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Formation mechanism of alkyl dicarbonates in Li-ion cells

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Abstract

The mechanism for the formation of alkyl dicarbonates in Li-ion cells was investigated. Alkyl dicarbonates are formed in graphite half-cells at 1.5 V versus Li/Li$^+$ or lower, and its concentration increased with lowering charging voltage. The results of the storage tests of solvents and electrolyte solutions in the presence of various kinds of lithium salts suggested that lithium alkoxides, which are formed by reductive decomposition of solvents, are the most probable active species for alkyl dicarbonate formation. The formation reaction proceeds through two-step nucleophilic reactions initiated by lithium alkoxides. At the first step, alkoxide anion attacks alkyl carbonate to generate an active nucleophile intermediate, which further attacks another alkyl carbonate to form alkyl dicarbonate at the second step.
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1. Introduction

Alkyl carbonates-based electrolyte solutions are used in most of commercially available Li-ion cells. Ethylene carbonate (EC) is chosen as a main solvent because of its high dielectric constant and high oxidative stability against the 4-V LiCoO$_2$ positive electrodes. Because EC is highly viscous, it is mixed with linear alkyl carbonates such as diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC), which have lower viscosities than EC, to obtain proper viscosity and ionic conductivity over a wide temperature range. One of the prominent properties of these EC-based solutions is an ability to form protective surface film, called the solid electrolyte interface (SEI), on graphite electrodes, which gives the solutions reductive stability. It is widely recognized that the SEI is formed by decomposition of the electrolyte solutions during the initial stage of charging [1–4]. Numerous studies have been performed to understand the decomposition of the electrolyte solutions on graphite electrode; however, most of these studies have focused on the composition and morphology of the SEI itself, rather than compositional changes of the solutions.

Because SEI is formed by reductive decomposition of solvents and electrolyte salts, part of the decomposition products are soluble and may deteriorate the properties of the electrolyte solution. Hence, understanding of this degradation compound formation is also important to obtain good performance of Li-ion cells. Yoshida et al. [5] first reported the formation of alkyl dicarbonates such as diethyl 2,5-dioxahexane dicarboxylate (DEDOHC), dimethyl 2,5-dioxahexane dicarboxylate (DMDOHC), and ethylmethyl 2,5-dioxahexane dicarboxylate (EMDOHC), which they referred to as trans esterification compounds in Li-ion cells using 1 M LiPF$_6$/EC + DEC (1:1, v/v), 1 M LiPF$_6$/EC + DMC (1:1, v/v), and 1 M LiPF$_6$/EC + EMC (1:1, v/v), respectively, after the initial charging. However, the mechanism for the alkyl dicarbonate formation is still controversial. Yoshida et al. reported that the formation of the alkyl dicarbonates is activated by the presence of lithium alkoxides; however, they did not explicitly describe the reason why lithium alkoxides have such a specific reactivity. On the other hand, Zhang et al. [6]

reported that DEDOHC is formed in 1 M LiPF$_6$/EC + DEC (1:1, v/v) in the presence of PF$_5$ gas. They proposed that the reactions of the solvents and PF$_5$, which is present in equilibrium with LiPF$_6$ in the solution are responsible for the formation of DEDOHC.

In the present study, electrolyte solutions in graphite and LiCoO$_2$ half-cells after cycling were analyzed by gas chromatography–mass spectroscopy (GC–MS) to obtain information about the formation of alkyl dicarbonates. In addition, storage tests of solvents and electrolyte solutions containing various kinds of lithium compounds were conducted to elucidate the mechanism for alkyl carbonate formation in Li-ion cells.

2. Experimental

2.1. Solvents and electrolyte solutions

Solvents and electrolyte solutions used in the present study were EC, DMC, EMC, DEC, DEDOHC, EC + DMC (1:1, v/v), EC + EMC (1:1, v/v), EC + DEC (1:1, v/v), and 1 M LiPF$_6$/EC, 1 M LiPF$_6$/DMC, 1 M LiPF$_6$/EMC, 1 M LiPF$_6$/DEC, 1 M LiPF$_6$/EC + DMC (1:1, v/v), 1 M LiPF$_6$/EC + EMC (1:1, v/v), 1 M LiPF$_6$/EC + DEC (1:1, v/v), and 1 M LiClO$_4$/EC + DEC (1:1, v/v). DEDOHC (water content < 20 ppm; viscous, colorless clear liquid) was purchased from Asahi Denka Kogyo Co., and the other solvents and electrolyte solutions were purchased from Tomiyama Pure Chemical Industries (battery grade, water content < 30 ppm).

2.2. Half-cell tests on alkyl dicarbonate formation

Graphite and LiCoO$_2$ half-cells were fabricated to clarify at which electrode and at what potential alkyl dicarbonates are formed. A mixture of artificial graphite powder (TIMCAL Graphite, SFG44) and poly(vinylidene difluoride) (PVdF) as a binder was coated on a copper foil to form graphite electrodes. A stack of the graphite electrode (active area: 2 cm × 2 cm), a polyolefin microporous separator (Celgard Inc., 2300, 25 μm), and a counter lithium foil (Honjo Metal Co. Ltd.) was inserted in a plastic laminate envelope, and an electrolyte solution of 1 M LiPF$_6$/EC + DEC (1:1, v/v) was injected. The envelope was finally sealed under dry atmosphere (dew point < −60 °C). LiCoO$_2$ electrode was prepared from LiCoO$_2$ powder (Nippon Chemical Industrial Co. Ltd.), conductive carbon powder, and PVdF on aluminum foil, and LiCoO$_2$ half-cells were prepared in a similar manner. Nine graphite half-cells were prepared and charged to different voltages. Four of them were charged to 1.2, 0.9, 0.5, and 0.0 V versus Li/Li$^+$ at a constant current of 0.7 mA (0.1 CA). The other five graphite half-cells were charged to 3.2, 2.0, 1.5, 1.2, and 0.9 V versus Li/Li$^+$ at 0.1 CA, and then hold at the respective constant voltages for 90 h in total. These graphite half-cells were discharged to 2.0 V versus Li/Li$^+$ at 0.1 CA. A LiCoO$_2$ half-cell was charged to 4.3 V versus Li/Li$^+$ at 1.1 mA (0.1 CA), and then discharged to 3.0 ver-

sus Li/Li$^+$ at 0.1 CA. All the charge and discharge tests were carried out at 25 °C. After discharged, these half-cells were disassembled under dry atmosphere, and the compositions of the electrolyte solutions were analyzed with a gas chromatograph (Hewlett-Packard, HP6890) equipped with a capillary column (Agilent J&W, HP-50+), and further identified with a mass spectrometer (JEOL, JMS-600 W). The ionization for MS was carried out by electron impact (EI), in which the voltage and the current for acceleration were set at 70 eV and 100 μA, respectively. The minimum detection limit of GC–MS analysis was about 1 ppm.

2.3. Storage tests in the presence of various kinds of lithium compounds

Catalysis of lithium compounds for the ester exchange reactions between linear alkyl carbonates was closely examined by Takeuchi et al. [7]. But, an examination for catalysis of lithium compounds for alkyl dicarbonate formation was inadequate though Yoshida et al. pointed out that lithium ethylene glycoxide, which was reduction product of EC, activated alkyl dicarbonate formation. Consequently, in order to elucidate catalysis in alkyl dicarbonate formation, storage tests were conducted for solvents and electrolyte solutions in the presence of various kinds of lithium compounds including several lithium alkoxides. As lithium compounds, lithium carbonate (Li$_2$CO$_3$), lithium fluoride (LiF), lithium hydroxide (LiOH), lithium formate (HCO$_2$Li), lithium acetate (CH$_3$CO$_2$Li), lithium methoxide (CH$_3$OLi), lithium ethoxide (C$_2$H$_5$OLi), and lithium ethylene glycoxide (CH$_2$OLi)$_2$ were tested. Li$_2$CO$_3$, LiF, and LiOH (Aldrich) were used after dried in vacuum at 250 °C for 3 h. HCO$_2$Li and CH$_3$CO$_2$Li were obtained by dehydration of HCO$_2$Li–H$_2$O (Aldrich) and CH$_3$CO$_2$Li–2H$_2$O (Aldrich), respectively, in vacuum at 250 °C for 3 h. Complete dehydration was confirmed by their weight losses. CH$_3$OLi, C$_2$H$_5$OLi, and (CH$_2$OLi)$_2$ were prepared from methanol, ethanol, and ethylene glycol, respectively, in the presence of an excess amount of lithium foil under dry atmosphere. These lithium compounds were mixed by 1 wt.% each with various solvents and electrolyte solutions mentioned earlier under dry atmosphere. The mixtures were sealed and stored on a rotary shaker at 25 °C for 1200 h at maximum. After the storage tests, the compositions of the mixtures were analyzed by GC–MS.

2.4. Molecular orbital calculations of charge densities

To evaluate the formation mechanism of alkyl dicarbonate, charge density calculations may be useful. Charge densities on the ionized oxygen atoms in alkoxide anions, carboxyl anions, and intermediate anions that may be generated in alkyl dicarbonate formation were calculated using functional density theory (DFT) using Gaussian 98W [8–10]. Molecular structures of each anions were optimized with HF/6-31G* in advance. Vibrational frequency calculation was performed

with the correspondence basis sets to confirm that the geometries are at the minimum of the potential energy surface and to make zero-point energy corrections. Finally, single-point energies were calculated at the B3LYP/6-311 + G (2d, p) by using the optimized geometries obtained and atomic charges (SCF densities) of the ionized oxygen atoms were evaluated. Charge densities on the carbon of EC and DEC were also calculated with same procedure.

3. Results and discussion

3.1. Half-cell tests on dialkyl carbonate formation

Fig. 1 shows gas chromatograms of the electrolyte solutions sampled from the graphite half-cell charged to 0.0 V versus Li/Li$^+$ and from the LiCoO$_2$ half-cell charged to 4.3 V versus Li/Li$^+$. While only the solvents EC and DEC, were detected from the LiCoO$_2$ half-cell (Fig. 1b), DEDOHC was detected at around 6 min in addition to the solvents from the graphite half-cell (Fig. 1a). It is clear that the alkyl dicarbonate was formed at the graphite electrode. Because the LiCoO$_2$ half-cell contained LiPF$_6$ and lithium metal, it is considered that their contributions to alkyl carbonate formation would be small. Fig. 2 shows the concentrations of DEDOHC formed in graphite half-cells charged at different voltages. DEDOHC began to be formed at 1.5 V versus Li/Li$^+$, and its concentration increased with a drop in charging voltage. This fact indicates that alkyl dicarbonates are formed via reductive decomposition of the solvents.

3.2. Storage tests in the presence of various kinds of lithium compounds

The results of the storage tests of solvents and electrolyte solutions in the presence of various lithium compounds are summarized in Table 1. Newly formed degradation compounds were detected only from EMC, DEDOHC, and EC + linear alkyl carbonates in the presence of lithium alkoxides, regardless of the co-existence of LiPF$_6$. The degradation compounds identified by MS were listed in Table 2. In EMC + 1 wt.% lithium alkoxide, DMC, and DEC were detected from the solutions. These compounds are ester exchange products of EMC as was reported by Takeuchi et al. [7]. They reported that alkoxide anions, which are formed
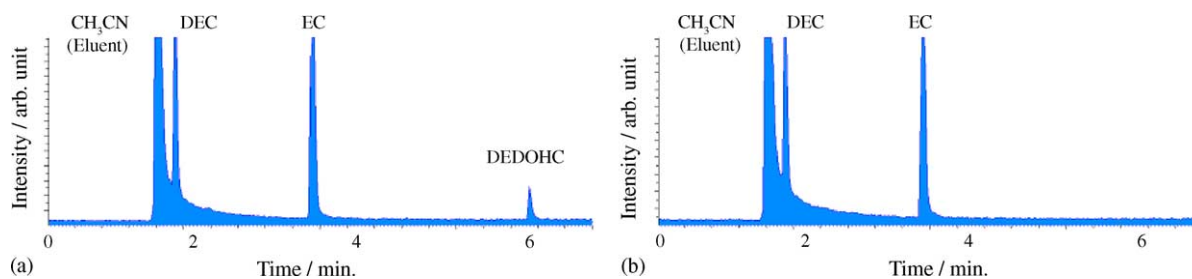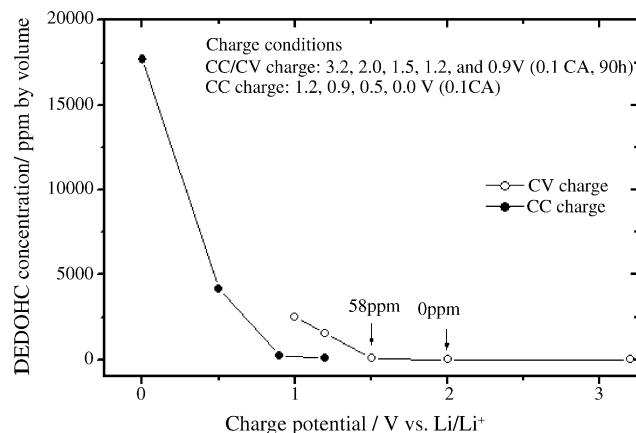

Fig. 2. Variation of DEDOHC concentration in graphite half-cells with charging voltage. The electrolyte solution: 1 M LiPF$_6$/EC + DEC (1:1, v/v).
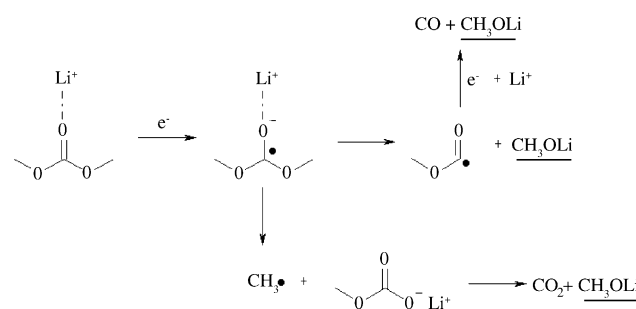

Fig. 3. Possible formation scheme for CH$_3$OLi originated in reduction of DMC.

by the reduction of linear alkyl carbonates, act as active intermediates to promote the ester exchange reactions. Alkyl dicarbonates such as DEDOHC, DMDOHC, and EMDOHC were formed in EC + linear alkyl carbonate mixtures only in the presence of lithium alkoxides. DEDOHC decomposed to EC and linear alkyl carbonate only in the presence of lithium alkoxides as well. Hence, it must be reasonable to presume that lithium alkoxides work as active intermediates to promote alkyl dicarbonate formation as in the case of ester exchange reaction.

Lithium alkoxides such as CH$_3$OLi and C$_2$H$_5$OLi are common reduction products detected by many researchers as components of SEI or soluble species into electrolyte. Possible formation scheme for CH$_3$OLi is shown in Fig. 3

Fig. 1. Gas chromatograms for the electrolyte solutions sampled from (a) graphite half-cell charged to 0.0 V vs. Li/Li$^+$ and (b) LiCoO$_2$ half-cell charged to 4.3 V. The electrolyte solution: 1 M LiPF$_6$/EC + DEC (1:1, v/v).

Table 1

Results of storage tests of solvents and electrolyte solutions in the presence of various lithium compounds

Solution	Lithium compounds							
	LiF	LiOH	Li_2CO_3	HCOOLi	CH_3COOLi	CH_3OLi	C_2H_5OLi	$(CH_2OLi)_2$
EC	×	×	×	×	×	×	×	×
EMC						o	o	
DEC	×	×	×	×	×	×	×	×
DEDOHC						o	o	
EC + DEC (1:1, v/v)	×	×	×	×	×	o	o	o
1 M $LiPF_6$/EC	×	×	×	×	×	×	×	×
1 M $LiPF_6$/EMC						o	o	
1 M $LiPF_6$/DEC	×	×	×	×	×	×	×	
1 M $LiPF_6$/EC + EMC (1:1, v/v)						o	o	
1 M $LiPF_6$/EC + DEC (1:1, v/v)	×	×	×	×	×	o	o	o
1 M $LiClO_4$/EC + DEC (1:1, v/v)						o	o	

o, newly formed degradation compounds were detected; ×, newly formed degradation compounds were not detected.

Table 2

MS analysis results for the detected degradation compounds in the mixtures after storage

Solution	Lithium compounds		
	CH_3OLi	C_2H_5OLi	$(CH_2OLi)_2$
EMC	DMC, DEC	DMC, DEC	
DEDOHC	EC, EMC, DEC, EMDOHC	EC, DEC	
EC + DEC (1:1, v/v)	EMC, DMDOHC, EMDOHC, DEDOHC	DEDOHC	DEDOHC
1 M $LiPF_6$/EMC	DMC, DEC	DMC, DEC	
1 M $LiPF_6$/EC + EMC (1:1, v/v)	DMC, DEC, DMDOHC, EMDOHC, DEDOHC	DMC, DEC, DMDOHC, EMDOHC, DEDOHC	
1 M $LiPF_6$/EC + DEC (1:1, v/v)	EMC, DMDOHC, EMDOHC, DEDOHC	DEDOHC	DEDOHC
1 M $LiClO_4$/EC + DEC (1:1, v/v)	EMC, DMDOHC, EMDOHC, DEDOHC	DEDOHC	

[5,7,11–13]. Both one-electron reduction and two-electron reduction are possible [14]. While C_2H_5OLi is soluble in solvent as Aurbach et al. [12] suggested a graphite electrode used in the half-cell test was repeatedly rechargeable in 1 M $LiPF_6$/EC + DEC (1:1, v/v) because graphite surface was covered by stable film (SEI) composed of reduction products from EC and $LiPF_6$, such as lithium alkyl carbonate $(CH_2OCO_2Li)_2$, Li_2CO_3, and LiF. This SEI formation takes place at potential below 0.8 V [17] versus Li/Li^+ and accompanies consumption of electric charge though alkyl dicarbonate formation begins at around 1.5 V versus Li/Li^+ and it can proceed with no electrolysis as the results of the storage tests demonstrated.

3.3. Mechanism for alkyl dicarbonate formation

It was reported that alkali metal alkoxides initiate anionic polymerization of some vinyl monomers as base catalysts because the alkoxide anions are strong nucleophiles [15,16]. If lithium alkoxides act as nucleophiles to promote alkyl dicarbonate formation as was proposed in the vinyl polymerization, the formation of DEDOHC in the 1 M $LiPF_6$/EC + DEC (1:1, v/v) + 1 wt.% C_2H_5OLi mixture can be described in a scheme shown in Fig. 4. The nucleophile, alkoxide anion, can attack four possible carbon atoms of EC and DEC as shown in routes 1–4. DEDOHC is formed through route 2. Route 4 regenerates DEC. The other routes may be possible; however,
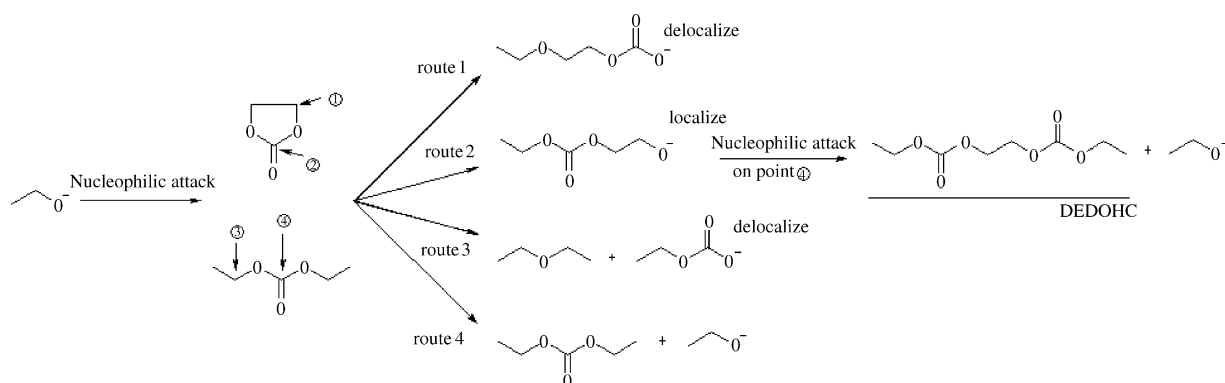

Fig. 4. Reaction scheme for DEDOHC formation in 1 M $LiPF_6$/EC + DEC (1:1, v/v) in the presence of 1 wt.% C_2H_5OLi.

Table 3
Calculated charge densities on the ionized oxygen of intermediate anions, alkoxide anions, and carboxyl anions calculated

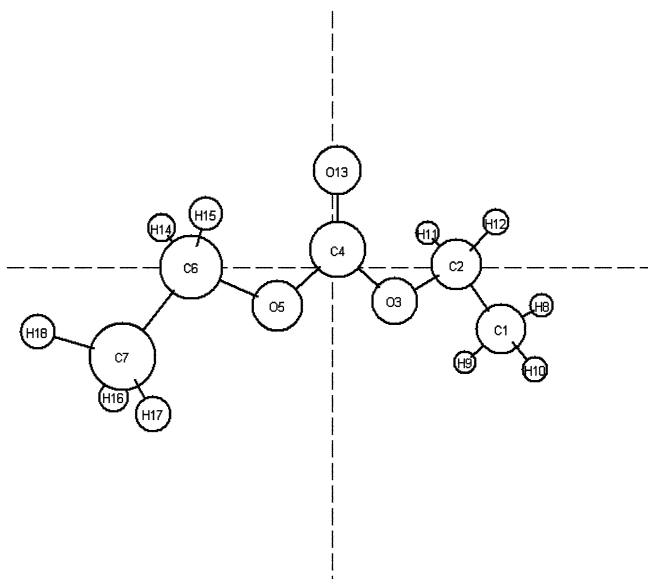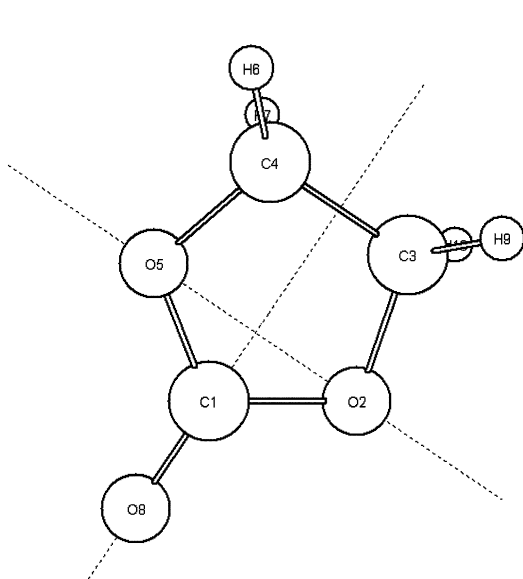| Intermediate anion	Charge	Alkoxide anion	Charge	Carboxyl anion	Charge
$C_2H_5OC_2H_4OCOO^-$	−0.636	CH_3O^-	−0.843	$HCOO^-$	−0.588
$C_2H_5OCO_2C_2H_4O^-$	−0.773	$C_2H_5O^-$	−0.782	CH_3COO^-	−0.649
$C_2H_5OCOO^-$	−0.649	$(CH_2O^-)_2$	−0.819		

the corresponding products were not detected in the mixture after storage as shown in Table 2. One possible reason is that the intermediate anions formed in routes 1 and 3 were less nucleophilic than that in route 4. This is due to charge delocalization over the oxygen atoms in carbonate groups of the intermediates in routes 1 and 3, whereas the charge of the intermediate in route 2 was localized on an oxygen atom.

Consequently, it is proposed that alkyl dicarbonate formation proceeds through two-step nucleophilic reactions. At the first step, the alkoxide anion attacks to an alkyl carbonate to generate an active nucleophilic intermediate, which further attacks another alkyl carbonate to form an alkyl dicarbonate at the second step. It was reported that solvent decomposition began at potentials below 1.5 V versus Li/Li$^+$ [17,18]. It was also reported that formation of alkoxide anions by solvent reduction took place above 1.46 V versus Li/Li$^+$ [7]. In addition, alkyl dicarbonates were formed in graphite half-cells at charging voltage of 1.5 V versus Li/Li$^+$ or lower as shown in Fig. 2. These results support the above proposal. As concentration of alkoxide anions increase in electrolyte with process of charging, alkyl dicarbonate formation should be enhanced as shown in Fig. 2.

Charge densities on the oxygen atoms of the intermediates estimated by MO calculations are summarized in Table 3, together with those of the alkoxide anions and carboxyl anions tested in the present study. The negative charge density on the ionized oxygen atom of the intermediate ($C_2H_5OCO_2C_2H_4O^-$) formed in route 2 is much higher than those of the other intermediates; besides, its value is approximately the same as that of the original alkoxide anion ($C_2H_5O^-$). Furthermore, charge on the ionized oxygen atom of the intermediate ($C_2H_5OCO_2C_2H_4O^-$) localized as with the original alkoxide anion ($C_2H_5O^-$). It is therefore reasonable to consider that the intermediate in route 2 can further attack DEC to form DEDOHC because it has a high nucleophilicity comparable to the original alkoxide anion. Charge densities on the carbon atoms of EC and DEC are summarized in Table 4. In each solvent molecule, the carbonate carbon (C1 for EC and C4 for DEC) is much more positively charged than the other carbon atoms. Moreover, LUMO extends widely at the carbonate carbon of EC as shown in Fig. 5, and should be vulnerable to nucleophilic attack of alkoxide anions. This property is consistent with the progress of alkyl dicarbonate formation through route 2.

Zhang et al. [6] reported that PF$_5$, which is formed from LiPF$_6$, works as an active species for the formation of DEDOHC in 1 M LiPF$_6$/EC + DEC as mentioned earlier. However, in the present study, DEDOHC was formed even in the EC + DEC (1:1, v/v) + 1 wt.% lithium alkoxide mixtures in the absence of LiPF$_6$. The effect of LiPF$_6$ addition on the formation of DEDOHC in EC + DEC (1:1, v/v) + 1 wt.% C_2H_5OLi is shown in Fig. 6. The rate of DEDOHC formation

Table 4
Calculated charge densities on the carbons of EC and DEC

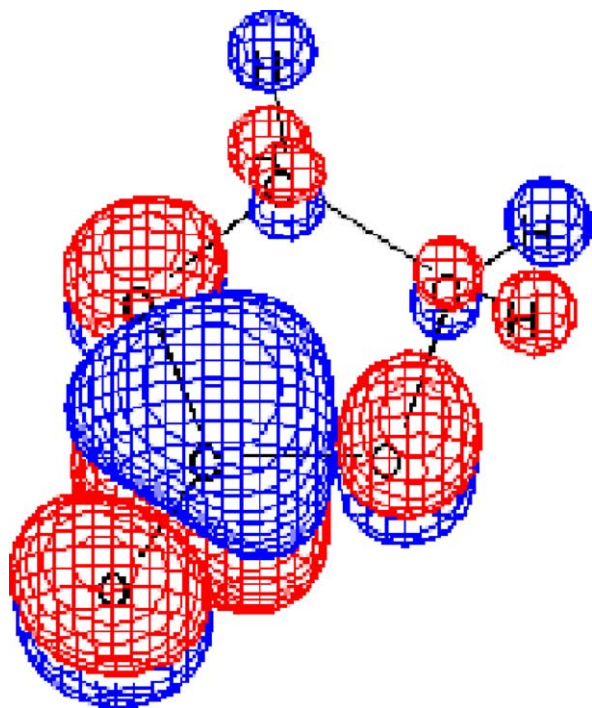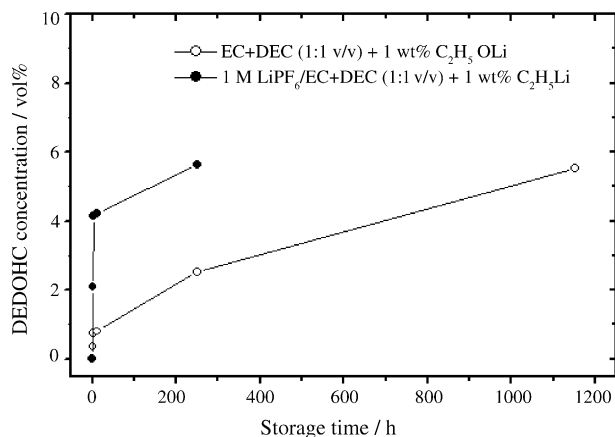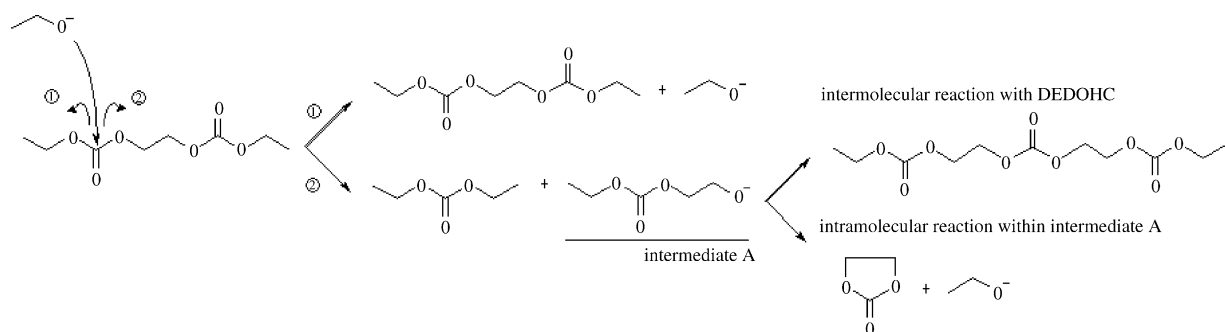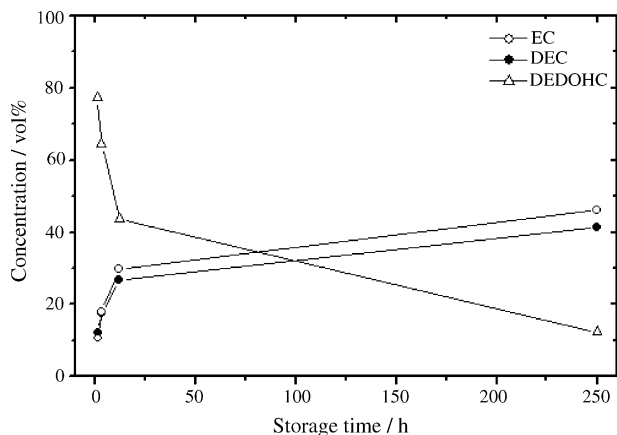| Carbon in EC	Charge	Carbon in DEC	Charge
C1	0.444	C1 and C7	−0.304
C3 and C4	−0.045	C2 and C6	−0.036
		C4	0.501

Fig. 5. LUMO contour map for EC.

Fig. 6. Variations of DEDOHC concentration in the EC + DEC (1:1, v/v) + 1 wt.% C_2H_5OLi and 1 M $LiPF_6$/EC + DEC (1:1 v/v) + 1 wt.% C_2H_5OLi mixtures with storage time.

Fig. 8. Variations of the concentrations of DEDOHC, EC, and DEC with storage time in the DEDOHC + 1 wt.% C_2H_5OLi mixture.

was greatly accelerated in the presence of 1 M $LiPF_6$. This result indicates that PF_6^- anion or a small amount of PF_5, which is present in equilibrium with $LiPF_6$, plays a catalytic role in DEDOHC formation, rather than an active species. PF_5 in the electrolyte is supposed to be associated with alkyl carbonates due to its strong Lewis acidity [19], which enhances the positive charge densities on the carbon atoms of the carbonate groups. The presence of a small amount of PF_5 in the solution therefore accelerates the rate of nucleophilic attack of alkoxides anion.

Takeuchi et al. [7] reported that the ester exchange reactions in an equimolar mixture of DMC and DEC were promoted not only by lithium alkoxides, but also by lithium metal. In the present study, however, alkyl dicarbonates were not detected in the graphite half-cells charged at 2.0 V versus Li/Li$^+$ and higher and the LiCoO$_2$ half-cell, in both of which lithium metal was used as counter electrodes. Consequently, lithium metal has no or little ability to promote alkyl dicarbonate formation. This fact suggests that graphite surface, on which many kinds of functional groups such as phenolic groups are present, plays an important role in alkyl dicarbonate formation as well as lithium alkoxides formed from solvents. For example, the phenolic groups can be lithiated during the initial charging to be a strongly nucleophilic functional groups that are analogous to lithium alkoxides [20–22].
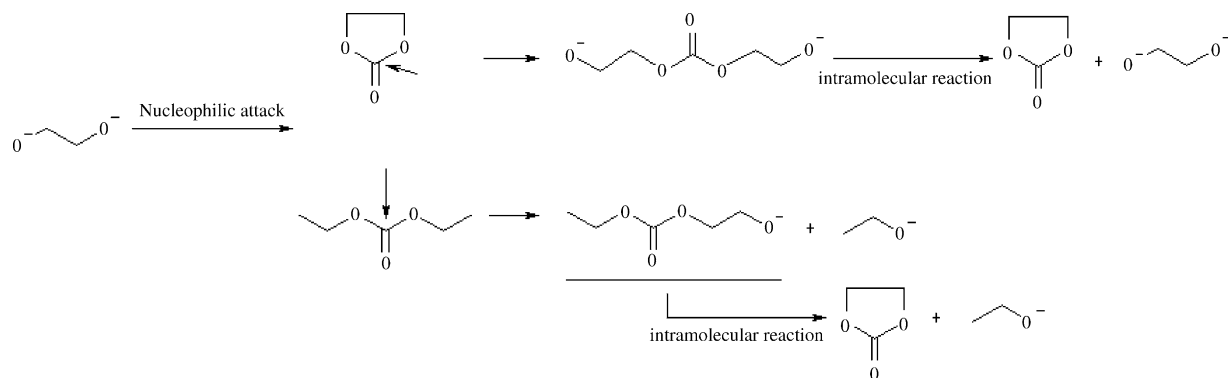

Fig. 7. Reaction scheme for the decomposition of DEDOHC in the presence of 1 wt.% C_2H_5OLi.

Fig. 9. Reaction scheme for EC and DEC regeneration in 1 M $LiPF_6$/EC + DEC (1:1, v/v) in the presence of 1 wt.% C_2H_5OLi.

However, further investigation is needed to clarify the role of graphite surface in alkyl dicarbonate formation.

3.4. Decomposition of DEDOHC in the presence of lithium alkoxide

In the presence of 1 wt.% C_2H_5OLi, DEDOHC decomposed to form EC and DEC, which is a reverse reaction of DEDOHC formation as shown in Tables 1 and 2. Through analogy from the scheme for DEDOHC formation mentioned above, the mechanism for EC and DEC formation can be described in a scheme shown in Fig. 7. Two reaction pathways are possible depending on the direction of bond cleavage upon the first attack of the ethoxide anion. One is regeneration of DEDOHC, and the other is the formation of DEC and an intermediate A. An intramolecular reaction of intermediate A will lead to the formation of EC and an ethoxide ion. If intermediate A attacks another DEDOHC molecule, a tricarbonate compound will be formed. While considerable amounts of EC and DEC were detected in the mixture, no tricarbonate compound was detected even after 250-h storage. Fig. 8 shows the variations of DEDOHC, EC, and DEC concentrations in the mixture with storage time. The concentrations of EC and DEC increased with storage time at an expense of DEDOHC. It should be noted that nearly equal amounts of EC and DEC were formed at each storage time. It is therefore considered that the intramolecular reaction is dominant in the reaction scheme in Fig. 7. A similar intramolecular reaction was also observed in the 1 M $LiPF_6$/EC + DEC (1:1, v/v) + 1 wt.% $(CH_2OLi)_2$ mixtures, in which EC formation can be described in a scheme shown in Fig. 9.

4. Conclusions

Alkyl dicarbonates are formed on graphite electrode at potentials of 1.5 V versus Li/Li+ or lower. The results of the storage tests of solvents and electrolyte solutions suggested that lithium alkoxides, which are formed by decomposition of solvents at around 1.5 V versus Li/Li+, are the most probable active species for alkyl dicarbonate formation. The

formation reaction proceeds through two-step nucleophilic reactions initiated by lithium alkoxides. At the first step, alkoxide anion attacks alkyl carbonate to generate an active nucleophile intermediate, which in turn attacks another alkyl carbonate to form alkyl dicarbonate at the second step. The rate of alkyl dicarbonate formation was enhanced in the presence of $LiPF_6$. This fact indicated that a small amount of PF_5, which is present in equilibrium with $LiPF_6$, plays a catalytic role in DEDOHC formation, rather than an active species. Alkyl carbonates were not formed on lithium metal, which implied that functional groups such as phenolic groups on graphite surface play an important role in alkyl dicarbonate formation.

Because alkyl dicarbonates such as DEDOHC are viscous liquid, their formation should lower the ionic conductivity of the electrolyte solutions, which deteriorates the performance of Li-ion cells. The effects of alkyl dicarbonate on the performance of Li-ion cells will be reported in near future.

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