Application of LiBOB as an Electrolyte Salt For 4 V Class Lithium Ion Rechargeable Cells

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$LiPF_6$ is widely used as an electrolyte salt for most of the lithium ion rechargeable cells, although it has unfavorable properties like poor stability toward heat and moisture. Recently, Angell *et al.* have reported a new Li salt, lithium bis(oxalato)borate (LiBOB), which has good chemical stability.[1,2] Therefore, we have examined its performances in a 4 V class lithium ion rechargeable cell, which consists of a graphite anode and a lithium cobalt oxide cathode.

LiBOB was prepared by the method described in the literature.[1] The solubility of this salt was examined first in a mixed solvent system of ethylene carbonate and ethyl methyl carbonate (EC-EMC, 3:7 in volume ratio). It is reported that the solubility of LiBOB at ambient temperature is higher than 1 mol dm^{-3} in dimethyl carbonate (DMC), propylene carbonate (PC), and other common solvents.[1] However, it was found that its solubility in the EC-EMC mixed solvent system is below 0.9 mol kg^{-1}-solvent.

The electrolytic conductivities of 0.85 mol dm^{-3} solutions of LiBOB, $LiPF_6$, and $LiBF_4$ are shown in Fig. 1. The LiBOB solution afforded the electrolytic conductivity between $LiPF_6$ and $LiBF_4$, and it kept a liquid sate at lower temperatures below -20°C, while the solutions of $LiPF_6$ and $LiBF_4$ froze. This observation that the LiBOB electrolyte is superior to the $LiPF_6$ and $LiBF_4$ electrolytes at low temperatures agrees with the previous report.[1]

The 2032-type coin cells were fabricated using a graphite anode, a $LiCoO_2$ cathode, a polyethylene separator, and one of the above electrolytes, and their cell performances were evaluated. The discharge capacities of each cell were measured at different discharge rates after charged in CC (0.2C)-CV (4.2 V) mode. Fig. 2 shows the discharge capacities of the cells using 0.85 mol dm^{-3} EC-EMC (3:7) solutions of LiBOB, $LiPF_6$, and $LiBF_4$, when discharge rate was varied from 0.2 to 1.5C at 25°C. The discharge capacities of each cell were represented by the ratio to the discharge capacity of the $LiPF_6$ cell at 0.2C. The discharge capacity of the LiBOB cell was inferior to $LiPF_6$ and $LiBF_4$ cells, and this behavior became more remarkable as the discharge rate was increased.

Fig. 3 shows Cole-Cole plots at 0°C for these cells at 100% state of charge after finishing the above discharge tests. LiBOB showed the largest circle, which indicates the poor electrochemical stability compared with $LiPF_6$ and $LiBF_4$. It was reported that LiBOB was oxidized over 4.5 V *vs.* Li^+/Li, and some oxidized products suffered reduction at 2-3 V.[1] This might be the reason why the discharge capacity of the LiBOB cell was lower than those of the $LiPF_6$ and $LiBF_4$ cells.

We will also report the results of cell storage tests at a high temperature from the viewpoint of the thermal stability of the Li salts.

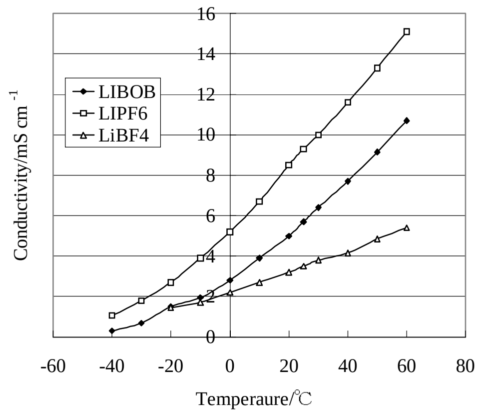

Fig. 1 Electrolytic conductivities of 0.85 mol dm^{-3} LiBOB, $LiPF_6$, and $LiBF_4$ in EC-EMC (3:7).

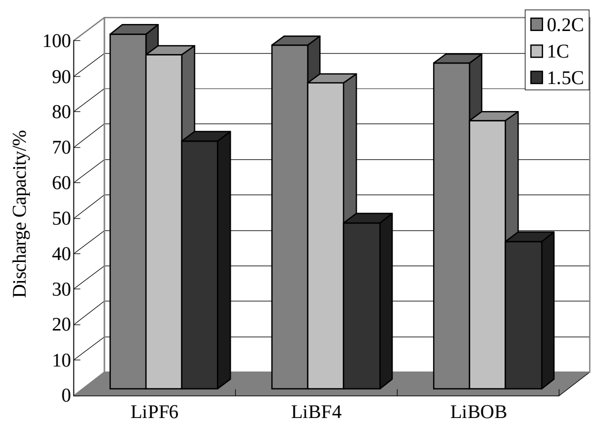

Fig. 2 Discharge capacities of 2032-type coin Li ion cells using 0.85 mol dm^{-3} LiBOB, $LiPF_6$, and $LiBF_4$ in EC-EMC (3:7). The discharge capacities were represented by the ratio to the discharge capacity of the $LiPF_6$ cell at 0.2C.

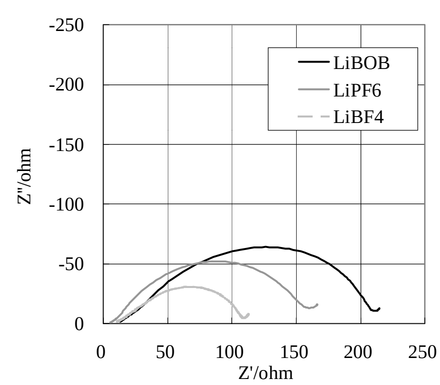

Fig. 3 Cole-Cole plots at 0°C of 2032-type coin Li ion cells using 0.85 mol dm^{-3} LiBOB, $LiPF_6$, and $LiBF_4$ in EC-EMC (3:7) at 100% state of charge after finishing the discharge tests.

1) W. Xu and C. A. Angell, *Electrochem. Solid-State Lett.*, **4**, E1 (2001).
2) K. Xu, S. Zhang, T. R. Jow, W. Xu, and C. A. Angell, *Electrochem. Solid-State Lett.*, **5**, A26 (2002).