

Discharge capacities of 18650-size test cells containing the six selected electrolytes were measured at room temperature and -20°C to evaluate the low-temperature performance of the electrolyte. For an illustration of the low-temperature performance, discharge curves of cells containing 1 M $\text{LiPF}_6/\text{EC-DMC}$ and 1 M $\text{LiPF}_6/\text{EC-EMC-EP}$ electrolytes at -20°C and room temperature are shown in Fig. 1. Relative discharge capacity values at -20°C compared to those at room temperature at various discharge rates (0.2–1.0 C) for various electrolyte compositions are shown in Table 3. It is evident that the discharge capacity at -20°C decreased as the discharge rate increased for all ternary electrolytes with a possible exception of the 1 M $\text{LiPF}_6/\text{EC-DEC-EP}$. However, the behavior at -20°C of the cell containing the binary control electrolyte (1 M $\text{LiPF}_6/\text{EC-DMC}$) was contrary showing increased capacity values as discharge rate increased. It is speculated that the increased capacity as the rate increased might be due to increase of cell temperature during discharge of the cell. Rate-dependent increase of cell temperature due to the exothermic discharge reaction of the Li-ion

Table 3
18650-size MCF/ LiCoO_2 cell discharge capacity values at -20°C vs. room temperature

Electrolyte ID	1 M LiPF_6 electrolyte composition	Discharge capacity as percentage of those at room temperature		
		0.2 C (280 mA)	0.5 C (700 mA)	1 C (1400 mA)
P	EC-DMC (1:1)	10–24	14–16.5	45–53
L	EC-DEC-EP (30:35:35)	57–63	69–72	62–65
M	EC-DEC-IPA (30:35:35)	72–75	39–48.5	32–35
G	EC-EMC-EP (30:30:40)	87–89	82–86	79–81
K	EC-DEC-MA (30:35:35)	83–92	77–80	72–80
F	EC-EMC-EA (30:30:40)	94	85–89.5	75–80
A	EC-DMC-MA (30:30:40)	94	92	89–91

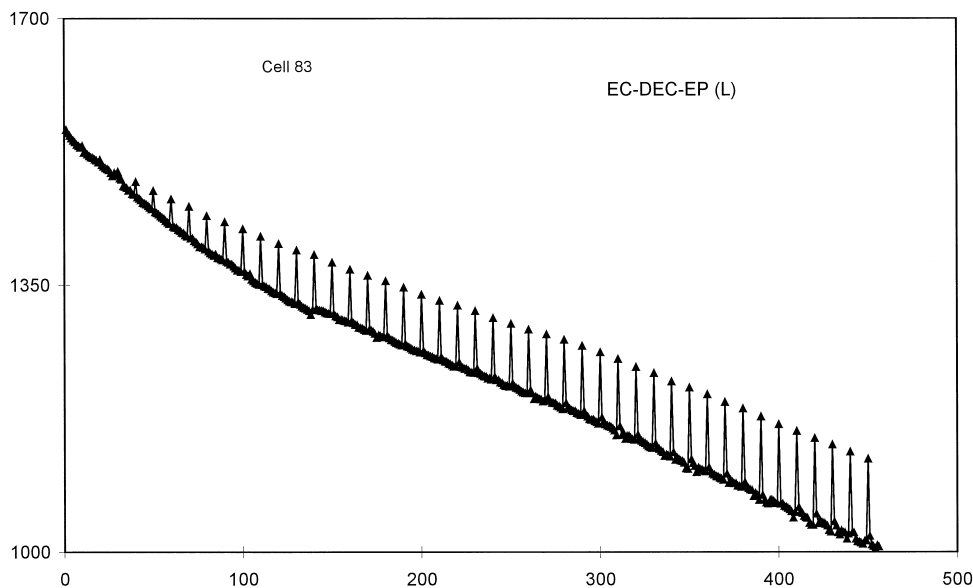


Fig. 2. Cycle life performance of 18650-size lithium-ion cells containing various 1 M LiPF₆ electrolyte solutions at 50°C.

cell has been reported [5,6]. The temperature increase of greater than 10°C at 1 C rate discharge was observed with a 18650-size cell. It appears conceivable that partially frozen EC–DMC electrolyte at –20°C might melt as the cell is discharged and improve the discharge capacity. The degree of melting, how soon it melts, and the resultant improvement of the capacity may depend on the discharge rate as observed for electrolyte P in Table 3. The capacity of cells with 1 M LiPF₆/EC–DEC–EP electrolyte increased as the rate is increased to 0.5 from 0.2 C but decreased when the rate is increased further to 1 C. It appears conceivable that the increase in capacity as the rate is increased to 0.5 from 0.2 C might be due to the domination of the effect of the temperature increase. The decrease in capacity as the rate increased to 1 from 0.5 C might be due to domination of the effect of the increased rate itself. The best performance at –20°C at high rate discharge was observed with 1 M LiPF₆/EC–DMC–MA (30:30:40) electrolyte (A) although it was not the best overall performer as discussed later, especially in cycle life.

3.3. Cycle life

Cycle life tests of 18650-size cells containing various electrolytes were carried out at room temperature as well as at 50°C. The results of the best performing cell of triplicate samples are shown for various electrolytes in Figs. 2 and 3. Although all test cells contained approximately the same amount of active materials, their initial discharge capacities varied considerably. Initial discharge capacity of cells containing P, A, F, and K electrolytes was in the neighborhood of 1620 mAh. The capacity of cells containing other electrolytes (L, M, and G) was considerably lower than this value both at room temperature and

50°C. It appears that the initial capacity is related to the quantity of irreversible capacity of the cell. The cells

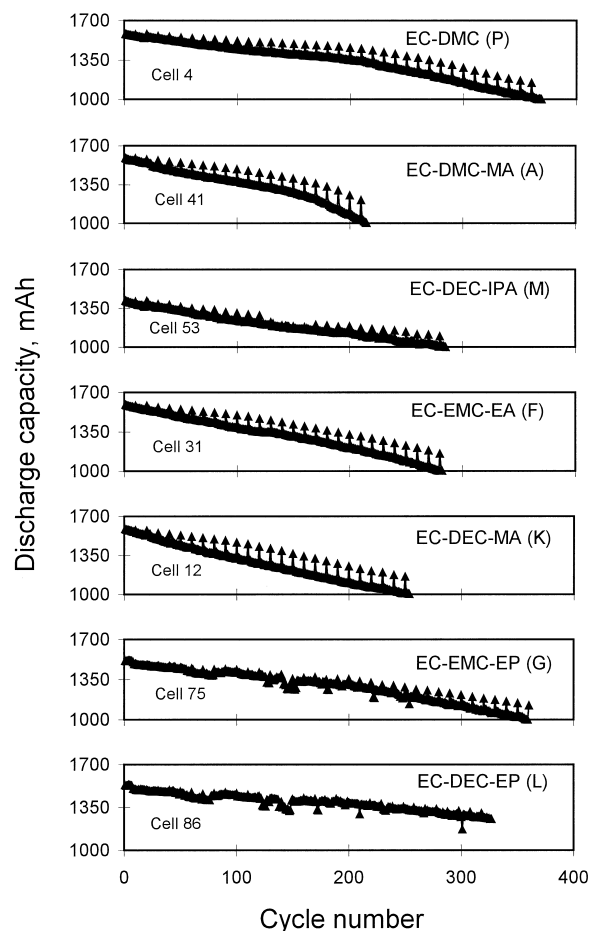


Fig. 3. Cycle life performance of 18650-size lithium-ion cells containing various 1 M LiPF₆ electrolyte solutions at room temperature.

Table 4

Correlation between irreversible capacity on first formation cycle and initial discharge capacity

Electrolyte ID	1 M LiPF ₆ electrolyte solution	Cell no.	Irreversible capacity (%)	Initial discharge capacity (mAh)
F	EC–EMC–EA (30:30:40)	38	6.26	1623
K	EC–DEC–MA (30:35:35)	18	6.27	1626
A	EC–DMC–MA (30:30:40)	50	6.77	1621
P	EC–DMC (1:1)	10	6.82	1616
G	EC–EMC–EP (30:30:40)	72	8.50	1557
L	EC–DEC–EP (30:35:35)	83	11.30	1554
M	EC–DEC–IPA (30:35:35)	59	14.46	1482

which show smaller initial capacity (electrolytes L, M, and G) showed larger irreversible capacity than those showing larger initial capacity as shown in Table 4.

The relationship between irreversible capacity and cycle life, however, is not clear. Two cells (electrolytes L and G) out of three (L, M, and G) which show larger irreversible capacity values than the other cells, showed substantially improved cycle life while the third cell (electrolyte M) showed similar cycle life to the remaining cells as shown in Figs. 2 and 3. However, it is apparent that the improved cycle life (electrolytes L and G) might be due to the presence of EP.

In order to determine relative cycle life of the test cells, cumulative discharge capacity values to a cutoff limit capacity value of 1 Ah during cycling were calculated. The cumulative capacity included only the capacities at 1 C rate (1400 mA) discharge excluding the capacities at 0.2 C

rate for convenience. This cumulative capacity is a measure of total capacity at 1 C rate discharge throughout useful cell life to 1 Ah capacity limit. Results are summarized in Table 5.

Cycle life at 50°C was reduced from the cycle life at room temperature by a factor of 1.3–1.7 for the ternary electrolytes of A, F, G, K and M. The temperature effect for the binary electrolyte (P) was much greater, showing 3.6 times greater cycle life for this electrolyte at room temperature than at 50°C. A quantitative effect of the temperature for electrolyte L is not available since the cycle life test is not completed. Since the temperature effect varies with the electrolyte compositions, it is difficult to predict the room temperature cycle life from value at 50°C. However, cycle life of the cells containing ternary electrolytes with EP (electrolytes G and L) are substantially better than those with the other electrolytes regard-

Table 5

Cycle life to 1 Ah and cumulative capacity to 1 Ah of 18650-size MCF/LiCoO₂ cells with various electrolytes at room temperature and 50°C

Electrolyte ID	1 M LiPF ₆ electrolyte solution	Room temperature			50°C		
		Cell no.	Cycle life	Cumulative capacity (Ah)	Cell no.	Cycle life	Cumulative capacity (Ah)
P	EC–DMC (1:1)	3	336	407.7	9	93	123.3
		4	372	444.5	10	105	136.7
		Ave.	354	426.1	Ave.	99	130.0
M	EC–DEC–IPA (30:35:35)	51	208	223.4	59	153	167.4
		53	285	306.4	60	152	164.2
		Ave.	247	264.9	Ave.	153	165.8
K	EC–DEC–MA (30:35:35)	12	254	291.2	18	172	199.3
		14	243	272.9	20	153	179.7
		Ave.	249	282.1	Ave.	163	189.5
F	EC–EMC–EA (30:30:40)	31	282	333.2	38	153	178.2
		33	236	272.5	39	151	179.9
		Ave.	259	302.8	Ave.	152	179.1
A	EC–DMC–MA (30:30:40)	41	215	260.2	50	131	153.5
		43	216	257.3	48	131	153.4
		Ave.	216	258.7	Ave.	131	153.5
G	EC–EMC–EP (30:30:40)	75	360	416.7	72	262	305.0
		76	315	369.5	73	242	277.7
		Ave.	338	393.1	Ave.	252	291.3
L	EC–DEC–EP (30:35:35)	86	> 670 expected		81	434	485.2
		87			83	456	511.3
					Ave.	445	498.2

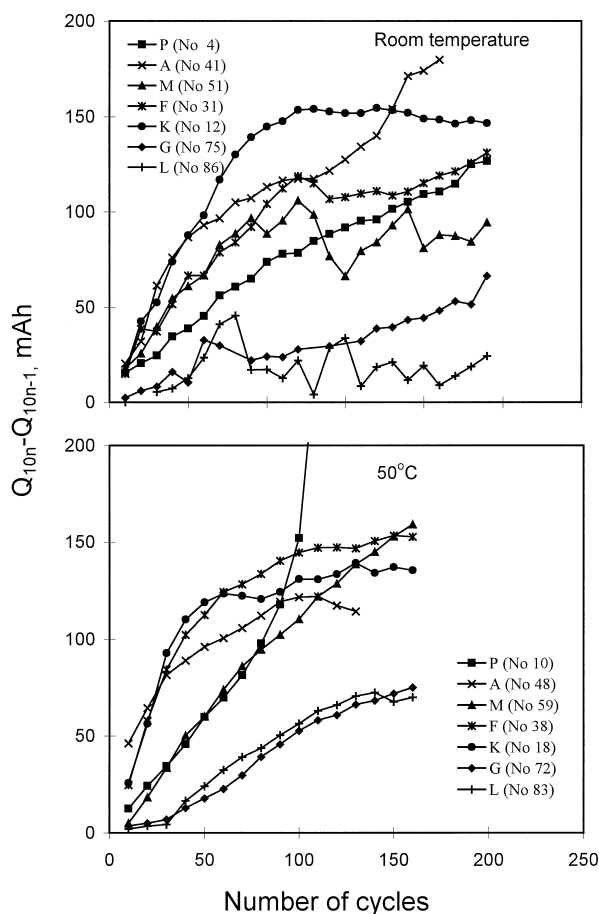


Fig. 4. Differential capacities ($Q_{10n} - Q_{10n-1}$, where n is cycles decade) of 18650-size lithium-ion cells during cycle life test at room temperature and 50°C.

less of the temperature as shown in Figs. 2 and 3 with an exception of electrolyte P at room temperature. Cycle life of the cell containing this electrolyte at room temperature was approximately the same as of electrolyte G, but that of electrolyte L is expected to be much greater than the others as shown in Fig. 3. Large temperature effect of the cells containing electrolyte P suggests that the mechanism of capacity fading with cycling in the later part of cycle life might be different from that of other cells although present evidence is insufficient for elucidation of the mechanism.

3.4. Rate capability and its change with cycling

In order to estimate the rate capability and its change with cycling, the differential capacities ($Q_{10n} - Q_{10n-1}$ where n = number of decades of cycle), were calculated as shown in Fig. 4. This differential capacity represents differences between capacities at 0.2 C rate (Q_{10n}) and those at 1 C rate (Q_{10n-1}) during cycling. Large differential capacity means large cell impedance and low rate capability. The differential capacity values were various with various electrolyte compositions at different temperatures

and increased with cycling at various rates as shown in Fig. 4. Although it is difficult to estimate quantitative effects of individual electrolyte components on the rate capability, the beneficial effect of EP is evident from the results as shown in Fig. 4. The cells with the electrolytes containing EP show substantially smaller differential capacities than the other cells by a factor of 2 or greater at all cycles during the cycling test both at room temperature and 50°C. Although the reason is not clear at this time, the present results indicate that EP is effective in reducing degradation of the rate capability with cycling.

4. Conclusions

We have studied a number of ternary electrolytes containing EC, a linear carbonate (DMC, DEC, or EMC), and a low freezing solvent (MA, EA, IAA, IPA, or EP) for performance at various temperatures, cycle life and rate capability of Li-ion cells containing them. The performance was various with various electrolyte compositions showing a significant effect of the low freezing solvents while the effect of the linear carbonates was relatively minor. Cells containing an electrolyte of EC–DMC–MA showed an excellent initial performance at -20°C although it is not attractive for a practical cell since it did not give a good cycle life relative to others. Two electrolyte compositions containing EP (EC–DMC–EP and EC–EMC–EP) were the most attractive for overall performance, i.e., initial performance at -20°C , cycle life and rate capability at room temperature and 50°C.

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