

Butyrolactone derivatives as electrolyte additives for lithium-ion batteries with graphite anodes

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Abstract

A series of butyrolactone derivatives with various side chains mainly at the 5-position were used as additives in 1 M LiClO₄–propylene carbonate (PC) electrolyte for lithium-ion batteries with graphite anodes. When more than 0.3 M of 2-acetyloxy-4,4-dimethyl-4-butanolide (AcBL1) was added to 1 M LiClO₄–PC solution, exfoliation of graphite, co-intercalation and decomposition of PC was suppressed and lithium insertion and extraction into/from graphite anode proceeded. ¹³C NMR measurements suggested that the suppression of PC co-intercalation and decomposition was due to the decrease of the number of PC molecules coordinated to the lithium ion and increase of AcBL1 coordination. Addition of butyrolactone derivatives with acetoxyl or carbonate groups at the 5-position into 1 M LiClO₄–PC solution led to better charge–discharge anode performance.

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Keywords: Butyrolactone; Lithium-ion batteries; Graphite anodes

1. Introduction

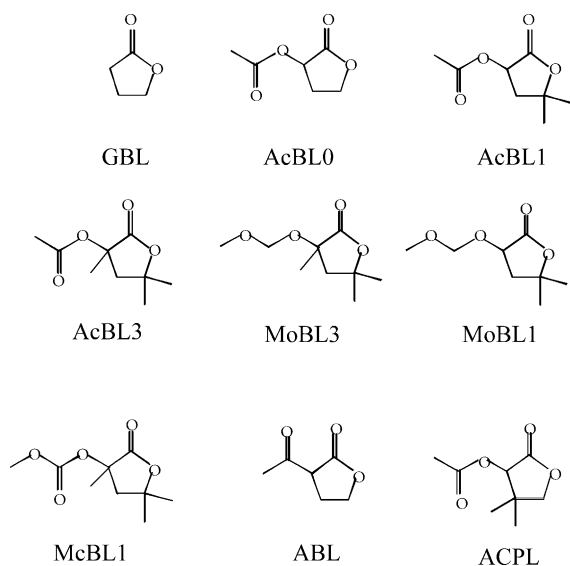
Carbons and ethylene carbonate (EC) with dimethyl carbonate (DMC) or diethyl carbonate (DEC) are usually chosen as anode materials and electrolytes for lithium-ion cells, respectively. Propylene carbonate (PC)-based electrolytes are more favorable from the view points of low-temperature behavior and flash points of the solvents. However, solvent co-intercalation into graphite anodes and decomposition have prevented the practical use of PC as electrolyte. A strategy to avoid the solvent co-intercalation and decomposition is to use electrolyte additives which ensure the formation of protective solid electrolyte interface (SEI) to decouple the anode interface and bulk properties. A number of electrolyte additives such as CO₂, N₂O, S_x²⁻, SO₂, chloroethylene carbonate, fluoroethylene carbonate, vinylpropylene carbonate, vinylene carbonate, catechol carbonates, 12-crown-4, ethylene sulfite, etc., has been evaluated [1–14]. However, new additives are still needed.

In this study, we introduce a series of butyrolactone derivatives with side chains mainly at the 5-position as PC-based electrolyte additives. These were easily prepared when using a new oxidation method proposed by Ishii and co-workers [15]. Furthermore, we have employed ¹³C NMR

measurement in order to understand the suppression of PC co-intercalation and decomposition on graphite anodes when the above butyrolactone derivatives were added to 1 M LiClO₄–PC. Recently, Abe et al. have reported the correlation between co-intercalation of lithium ions solvated by organic molecules and electrochemical intercalation of lithium ions in PC-based electrolyte containing them [16]. They indicated that solvents with higher Gutmann's donor number [17] than that of PC preferentially coordinate with lithium ions and accordingly co-intercalate into graphite. This co-intercalation process is believed to be the first step of the SEI formation, leading to reversible intercalation and de-intercalation of lithium ions. Yoshio et al. also suggested the Li⁺ ion coordination by solvents is an important factor for the suppression of PC decomposition on graphite anodes, based on conductivity measurements and donor numbers determined from the absorption peaks of bis-(1,3-propanediolato)vanadium in the desired solvent [18,19]. However, unfortunately these donor numbers only show the difference of coordination ability among solvents. On the other hand, ¹³C NMR measurement is a more powerful tool for directly investigating the ion–solvent interaction [20–23]. From this measurement, one can even estimate the number of solvents coordinated to a Li⁺ ion, which would provide useful information to understand the suppression of PC co-intercalation and decomposition on graphite anode.

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Scheme 1. Structure of butyrolactone derivatives.

2. Experimental

The electrolyte solutions were prepared by adding various amounts (0.1–1.0 M) of 4-butanolide (γ -butyrolactone, GBL) and its derivatives to 1 M LiClO_4 -PC solution (Kishida Chemical Co. Lithium Battery Grade). Butyrolactone derivatives; 2-acetyloxy-4-butanolide, 2-acetyloxy-4,4-dimethyl-4-butanolide, 2-acetyloxy-2,4,4-trimethyl-4-butanolide, 2-methoxymethoxy-4,4-dimethyl-4-butanolide, 2-methoxymethoxy-2,4,4-trimethyl-4-butanolide, 2-methoxycarbonyloxy-4,4-dimethyl-4-butanolide 2-acetyl-4-butanolide and 2-acetyloxy-3,3-dimethyl-4-butanolide abbreviated as AcBL0, AcBL1, AcBL3, MoBL1, MoBL3, McBL1, ABL and ACPL (Scheme 1), respectively, were prepared by using a new oxidation method proposed by Ishii and co-workers [15]. The water content in these samples was less than 100 ppm. The working electrode was a mixture of graphite powder (NG7) and PVdF (8 wt.%) deposited onto foamed Ni sheet. The graphite anodes were galvanostatically charged and discharged between 3.0 and 0 V versus Li/Li^+ at 15.5 mA/g. ^{13}C NMR data for the electrolyte solutions were acquired in CDCl_3 solution using Bruker DRX500 NMR spectrometer at room temperature. It has been reported that solvation of Li^+ ions by chloroform is almost negligible in mixtures of EC and chloroform, based on Raman spectroscopy [24]. The peak positions were calibrated using the central peak of CDCl_3 (76.90 ppm). The LUMO energies of the above butyrolactone derivatives

calculated by semi-empirical quantum calculation using MOPAC are summarized in Table 1. LUMO energies of all the additives in this study were lower than that of PC.

3. Results and discussion

3.1. Addition of AcBL1 into 1 M LiClO_4 -PC solution

Fig. 1 shows the first discharge curves for a graphite anode in 1 M LiClO_4 -PC solution containing various concentrations of AcBL1. As the AcBL1 content increased, the plateau at 0.95 V due to exfoliation of graphite and propylene evolution became shorter and was shifted to lower potential. On the other hand, a new plateau at 1.3–1.1 V was apparently observed when the AcBL1 content reached 0.7 M. Plateaus at 0.24, 0.18 and 0.1 V indicating lithium intercalation into graphite were also observed. As shown in Fig. 2, the charge capacity increased with increasing AcBL1 content except for 0.3 M, and the charge capacity reached 340 mAh/g in 1 M LiClO_4 -PC containing 1 M of AcBL1, which was similar to that observed in 1 M LiClO_4 -EC/DEC

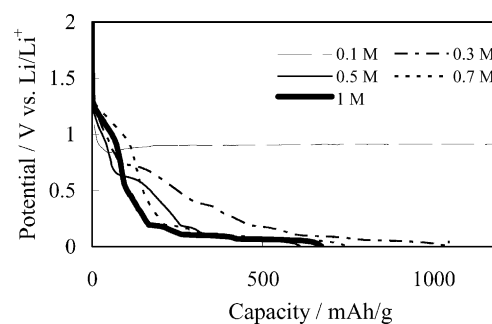
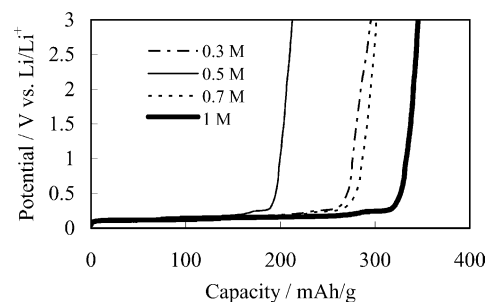
Fig. 1. First discharge curves of graphite electrode in LiClO_4 -PC containing various concentrations of AcBL1.Fig. 2. First charge curves of graphite electrode in LiClO_4 -PC containing various concentrations of AcBL1.

Table 1
LUMO energies of various butyrolactone additives

	ABL	McBL1	AcBL0	ACPL	AcBL1	AcBL3	MoBL1	GBL	MoBL3	PC
LUMO energy (eV)	0.338	0.435	0.571	0.608	0.688	0.750	0.923	1.05	1.09	1.20

Table 2
Chemical shifts of carbonyl carbons in the presence of 1 M of LiClO₄ with respect to those in the absence of LiClO₄

AcBL1 content/M	PC	AcBL1 lactone ring	AcBL1 side chain
0	0.83	–	–
0.3	0.57	0.53	0.60
0.5	0.59	0.54	0.63
0.7	0.54	0.50	0.53
1.0	0.39	0.38	0.34

solution. The smaller charge capacity of the graphite electrode in 1 M LiClO₄-PC containing lower AcBL1 content can be ascribed to the partial exfoliation of graphite.

Table 2 shows the ¹³C NMR chemical shifts of carbonyl carbons for PC and AcBL1 with respect to that of each solvent obtained for a mixture of PC and AcBL1 in the absence of LiClO₄. Positive shifts from those of the solvents in the absence of LiClO₄ indicate electronic deshielding of the nuclei due to electrostatic interaction between Li⁺ ions and the solvent molecules [20–24]. Therefore, in all cases, Li⁺ ions are bonded to carbonyl oxygen atoms of both PC and AcBL1. Unfortunately, it was not possible to distinguish a free and a bonded population, because the exchange of both sites with the lithium ion was rapid on the NMR time scale and only one peak for each carbonyl carbon atom was observed, as was the case in the literature [20–24]. However, the upfield shift of the peaks for the carbonyl carbon of PC with increasing AcBL1 content and downfield shift for AcBL1 indicated that a considerable amount of lithium ion was released from PC and bonded to AcBL1. The change of discharge curves along with the increase of AcBL1 concentration shown in Fig. 1 can be explained as follows. The decrease of the concentration of PC bonded to lithium ions and/or an incomplete SEI film formed due to AcBL1 reduction increases the overpotential for PC co-intercalation and decomposition around 0.95 V because of the limited supply of PC molecules to the anode and accordingly, lowers and shortens the corresponding plateau. On the other hand, the decomposition of AcBL1 is more readily observed at 1.2 V as a result of an increase of lithium ions solvated by AcBL1, since AcBL1 molecules for decomposition and/or co-intercalation are sufficiently supplied to the electrode surface. This phenomenon can occur because the reduction potential of AcBL1 is higher than that of PC, as one can imagine from the lower LUMO energy level of AcBL1 as shown in Table 1. As a result of the reduction of sufficient AcBL1 molecules, a protective SEI was successfully formed on the anode surface and this prevented further decomposition of AcBL1, exfoliation of graphite, and propylene evolution. Accordingly, lithium intercalation into graphite was observed. The effect of the concentration of lithium ions solvated by AcBL1 on the kinetics of the AcBL1 decomposition was also observed, when the charge–discharge measurements were performed in 1 M LiClO₄-PC containing various AcBL1 contents or at various current densities.

When the current density was low (7.8 mA/g), the potential plateau at 1.2 V was observed more clearly, and even in 1 M LiClO₄-PC containing 0.3 M of AcBL1, charge capacity reached 320 mAh/g. On the other hand, at higher current densities (>66 mA/g), the plateau at 1.2 V disappeared and the charge capacity was <180 mAh/g. In this case, the protective SEI layer was incomplete, and graphite exfoliation and propylene evolution was not prevented. In order to form an effective SEI layer on the graphite surface, an appropriate amount of additives bonded to Li⁺ ions are needed.

3.2. Addition of various butyrolactone derivatives into 1 M LiClO₄-PC

Fig. 3 shows the first charge–discharge curves for a graphite anode in 1 M LiClO₄-PC solution containing 1 M of various additives including AcBL1. Based on the potential profile and charge capacity, these additives may be classified into four categories, (1) ABL, (2) AcBL1, ACPL, McBL1, (3) MoBL1, AcBL0, AcBL3, and (4) MoBL3, GBL. When ABL was added to 1 M LiClO₄-PC solution, a long plateau at 1.7 V was observed and the potential did not reach that of lithium insertion. In the electrolyte solution containing AcBL1, ACPL and McBL1, after showing a relatively short plateau starting from 1.4 to 1.1 V, lithium insertion occurred and the charge capacities were 320–340 mAh/g, similar to that observed in 1 M LiClO₄-EC/DEC solution. When the electrolyte solution contained AcBL0, AcBL3 and MoBL1, though the potential profiles at the beginning of discharge were rather similar to those observed in the solution containing the above additives, the irreversible capacity was large and the charge capacity was <250 mAh/g. This can be because the electrode surface was not well covered with an effective SEI and the film may dissolve into solvents. A long potential plateau starting from 0.9 V, which was similar to that observed in 1 M LiClO₄-PC solution, appeared in the electrolyte containing GBL and MoBL3. It appears that the potential levels where the plateau begin corresponds to the LUMO energies of the additives, and in all cases, graphite exfoliation was suppressed apparently, which would be because the additive reduction potentials were higher than that of PC, reflecting their lower LUMO energy levels. Therefore, the anode charge–discharge behavior was greatly dependent on the additive reduction process. If the reduction products of the additives successfully form a favorable SEI layer, lithium insertion and extraction occurs reversibly.

In Table 3, the chemical shifts of the carbonyl carbon atoms of PC and additives obtained from ¹³C NMR measurements are summarized, together with the discharge and charge capacities at the first cycle obtained from Fig. 3. For all the additives, the positive shifts were observed for the carbonyl carbon atoms in the lactone ring or side chain. This indicates that considerable amounts of lithium ions are solvated by these additives. However, whereas the shift of

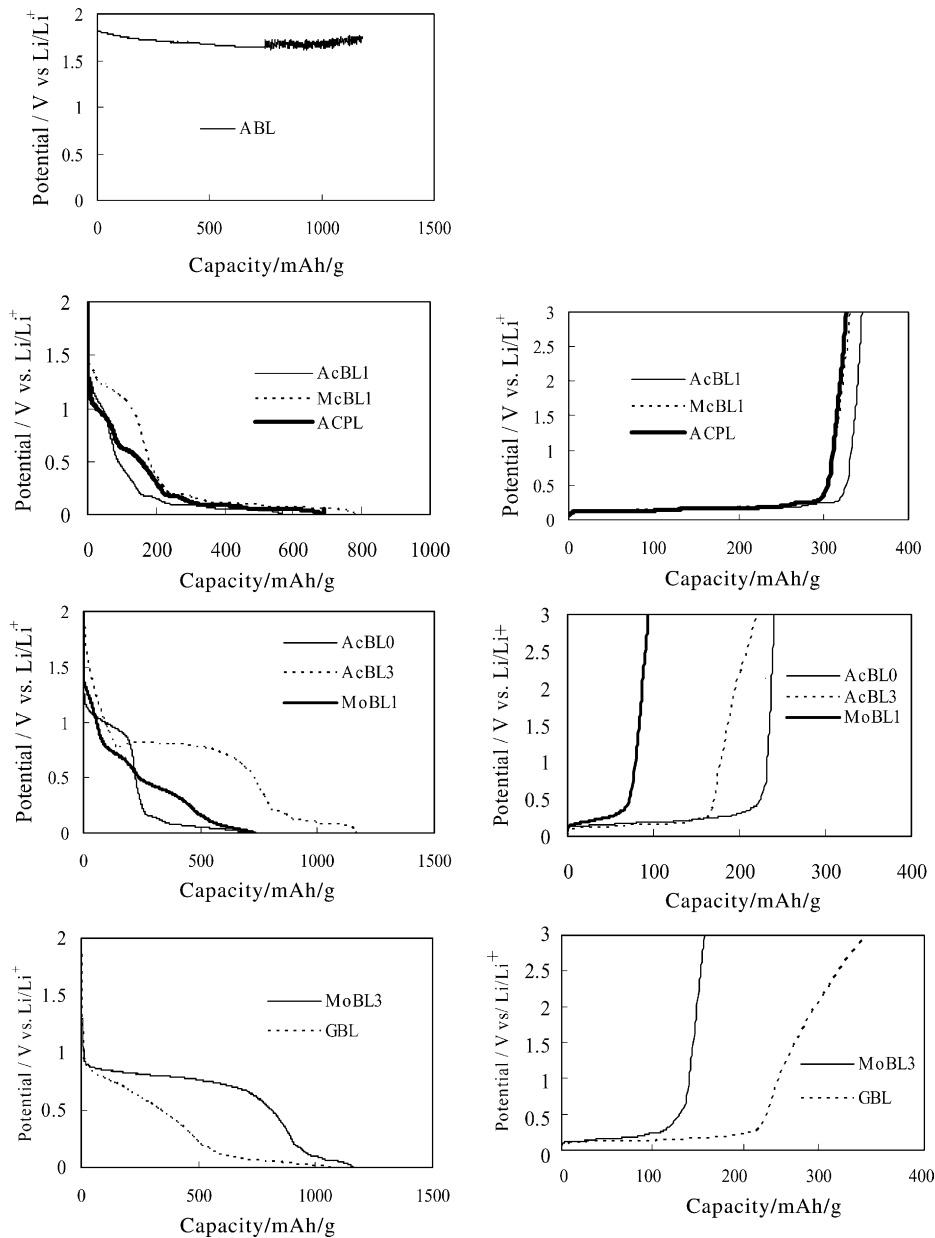


Fig. 3. First charge (right) and discharge (left) curves of graphite anode in 1 M LiClO_4 -PC solution containing 1 M of various additives.

Table 3

The difference of chemical shifts of carbonyl carbon atoms in PC and various additives (1 M) in the presence of LiClO_4 from those of PC or additives in the absence of LiClO_4 , together with the capacities at the first cycle

Additives	Carbonyl PC	Carbonyl lactone ring	Carbonyl side chain	First reversible capacity (mAh/g)	First irreversible capacity (mAh/g)
AcBL1	0.39	0.38	0.34	345	327
McBL1	0.68	0.55	0.06	332	325
ACPL	0.70	0.48	0.69	327	363
ABL	0.72	1.50	0.96	—	—
MoBL1	0.72	1.43	—	100	400
GBL	0.75	1.98	—	338	751
MoBL3	0.83	1.05	—	157	1007
AcBL3	0.88	0.82	0.76	221	946
AcBL0	0.93	0.79	1.21	240	477
No additive	0.83	—	—	—	—

carbonyl carbon atoms in PC apparently decreased in the solution containing McBL1, AcBL1 and ACPL, it was similar to that for the solution without the additives or even increased for the other additives. This means that while some of PC molecules bonded to Li^+ ion were replaced by the former additives, the latter additives interact with Li^+ ion almost without changing the number of PC molecules bonded to Li^+ ion. In addition, the larger shifts observed for carbonyl carbon atoms of the latter additives suggest the larger number of solvated additives. Therefore, the Li^+ ions solvated by the latter additives and PC are larger than those solvated by only PC. Chung et al. recently reported that intercalation of the larger cation into graphite is difficult and thus prevent exfoliation of graphite, based on the experimental data using various electrolyte solutions such as those containing tetrabutylammonium cation, *cis*- and *trans*-butylene carbonates [25]. This is in good agreement with data for chemically prepared lithium or lithium-solvent-graphite intercalation compounds [26]. Ternary graphite intercalation compounds of lithium ion solvated by large organic molecules were not formed. In this context, intercalation of lithium ions solvated by PC and additives, which is believed to be the first step of SEI formation would be rather difficult in electrolyte solutions containing additives other than AcBL1, McBL1 and ACPL. This would prevent favorable SEI formation, leading to poorer anode charge–discharge behavior. However, further information about the number of solvated molecules obtained by Raman spectroscopy for the electrolyte solution and co-intercalation and SEI formation processes based on surface morphology changes of graphite by in situ scanning probe microscopy during the first discharge process [26,27] are needed to prove the above hypothesis.

Several groups have proposed the strategy to select electrolyte components which facilitate SEI formation. Peled et al. indicated that the SEI precursor must be selected from materials with a high exchange current density for reduction [29]. Chung et al. focused more on intrinsic thermodynamic stability rather than kinetics of reduction [25]. Both concepts would be true for the selection of additives for PC-based electrolyte. However, according to the present study, it is also necessary to consider additive solvation behavior (preferential solvation and the size of solvated Li^+ ion) as suggested by Abe et al. [16] and Mizutani et al. [28]. The correlation between charge–discharge measurements and ^{13}C NMR data of the 1 M LiClO_4 –PC electrolyte solution containing various butyrolactone derivatives showed that reduction behavior of additives during first discharge is greatly affected by the concentration of additives bound to Li^+ ions. The solvation behavior of Li^+ ions in the presence of butyrolactone derivatives and PC appears to be complicated because ^{13}C NMR data obtained in this study suggested that both species are bonded to Li^+ ion at the same time.

In summary, a combination of thermodynamic data obtained by quantum calculation and Li^+ ion-additives interaction data from ^{13}C NMR measurements give us useful information to select additives for PC electrolyte in lithium-ion cells using graphite anodes.

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