Effects of Cyclic Carbonates as an Additive to GBL Electrolytes

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Lithium ion batteries are widely used for many portable electronic devices (e.g., laptop computers, cellular phones, and digital cameras). Ethylene carbonate (EC) with linear carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) are usually used as solvents constituting the electrolytes for lithium ion batteries.

However, since such liner carbonates have low boiling points and low flashing points, it is disadvantageous from the safety aspect.

On the other hand, □-butyrolactone (GBL) has a high boiling point, a high flashing point, a low freezing point, and a high dielectric constant, and it is a very preferable solvent constituting the electrolytes for lithium ion batteries.[1,2] However, GBL readily undergoes reductive decomposition on the surface of the negative electrode during charging, and it forms a passivation film with a large resistance, causing deterioration of battery performances.

In order to improve the battery performances, many electrolyte additives have been proposed.[3] For example, vinylene carbonate (VC)[4,5] was widely investigated as an additive for forming a passivation film. However, these additives were mainly investigated to carbonate-based electrolytes, and little is known about the suitability to GBL electrolytes.

In this work, the effects of cyclic carbonates selected from ethylene carbonate (EC), propylene carbonate (PC), vinylene carbonate (VC), vinylethylene carbonate (VEC),[6,7] and phenylethylene carbonate (PhEC)[8] were examined as an additive to GBL electrolytes.

Fig. 1 shows the first charge-discharge curves of LiCoO$_2$/Graphite cell in 1 M LiBF$_4$/GBL in the presence and absence of 5 wt% VC. The cells were charged to 4.2 V at 0.2C rate followed by a constant voltage charging to a cut-off current of 0.02C rate, and discharged to 3.0 V at 0.2C rate. Charge-discharge capacity was calculated based on the mass of LiCoO$_2$.

In the presence of VC, the discharge capacity increased and discharge voltage was higher. This means that VC undergoes reduction on the surface of the graphite prior to the reductive decomposition of GBL, producing an effective passivation film, and this passivation film suppressed the excessive decomposition of GBL. Therefore, the formation of the passivation film with a large resistance derived from decomposition of GBL was suppressed.

The first charge-discharge curves are shown in Fig. 2, when VC was replaced with VEC or PhEC. In order to be equal the molar ratio of GBL to additives in the electrolyte, 1 M LiBF$_4$/GBL with 6.6 wt% VEC and 9.5 wt% PhEC were used, respectively. Similar results were obtained as compared with VC.

We will report the various analytical data of the surface film formed on the graphite.

References:
1) N. Takami, T. Ohsaki, H. Hasebe, M. Yamamoto, *J. Electrochem. Soc.*, **149**, A9 (2002).
2) A. Chagnes, B. Carre, P. Willmann, R. Dedryvere, D. Gonbeau, D. Lemordant, *J. Electrochem. Soc.*, **150**, A1255 (2003).
3) M. Ue, in *Extended Abstracts of the Battery and Fuel Cell Materials Symposium*, Graz, Austria, April 18-22, p.53 (2004).
4) B. Simon, J.-P. Boeuve, *US Patent 5,626,981* (1997).
5) D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, *Electrochim. Acta*, **47**, 1423 (2002).
6) M. Kotato, T. Fujii, N. Shima, H. Suzuki, *WO 00/79632* (2000).
7) Y. Hu, W. Kong, H. Li, X. Huang, L. Chen, *Eectrochem. Commun.*, **6**, 126 (2004).
8) H. Suzuki, T. Sato, M. Kotato, H. Ota, H. Sato, *US Patent 6,664,008* (2003).
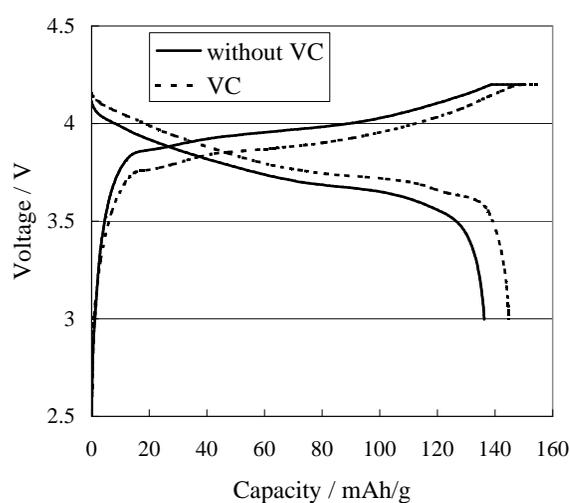
Fig. 1 Charge-discharge curves of LiCoO$_2$/Graphite cell in 1 M LiBF$_4$/GBL with and without VC.
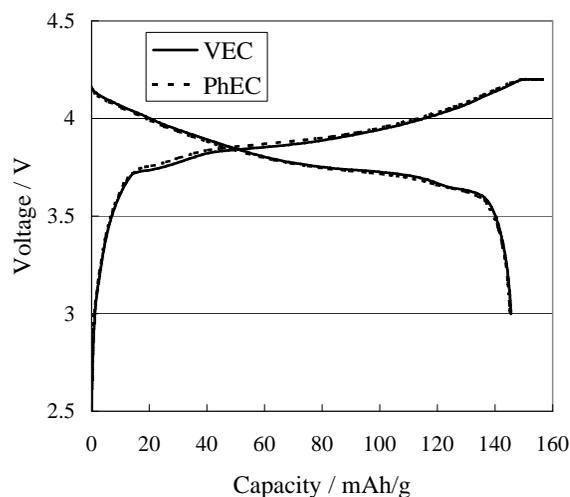
Fig. 2 Charge-discharge curves of LiCoO$_2$/Graphite cell in 1 M LiBF$_4$/GBL with VEC or PhEC.