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New thin lithium-ion batteries using a liquid electrolyte with thermal stability

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Abstract

New thin lithium-ion batteries (LIBs) using a laminated film bag, an organic liquid electrolyte, and a mesophase-pitch-based carbon fiber (MCF) anode exhibited high discharge performance, a very low swelling under a high-temperature storage, and excellent safety performance. A 1.5 M solution of $LiBF_4$ in an ethylene carbonate (EC)/γ-butyrolactone (GBL) mixed solvent was found to be a promising liquid electrolyte for the thin LIBs because the electrolyte has a high flame point of 129°C, a high boiling point of 216°C, a low vapor pressure, and a high conductivity of 2.1 mS/cm at −20°C. It was demonstrated that the thin LIB using B-doped MCF anode has a high energy density of 172 Wh/kg, high rate capability, high capacity at −20°C, and a long cycle life of 500 cycles. The safety of thin LIBs under overcharging tests and oven tests was superior to that of conventional prismatic LIBs and PLBs. The very low swelling and the excellent safety performance were attributable to the stability of $LiBF_4$–EC/GBL electrolyte against $LiCoO_2$ cathode material.

Keywords: Thin lithium-ion battery; Liquid electrolyte; Laminated film bag

1. Introduction

Prismatic lithium-ion batteries (LIBs) have been developed in order to achieve progress in terms of higher capacity, lighter weight, thinness, and safety. Recently, thin film and prismatic polymer lithium-ion batteries (PLBs) using polymer gel electrolytes were commercialized for some portable electronic devices. PLBs have the advantages of thinness and light weight due to the use of the laminated film bag [1,2]. However, PLBs are subject to some problems in that their performance is inferior in some respects to that of LIBs. We developed new thin LIBs whose performance and safety are superior to those of PLBs and prismatic LIBs. We named the thin LIB ‘‘advanced lithium-ion battery (ALB)’’ [3]. The ALB has been produced by A&T Battery Corp., since March 2000. By using an organic liquid electrolyte with thermal stability, the MCF anode, and the laminated film bag, the thin LIBs with high performance and safety were fabricated as thin cells with the thickness of between 0.5 and 4 mm. Herein, we report the performance, the safety, and the characteristics of materials of the new thin LIBs.

2. Experimental

Thin LIBs were constructed by using the MCF anode, a $LiCoO_2$ cathode, the organic liquid electrolyte, a separator, and an aluminum-plastic laminated film bag as the case. The electrolyte used for the thin LIBs was a 1.5 M solution of $LiBF_4$ in a mixture 1:3 by volume of EC and γ-GBL (1.5 M $LiBF_4$–EC/GBL). 1 M $LiPF_6$–EC/diethyl carbonate (DEC), 1 M $LiPF_6$–EC/methyl-ethyl carbonate (MEC), and 1 M $LiPF_6$–EC/propylene carbonate (PC) electrolytes were also used for the purpose of comparison with the 1.5 M $LiBF_4$–EC/GBL electrolyte. The MCF and the B-MCF were prepared at Petoca Co., Ltd., and graphitized. The B-MCF was highly graphitized to enhance the capacity [4]. The anode and the cathode construction were the same as those described previously [5,6]. The charge–discharge characteristics were evaluated between 4.2 and 3 V at 20°C.

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3. Results and discussion

3.1. Liquid electrolyte

The electrolyte of thin LIBs using the laminated film bag must be more thermally stable than that of conventional prismatic LIBs using a metallic can. A promising electrolyte is a solution consisting of high-viscosity solvents such as EC, PC, and GBL because the high-viscosity solvents have high boiling points, high flash points, and low vapor pressure. For the thin LIBs in the high temperature condition, the vapor pressure of the promising electrolytes must be also lower than those of the EC/DEC and the EC/MEC electrolytes used for the prismatic LIBs. Fig. 1 shows change of vapor pressure of 1 M $LiPF_6$–EC/DEC (1:1) electrolyte and 1.5 M $LiBF_4$–EC/GBL (1:3) electrolyte with temperature. In the high-temperature range of 60–100°C, the EC/GBL electrolyte showed very low vapor pressure in comparison with the EC/DEC electrolyte. However, it is necessary for the thin LIBs using the high-viscosity solvents to enhance the charge–discharge performance of anode. In the $LiBF_4$–EC/GBL electrolyte, even the highly graphitized B-MCF anode exhibited the high reversibility and high capacity. The reversible capacity of 342 mAh/g and the coulombic efficiency of 93.2% were obtained at the first cycle. The capacity of B-MCF anode was larger than that of MCF anode. The efficiency in the $LiBF_4$–EC/GBL electrolyte is comparable to that in the $LiPF_6$–EC/DEC electrolyte [5]. The efficiency in the $LiPF_6$–EC/PC electrolyte was a low value of 59% because the electrolytes containing PC lead to a large gas evolution on the graphite anode at the first charge [7]. On the other hand, the $LiBF_4$–EC/GBL electrolyte had high conductivities in the lower temperature range of −40 to 0°C. The conductivity of 1.5 M $LiBF_4$–EC/GBL (1:3) electrolyte at −20°C was 2.1 mS/cm which is higher than those of 1 M $LiPF_6$–EC/DEC (1:1) electrolyte and 1 M $LiPF_6$–EC/PC (1:1) electrolyte. Therefore, we propose that the $LiBF_4$–EC/GBL electrolyte should be used for thin LIBs using the laminated film bag because it has the advantages of a high boiling point of 216°C, a high flash point of 129°C, a low vapor pressure of 24.6 mmHg at 80°C, high conductivities of 6.04 mS/cm at 20°C and 2.1 mS/cm at −20°C, and a high coulombic efficiency of 93% at the first cycle.

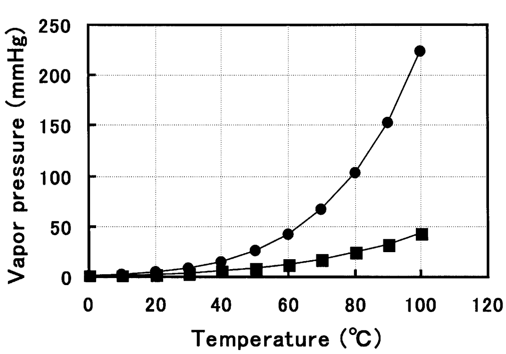

Fig. 1. Change of vapor pressure with temperature in (●) 1 M $LiPF_6$–EC/DEC (1:1) and (▲) 1.5 M $LiBF_4$–EC/GBL (1:3).

3.2. Performance test data

Table 1 shows main specifications of thin LIBs with thickness of 1.2 and 3.6 mm. The energy densities of the thin LIBs were higher than those of prismatic LIB [6] and thin PLBs [1,2]. Specifically, by using the B-MCF anode, the 363562B-type LIB had the highest energy density of 172 Wh/kg. Fig. 2 shows the discharge curves of the thin LIBs at various discharge rates between 0.2 and 3 C. The capacities at 3 C rate discharge of the 123562-type and the 363562B-type LIBs were 85 and 88% of their capacities at the 0.2 C rate discharge, respectively. Such a rate capability is superior to that of PLB [1,2]. Fig. 3 shows the dependence of capacity ratio of the thin LIBs on temperature. At −20°C, the capacities of the 123562-type at 0.5 C rate discharge and the 363562B-type at 1 C rate discharge were 88 and 50% of those at 20°C, respectively. The excellent high-rate capability and low-temperature characteristics are due to the rapid deintercalation of lithium ions from the MCF anode [5,6]. Fig. 4 shows the charge–discharge cycle life of 123562-type and 363562B-type LIBs. The 363562B-type LIB maintained 80% of its initial capacity after 500 cycles in a rapid charge–discharge cycling test of 1 C rate. The 123562-type LIB maintained 70% after 500 cycles. Thus, it has been demonstrated that the thin LIBs have good cycle

Table 1
Specifications of thin LIBs

Type	123562	363562	363562B
Dimensions (mm)	1.2 × 35 × 62	3.6 × 35 × 62	3.6 × 35 × 62
Thickness (mm)	1.2	3.6	3.6
Capacity at 0.2 C (mAh)	130	570	680
Average voltage at 0.2 C (V)	3.8	3.8	3.8
Weight (g)	4.0	13.5	15
Charge voltage (V)	4.2	4.2	4.2
Rate current at 1 C (mA)	130	570	650
Cathode material	$LiCoO_2$	$LiCoO_2$	$LiCoO_2$
Anode material	MCF	MCF	B-MCF
Energy density per weight (Wh/kg)	120	160	172

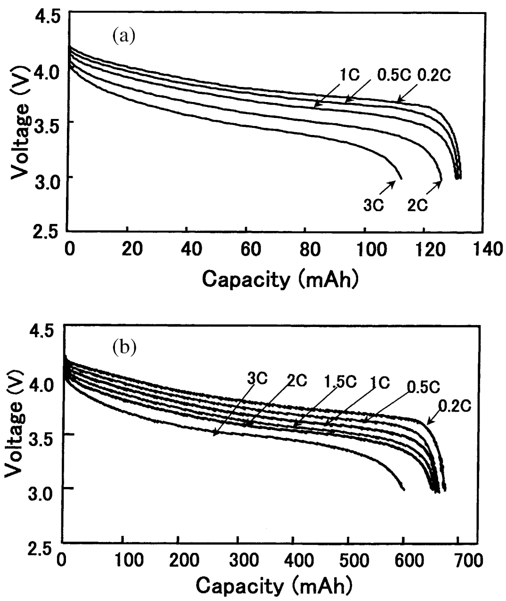

Fig. 2. Discharge curves of (a) 123562-type and (b) 363562B-type LIBs at various discharge rates.

life. We consider that the good cycle life of thin LIBs is attributable to use of the MCF anode [5,6].

On the other hand, the 363562B-type LIB after charging at 4.2 V was stored for 24 h at 85°C to investigate swelling because the laminated film bag is expanded by an evolution of gas. The swelling at 85°C storage of the thin LIB using the $LiBF_4$–EC/GBL electrolyte was very small, less than 0.1 mm. The swelling of thin LIB using 1 M $LiPF_6$–EC/MEC electrolyte was large, more than 1 mm. The $LiBF_4$–EC/GBL electrolyte is electrochemically and thermally stable in the oxidation condition of the $LiCoO_2$, since the GBL solvent is not only thermally stable but also electrochemically stable under the oxidation [8]. The $LiBF_4$–EC/GBL electrolyte in the high-temperature storage produces little evolution of gas. The MEC solvent on the $LiCoO_2$ electrode after full charging at 85°C decomposes and produces a large amount of gas.

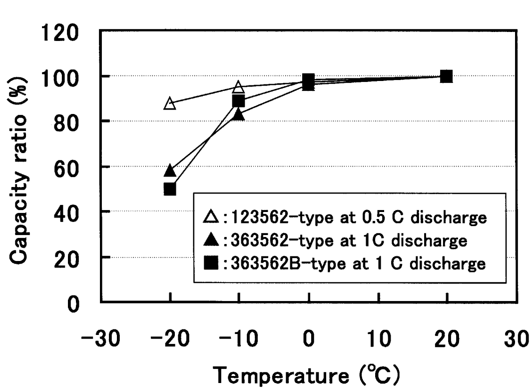

Fig. 3. Dependence of discharge capacity ratio on temperature.

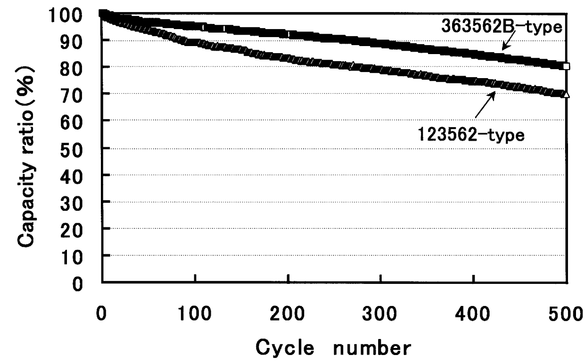

Fig. 4. Change in capacity as a function of cycle number for 123635-type and 363562B-type LIBs during charge–discharge cycle at 1 C rate.

3.3. Safety test data

It is necessary for the thin LIBs to be sufficiently safe to permit use with the laminated film bag. The 363562B-type LIB using the $LiBF_4$–EC/GBL electrolyte exhibited excellent safety performance of no rupture and no fire in an external short circuit test, overcharge tests, oven tests, a nail penetration test, and a crush test. Specifically, the thin LIB withstood overcharge tests up to 12 V, 5 C rate as well as oven tests up to 170°C for 1 h at 4.4 V. From the results of safety tests of prismatic LIBs and PLBs currently available, the PLBs could not withstand oven tests at 150°C for 1 h at 4.4 V. The prismatic LIBs could not withstand overcharging test up to 12 V, 3 C rate. Thus, it has been demonstrated that the thin LIBs have safety superior to that of conventional prismatic LIBs and PLBs (Table 2). We consider that the safety performance in overcharge tests and oven tests is closely related with thermal stability of the electrolyte against cathode materials. Fig. 5 shows differential scanning calorimeter (DSC) profiles of unwashed $LiCoO_2$ after charging up to 4.2 V in the $LiBF_4$–EC/GBL electrolyte and the $LiPF_6$–EC/MEC electrolyte. The DSC peak of $LiCoO_2$ in the $LiBF_4$–EC/GBL electrolyte was smaller and shifted to higher temperature than that of the $LiPF_6$–EC/MEC electro-

Table 2
Safety test data of 363562B-type LIB and Prismatic LIB

Items	363562B-type LIB	Prismatic LIB
Capacity (mAh)	680	540
Size (mm)	3.6 × 35 × 62	4.8 × 30 × 48
Overcharge test		
1 C, 12 V	NR, NF (74°C)	NR, NF (111°C)[a]
2 C, 12 V	NR, NF (122°C)	GE, F
3 C, 12 V	NR, NF (119°C)	GE, F
5 C, 12 V	NR, NF (130°C)	GE, F
Oven test		
150°C, 4.4 V	NR, NF (154°C)	NR, NF (163°C)
170°C, 4.4 V	NR, NF (177°C)	GE, F

[a] NR: no rupture, NF: no fire, GE: gas evolution, F: fire.

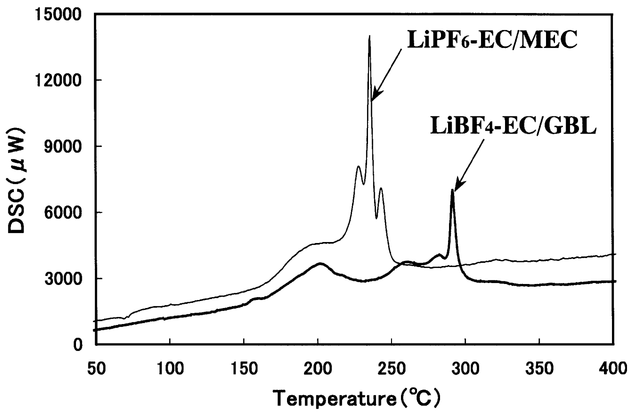

Fig. 5. DSC profiles of unwashed $LiCoO_2$ after charging up to 4.2 V in 1.5 M $LiBF_4$–EC/GBL (1:3) and 1 M $LiPF_6$–EC/MEC (1:2).

lyte. The $LiBF_4$–EC/GBL electrolyte has the thermal stability against the oxidation. The safety of thin LIBs is attributable to use of the $LiBF_4$–EC/GBL electrolyte whose flame point, boiling point, and oxidation temperature are higher than those of any prismatic LIB currently available. Finally, the high discharge performance, the excellent stability for high-temperature storage, the long cycle life, and the excellent safety performance of thin LIBs were attributable to high performance of the MCF anode and the stability of the $LiBF_4$–EC/GBL electrolyte against $LiCoO_2$ cathode material.

4. Conclusions

The $LiBF_4$–EC/GBL as the thermally stable liquid electrolyte and the MCF anode were applied to thin LIBs with thickness of 1.2 and 3.6 mm using the laminated film bag. The thin LIBs exhibited high discharge performance, very low swelling under a high-temperature storage, and excellent safety performance. The thin LIBs using the B-MCF anode had the highest energy density of 172 Wh/kg, high rate capability between 0.2 and 3 C rate discharge, a high capacity at -20°C, and a long cycle life of 500 cycles. The thin LIBs under overcharge tests and oven tests exhibited excellent safety performance. The DSC profiles of unwashed $LiCoO_2$ indicated that the $LiBF_4$–EC/GBL electrolyte had thermal stability against $LiCoO_2$ cathode material after charging up to 4.2 V. The excellent performance and safety data confirm that the thin LIB using the $LiBF_4$–EC/GBL electrolyte and the MCF anode is the most promising thin rechargeable battery with high energy density, high discharge performance, very low swelling for high-temperature storage, and excellent safety.

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