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Functional electrolytes: Novel type additives for cathode materials, providing high cycleability performance

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Abstract

We present the results of novel type additives to improve the cathode cycleability performance. Benzene derivatives (biphenyl and *o*-terphenyl) and heterocyclic compounds (furan, thiophene, *N*-methylpyrrole and 3,4-ethylenedioxythiophene), which have lower oxidation potentials than those of electrolyte solvents are picked up. We use MO calculations in the selection of additives and prove that the calculated HOMO values agree well with the measured oxidation potentials. To clarify the additive performance, electrochemical properties and cycleability of the additive are investigated. The additives are found to be decomposed on cathode to form very thin film. We have named this resulting novel-type thin surface film as electro-conducting membrane (ECM) since it is different from solid electrolyte interphase (SEI) by the point of its electro-conductivity. The nature and the component of ECM are studied with X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) in details. It is concluded that these additives, which were formerly known as overcharge protecting proofs, contribute to improve cathode cycleability by forming very thin cathode surface layer in the case of slight amount of addition.
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1. Introduction

Lithium-ion batteries (LIB) have been commercialized for over 10 years and playing a very important role in our life today because they combine a large power source with small size and light weight. The cell voltage of the batteries can reach as high as 4 V, which may ensure both high energy and power densities. LIB has made rapid progress, especially, in energy density development. The capacity of 18650 cylindrical cell was just 1000 mAh in 1993. Average increase of capacity led to 1500 mAh in 1997, which was thought to be the maximum capacity increase from the point of battery design. The reason was the formation of solid electrolyte interphase (SEI) by the decomposition of electrolyte at the carbon anode surface [1]. It was thought to be inevitable to avoid SEI film formation in the battery reactions, however, we have proposed a control of SEI film formation

with a new concept of electrolyte, "Functional Electrolytes", which improves battery performances by the deliberate formation of SEI film with a small amount of additives. So far the composition and the role of SEI film have been extensively studied [2]. In the earliest research, CO_2, N_2O, SO_2 [3], Cl-EC [4] and crown ether [5] are evaluated in compatible with graphite anode to suppress propylene carbonate (PC) decomposition. However, during our continuous effort, we have been developing several additives to suppress PC decomposition on graphite anode [6]. Owing to the development of anode additives, highly graphitized carbons, which have as high capacity as 350 mAh g^{-1}, become able to be used without serious electrolyte decomposition. We have started commercial production of the electrolyte in 1997, which we call as the first generation of "Functional Electrolytes" [7]. After we have commercialized "Functional Electrolytes", researches for the electrolytes have been mainly focused on electrolyte additives. Concerning about the electrolyte solvents, highly graphitized carbons are not generally compatible with PC, an excellent solvent with high conductivity

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and low melting point, since PC decomposes at the initial charging stage on anode. The emergence of anode additives has enabled to use graphite anode with PC. We have also proposed to use PC-based electrolyte with graphite anode as a fingerprint-solvent system in developing additives to suppress electrolyte decomposition on graphite anode [6]. For the anode additives, we have introduced some olefinic carbonates and esters such as catechol carbonate, vinyl acetate (VA) and so on [6]. These additives are deliberately decomposed on anode to form a new-type SEI film, which modifies anode surface.

Recent increase of the LIB capacity reaching to over 2400 mAh is due to the elevation of the charging cut-off voltage to use more lithium-ions in $LiCoO_2$. On the condition of the new battery operations, however, we need to modify the cathode surface, since electrolyte decomposition tends to occur more easily. From such a point of view, we have investigated several cathode additives as a new generation of "Functional Electrolytes" to control the formation of cathode surface film. Once we take a closer look at overcharge protection, a novel task for this kind of additives is found. That is, we have found that amount of addition of overcharging proof extensively affects the battery performance. For example, biphenyl (BP) is known to work as overcharging proof, since the gas evolution occurs at higher voltage (decomposition at 4.5 V versus Li/Li^+) and the gas opens the safety cap at a certain pressure. In the present work, we have found an interesting result that cathode surface modification by the electrolyte additives exerts a significant influence on the battery performance. We herein have examined appropriate amount of addition and found that slight amount (0.1 wt.%) of BP decomposes to construct very thin surface film, improving cathode conductivity. What is more interesting, BP decomposes at the active sites of cathode surface. Consequently further electrolyte decomposition is prevented to provide satisfactory cathode cycle performance. In this case, unfortunately, the effect of overcharge protection has to be sacrificed.

We have formerly introduced the first generation of "Functional Electrolytes", which improves graphite anode surface. Now several types of functional electrolytes have been developed and commercially produced. The categories of the functional electrolytes include: (i) the additives designed for better SEI performance of carbon anode as mentioned above [6], (ii) the additives such as trialkyl phosphate [8], R-COOR′ [9], to improve wettability of the poly olefin separator, (iii) organic species to protect overcharge (BP [10] and *o*-terphenyl (OTP) [11]), and (iv) the cathode cycle improving agents addressed herein. In this paper, we report the additives to improve the cathode cycleability, as the new generation of "Functional Electrolyte", which controls the formation of new-type cathode surface film (Electro-Conducting Membrane (ECM)). Specifically benzene derivatives and aromatic heterocyclic compounds are examined. Additive-selection by MO calculations, electrochemical properties of additives and cathode film analyses (AES and XPS) are addressed.

2. Experimental

The additives were commercially available from Aldrich and were used after appropriate purification (distillation or recrystalization). Electrolytes were used as received (UBE Industries Ltd.). Electrolyte solvents such as PC, ethylene carbonate (EC), dimethyl carbonate (DMC) and methylethyl carbonate (MEC) stored under a nitrogen atmosphere. Anode preparation was as follows: 90 wt.% of graphite powder suspended in a solution of 10 wt.% of poly(vinylidene)fluoride (PVdF) (Kureha) in 1-methyl-2-pyrrolidone (Wako Pure Chemical Industries) was spread on the copper foil current collector, dried at 100 °C overnight, pressed at 100 kg cm^{-2}, then finally dried under vacuum at 130 °C for 3 h. $LiCoO_2$ cathode was made from 90 wt.% of $LiCoO_2$ (Nihon Kagaku Kogyo Co.), 5 wt.% of acetylene black and 5 wt.% of PVdF. The preparation of the cathodes was very similar to the method of anode preparation. Instead of copper foil, aluminum foil was used for the cathode current collector. Electrolyte preparation and cell assembly were carried out under a dry argon atmosphere in a glove box. Polypropylene separator (Hoechst) was used for coin cell and cyclindrical cell. The coin cell-size was 20 mm diameter and 3.2 mm height. The coin cell was charged at constant current of 0.8 mA to reach 4.3 V over 5 h and then discharged to 2.7 V. 18650 Cyclindrical cell was initially charged at a constant current (0.02 C) for 2 h, then at 1 C up to 4.3 V, followed by constant voltage charge for 2 h, then the cell was discharged to 2.7 V at a constant current of 1 C. Charge–discharge cycle was repeated 200 times at appropriate temperature. For the measurement of cathode cyclic voltammetry (CV) and AC impedance, 1 M $LiPF_6$ dissolved in PC with additive was prepared. In the case of anode CV and AC impedance, 1 M $LiPF_6$-EC/MEC = 3/7 (by volume) with 2 wt.% additive was prepared. The water content of electrolytes was determined by Karl–Fischer titration and the value was within 10 ppm. CV and impedance measurement was carried out in glass cells with three electrodes. Graphite electrode or $LiCoO_2$ electrode was served as working electrode. The amount of active material was ca. 10 mg, respectively. Lithium metal foil was applied for counter and reference electrodes. ALS model 608A was used to measure CV and impedance. Cathode CV was started from OCV, then cycles from 5 to 3 V with 0.1 mV s^{-1} for one cycle. Anode CV was measured for three cycles from 0 to 2 V with 1 mV s^{-1}. After CV measurement, AC impedance was observed immediately at open circuit voltage conditions. Frequency of impedance ranges from 100 kHz to 10 mHz. The impedance of the electrode surface film was calculated from a diameter of semi circle of the cole–cole plot.

We carried out cathode film analyses with $LiCoO_2$ electrode used for the cyclindrical cell. After 200 times charge–discharge cycles at 45 °C, the electrode was recovered from the cell and was rinsed with DMC, then was dried in vacuum at room temperature to evaporate the DMC. The X-ray photoelectron spectroscopy (XPS) analysis was

performed with PHI, 1600S using a focused monochromatized Mg Kα radiation (400 W). Cathode film thickness was measured by the auger electron spectroscopy (AES) (PHI, SAM670Xi). Ar ion was used for etching. After the measurement of depth profile, we defined the thickness of the film as the point where the sum of Co and O atomic concentration reaches 90%.

MO calculations were accomplished by a semi-empirical method (PM3) with winMOPAC ver. 3.5.

3. Results and discussion

3.1. Additive candidates

We have investigated additives for the cathode to improve the LIB performance. As the representative overcharging proof, BP is known. At the higher voltage, BP decomposes to produce gas, which opens safety cap at a certain pressure, and then the battery stops operations. To get enough gas pressure inside the battery, at least several percentage addition of BP is required. The decomposed products will leave very thick film covering the cathode surface (a Li$^+$-conducting insulator), which makes the cathode inert and unusable anymore. In this case, we assume that the decomposed products on cathode are mainly derived from BP decomposition. If we can control the thickness of cathode surface film, we would be able to improve the cathode surface chemistry, since polymerized benzene is known to have electro-conductivity [12].

Our design concepts of selecting cathode additives are as follows: (1) the additive is chemically stable in electrolyte, (2) the additive has lower oxidation potentials than those of electrolyte solvents, (3) the additive is decomposed on cathode to form protective layer in charging, (4) the resulting cathode surface film has not only Li$^+$ conductivity but also electro-conductivity and (5) the additive does not show any harmful influence on anode in charge–discharge cycles. We herein have studied the structure of the additives as well as their most effective amount of addition.

We assume that cathode surface has uneven high voltage spots (active sites). In charging, the potential of cathode surface does not always elevate equally, causing tiny uneven high voltage spots. At the active sites, strongly oxidative species are produced and the electrolyte decomposition occurs. The reason why such active sites would arise is: (1) cathode materials are unevenly spread over on the collector in preparing cathode and (2) decomposed products of electrolyte cover the cathode surface unevenly as charge–discharge cycles progress. Accordingly we assume that the cathode additives are predominantly decomposed at the active sites on cathode surface before the solvent decomposition to form cathode protective layer. Generally cathode materials are less conductive so that conducting materials (e.g. acetylene black etc.) are mixed in preparing cathode. Hence, we envisage the increase of cathode conductivity by the formation of conducting polymer layer derived from the additive decomposition. According to our concepts, we have picked up aromatic compounds such as biphenyl (BP), o-terphenyl (OTP), dibenzyl (DBZ), diphenyl ether (DPE), furan, thiophene (TPN), N-methylpyrrole (MPL) and 3,4-ethylenedioxythiophene (EDT) as additive candidates (Fig. 1).

3.2. Molecular orbital (MO) calculations

In the selection of additives, we have used MO calculations as the first screening technique. It is known that HOMO (the highest occupied molecular orbital) energy correlates to the potential of oxidative decomposition and LUMO (the lowest unoccupied molecular orbital) energy corresponds to the potential of reductive decomposition, respectively. As a screening index, we set up −9 eV of HOMO, which is much higher than the value of electrolyte solvents (EC: −11.8 and DMC: −11.6 eV). Actually the calculated HOMO values of additives are region from −9.64 to −8.87 eV (Table 1). These high HOMO energy compounds are supposed to be decomposed on cathode prior to the solvents since they are good electron donors.
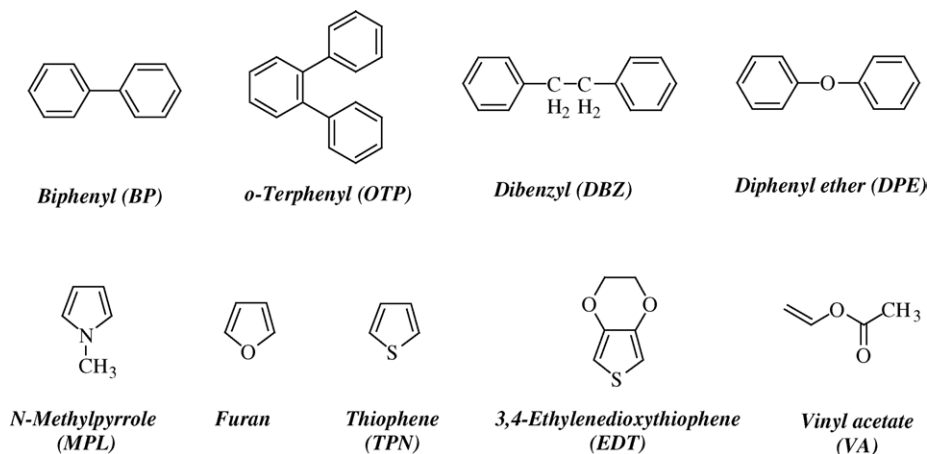

Fig. 1. Chemical structures of the investigated additives.

Table 1
HOMO energies and measured oxidation potentials of additives, together with EC and DMC

Compound	BP	OTP	DBZ	DPE	MPL	Furan	TPN	EDT	VA	EC	DMC
HOMO (eV)	−8.92	−9.34	−9.46	−9.11	−8.87	−9.38	−9.64	−8.98	−9.95	−11.8	−11.6
Oxidation potential (V) vs. Li/Li^+	4.5	4.5	4.6	4.5	3.8	4.3	4.4	4.0	5.1	5.5	5.3

3.3. Electrochemical properties of additive

Table 1 summarizes the electrochemical properties of the additive candidates together with the typical electrolyte solvents (EC and DMC) and anode additive (VA), including HOMO energies and oxidation potentials. The oxidation potentials are measured by linear sweep voltammetry at a Pt electrode with three-electrode cells (Fig. 2). Their decomposition potentials are estimated from the points where the current goes over 0.1 mA as a threshold value. As we have expected, the cathode additives, with high HOMO energies, have lower oxidation potentials than those of the solvents.

To investigate effective amount of the additive, cyclic voltammetry at a $LiCoO_2$ electrode with three-electrode cells were measured (Fig. 3). Sweeping from OCV to 5 V (versus Li/Li^+), two oxidative current peaks are observed at 3.9 and 4.6 V for each sample, which are related to Li^+ extraction. In the case of 2 wt.% BP addition, high current is observed at 4.5 V, which indicates that considerable amount of BP has decomposed. When sweeping from 5 to 3 V, for the electrolytes without additive and with 0.1 wt.% BP, there are reductive current peaks at 4.3 and 3.7 V, which show Li^+ insertion into $LiCoO_2$. However, for the electrolyte with 2 wt.% of BP addition, little reductive current is observed, which suggests that further Li^+ insertion is inhibited by the thick BP decomposed products piled over the electrode. These results indicate that the amount of addition exerts crucial influence on the thickness of cathode surface film. The thick film must have prevented Li^+ insertion.

In addition to the voltammetric measurement, AC impedance is also used to probe the nature of cathode surface layer. Impedance measurements at 25 °C were conducted
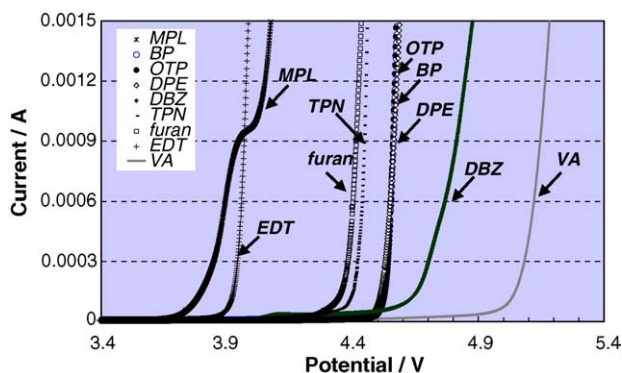
right after CV. Even after only one cycle, the surface film resistance of $LiCoO_2$ drastically increased to 1.32 Ω in the case of 2 wt.% BP addition, compared with the 0.72 Ω of 0.1 wt.% BP (Fig. 4). The results of impedance agree well with the fact of CV measurement. In the case of 2 wt.% addition, Li^+ intercalation is prevented by the BP decomposed products, supporting higher impedance value. As the similar impedance values of BP 0.1 wt.% and pristine electrolyte suggest both of the electrolytes are proved to show successful Li^+ intercalation. The results of CV and impedance imply the successful formation of ECM in the case of slight amount of BP addition.
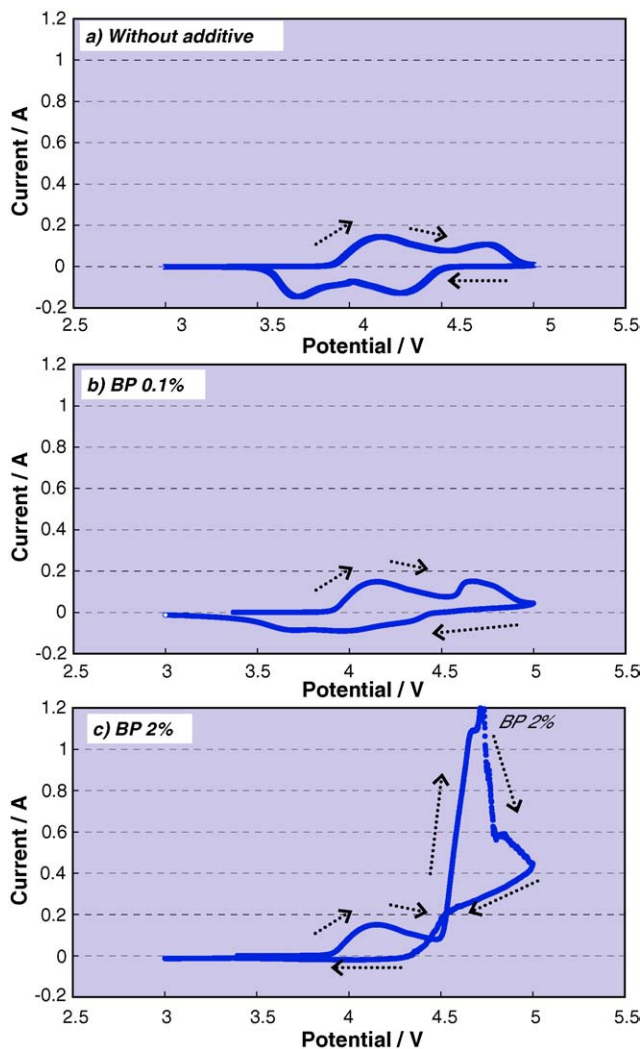

Fig. 2. Linear sweep voltammetries of Pt electrode in 1 M $LiPF_6$ PC electrolyte with 2 wt.% of various additives at 25 °C.

Fig. 3. Cyclic voltammograms of $LiCoO_2$ in 1 M-$LiPF_6$ PC (a) without additive, (b) with 0.1 wt.% BP and (c) with 2 wt.% BP at 0.1 mV s^{-1}.
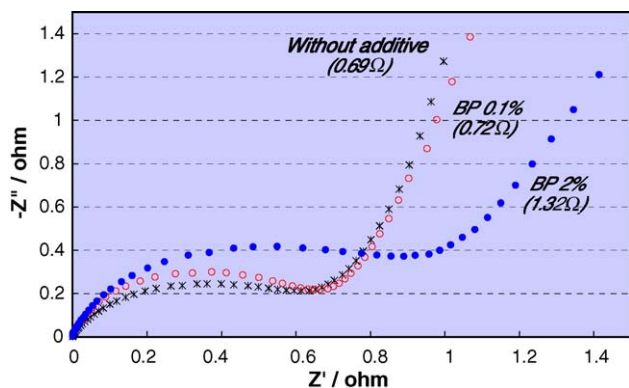
Fig. 4. AC impedance plots of LiCoO2 electrode cells possessing electrolytes with several amount of BP at room temperature after one cycle.

By measuring LiCoO2 cyclic voltammetry and AC impedance, we have confirmed the cathode additive, BP, works on LiCoO2 electrode. In order to clarify that the cathode additive does not work on graphite anode, we examined CV and AC impedance with a natural graphite electrode. 2 wt.% of the cathode additives are used as a noticeable amount with 1 M LiPF6-EC/MEC = 3/7 to know the obvious results. Fig. 5 shows the first and the third cycles of CV measurements at natural graphite with three-electrode cells in the case of representative BP and the pristine electrolyte.
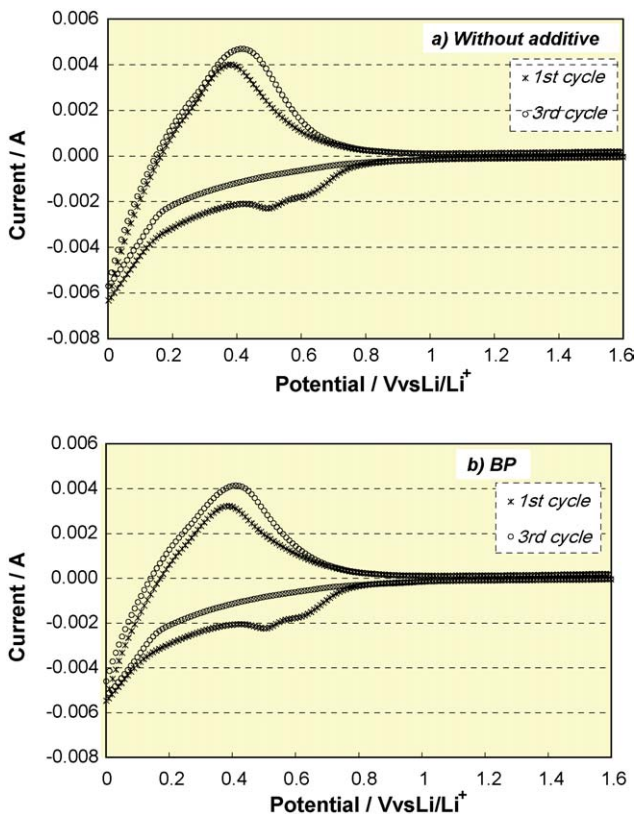

Fig. 5. The first and third cyclic voltammograms of graphite in 1 M LiPF6-EC/MEC = 3/7 with 2 wt.% of various additives at 1 mV s^{-1}, (a) without additive and (b) BP.
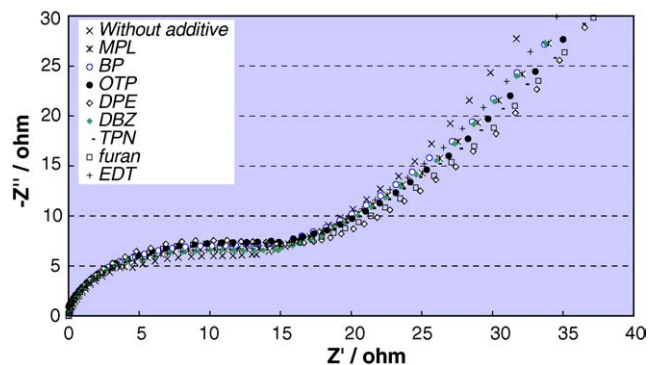

Fig. 6. AC impedance plots of graphite electrode cells possessing electrolytes with various additives at 25 °C after three cycles of voltammetries.

For all the electrolytes with additives, no peaks other than EC decomposition are observed and the cyclic voltammograms are quite identical to the pristine electrolyte, indicating that all the additives are stable on graphite anode.

AC impedance of natural graphite electrode is measured after three cycles of CV (Fig. 6). All the electrolytes with additives show identical impedance value of 13 Ω with the pristine electrolyte. Although 2 wt.% addition of cathode additives exerts serious influence on cathode, in the case of anode, no significant difference between pristine and additive-containing electrolyte is observed, which demonstrates the stable character of cathode additives on graphite anode.

3.4. Charge–discharge cycle

In order to prove the influence of additives on the LIB cycle performance, we investigated the cycle life of the electrolytes with 0.1 and 2 wt.% of representative BP, comparing with the pristine electrolyte (1 M LiPF6-EC/MEC = 3/7). Cylindrical cells are used and the test was undertaken at 45 °C as the upper limit of 4.3 V (Fig. 7). On such a severe condition, oxidative decomposition of electrolytes is liable to occur so that we can distinguish the effect of additives clearly. As
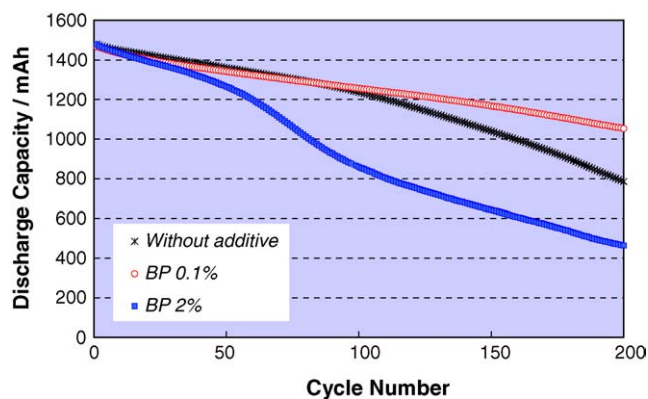

Fig. 7. Cycle performance of LiCoO2/graphite cyclindrical cells in 1 M LiPF6-EC/MEC = 3/7 without additive, with BP 0.1 wt.% and with BP 2 wt.% within 2.7–4.3 V at 45 °C.
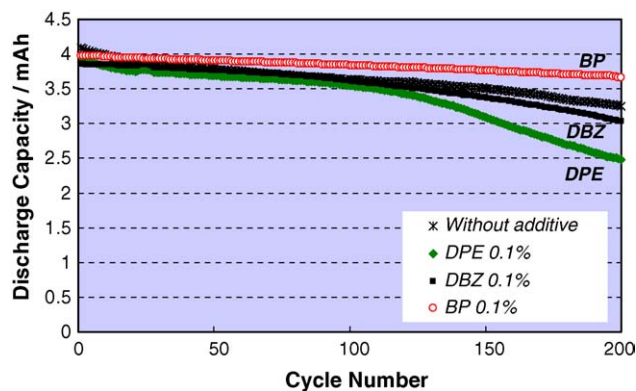
Fig. 8. Cycle performance of LiCoO$_2$/graphite coin cells in 1 M LiPF$_6$-EC/MEC = 3/7 without additive, with BP 0.1 wt.%, with DBZ 0.1 wt.% and with DPE 0.1 wt.% within 2.7–4.3 V at 25 °C.

we have expected, the amount of additive is proved to control the cycleability. In the case of a slight amount addition (0.1 wt.%), the cycle proceeds with higher capacity preservation than the electrolyte without additive. When the 2 wt.% of BP is added, BP gradually decomposes on cathode to produce Li$^+$ insulator, leading to the big capacity fading. These results agree well with the CV and impedance measurements with the high cathode surface resistance in 2 wt.% of BP addition.

Coin-cell cycle performance of benzene derivatives is examined with the additive amount standardized to 0.1 wt.% (Fig. 8). BP shows improved cycle performance, however, both the electrolytes with DPE and DBZ are inferior to the pristine electrolyte. Though all the additives have similar oxidation potentials to be decomposed on cathode, the
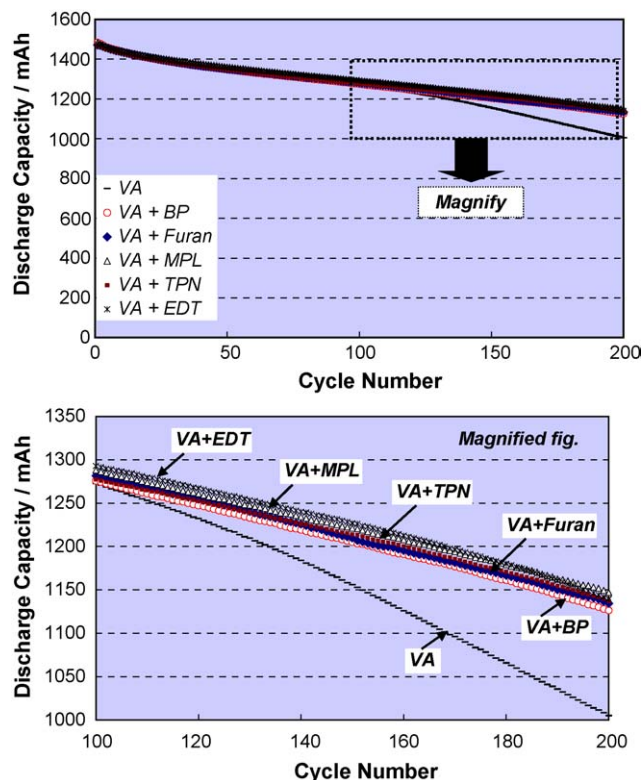

Fig. 9. Cycle performance of LiCoO$_2$/graphite cylindrical cells in 1 M LiPF$_6$-EC/MEC = 3/7 + VA (1 wt.%) as a base electrolyte within 2.7–4.3 V at 45 °C. 0.1 wt.% of cathode additives (BP, MPL, Furan, TPN and EDT) are used.
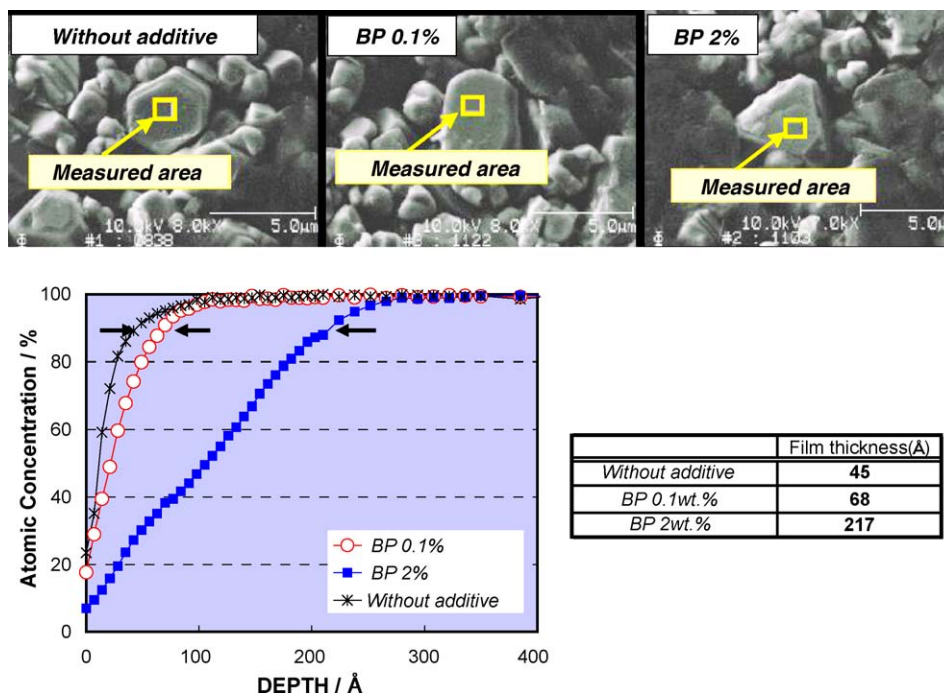

	Film thickness(Å)
Without additive	45
BP 0.1wt.%	68
BP 2wt.%	217

Fig. 10. AES measurement of LiCoO$_2$ cathode surface film thickness. LiCoO$_2$ electrodes used for the cyclindrical cells after 200 times charge–discharge cycles at 45 °C in 1 M LiPF$_6$-EC/MEC = 3/7 without additive, with BP 0.1 wt.% and with BP 2 wt.% were examined.

results of cycleability differ. This clearly shows the nature of decomposed products on cathode is different. We believe the cycleability depends on the surface film character. That is, the additive structure controls the nature of ECM. For BP and OTP, benzene rings are directly connected in their molecular structure, meanwhile, the structures of DBZ and DPE are divided by carbon or oxygen atom, respectively leading to the formation of inferior conductive surface films.

In order to obtain more concrete evidence of cathode additive performance, VA, the well-known anode additive [6] is conducted for the cycle test of cylindrical cells together with several new cathode additives. For the further cathode additive development, 5-membered heterocyclic compounds such as MPL, furan, TPN and EDT are evaluated (Fig. 9). These compounds are well-known monomers of conducting polymers [13–17].

Obviously all the cathode additives show improved effect with higher capacity retention than the electrolyte without cathode additive. On this test condition, cathode is exposed to significantly severe situation such as higher temperature as 45 °C and higher voltage as 4.3 V, as the consequence, the effect of cathode is clearly demonstrated in contrast to the anode. Accordingly, in spite of VA addition, capacity degradation begins at around 100 cycles when cathode additives are absent. Every electrolyte with heterocyclic compound shows satisfactory cycle performance similar to the BP electrolyte. These results indicate that monomers of the conducting polymers can be good cathode additives when they have lower oxidation potentials than those of electrolyte solvents. The reason why these cathode additives can improve the cycleability is the successful formation of the polymerized thin films to suppress the significant electrolyte decomposition on cathode active sites.

3.5. ECM analyses

We carried out cathode film analyses with AES and XPS of $LiCoO_2$ electrode used for the cyclindrical cell after 200 times charge–discharge cycles at 45 °C in 1 M $LiPF_6$-EC/MEC = 3/7 without additive, with BP 0.1 wt.% and with BP 2 wt.%. As shown in SEM figures, it is difficult to see if a thin layer covers the cathode by their outward appearance. We measured AES depth profiles of the cathode surface to elucidate the film thickness. The film thickness was defined at the point where the sum of Co and O atomic concentration reaches 90%. In AES measurement, we ignored Li atom in the depth measurement of $LiCoO_2$, since detectable sensitivity of Li atom was extremely lower than those of Co and O. Around the 100% range of Co + O atomic concentration, the depth varied so significantly that we could not evaluate the accurate film thickness. Accordingly we set up the threshold value as 90%. As shown in SEM figures (Fig. 10), we measured the flat and uniform surface of cathode as much as possible. BP 0.1 wt.% electrolyte and pristine electrolyte produce very thin films of 68 and 45 Å, respectively. On the other hand, the electrolyte with BP 2 wt.% affords thick film
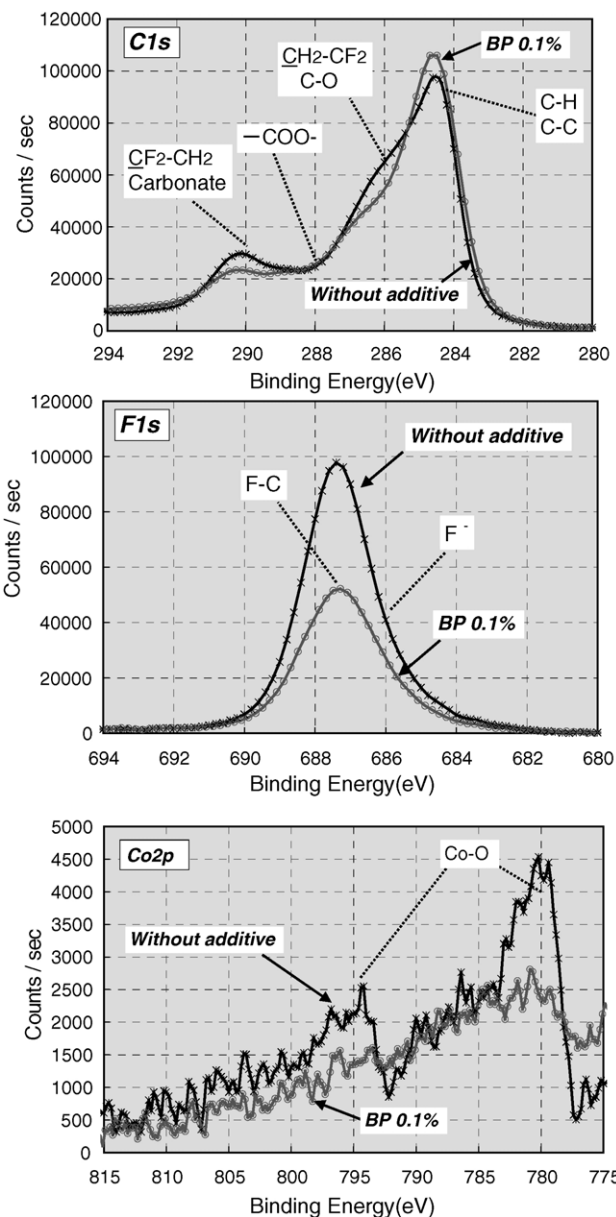

Fig. 11. XPS analysis of cathode surface film component. $LiCoO_2$ electrodes used for the cyclindrical cells after 200 times charge–discharge cycles at 45 °C in 1 M $LiPF_6$-EC/MEC = 3/7 without additive and with BP 0.1 wt.% were examined.

of 217 Å (Fig. 10). The thickness of the cathode surface is well corresponds to the results of $LiCoO_2$ voltammetry. When the amount of BP addition increases, the resulting thick surface film prevents Li^+ from inserting into the cathode successfully (Figs. 3 and 4).

Fig. 11 shows the results of XPS. In the C 1s spectra, the peaks resulted from binder PVdF and carbonate peaks decreased and C–H/C–C peak of organic components increased. In the F 1s spectra, the binder F–C peak is lowered and the Co–O peaks by $LiCoO_2$ are reduced in the Co 2P spectra. These XPS results indicate that the surface of cathode materials is covered with organic compounds and

both binder and LiCoO$_2$ are hard to be seen when 0.1 wt.% of BP exists. Moreover, in the C 1s spectra, the peaks of carbonate and esters do not increase. This implies the film over the cathode is originated not from electrolyte component but from the cathode additives.

4. Conclusions

In the case of slight amount of addition, we have proved that BP, OTP, furan, MPL, TPN and EDT improve cycleability of LIB because they form useful ECM. We propose that additive oxidation and electrochemical polymerization are the key reaction of the cathode surface modification. A general reaction mechanism for oxidative polymerization can be formulated as follows. At the initial charging process, the additives with lower oxidation potentials than those of electrolyte solvents are decomposed at the uneven high voltage sites on cathode to form radical cation species. Such radicals tend to react with another additive molecular, which has lower oxidation potential, to form conducting surface film, since these additives are widely known as monomer-units of conducting polymers. The newly produced ECM covers the active sites on cathode to protect further electrolyte decomposition. Moreover, the thin film is expected to help electro-conductivity of cathode since it is a polymeric film composed by the monomer of conducting polymer with excellent conductivity [18]. As a consequence, we conclude that both the suppression of the electrolyte decomposition and the assistance of cathode conductivity have led to the improvement of cycleability.

An important thing to remember is that the ECM should be controlled very thin in order to obtain good cycleabilty. Even though the conducting polymer is formed on cathode, the battery performance will lower unless the film thickness is controlled as thin as several nanometer. That is, we have clarified the amount of additive exerts a crucial influence on the behavior to the cathode surface. 0.1 wt.% addition of the additive leads to the formation of several nm of thin surface layer, which protects further electrolyte decomposition on the cathode active sites. In the case of slight amount addition, the additives are completely decomposed at the initial charging process; hence they do not work as overcharging proofs. On the contrary, in the case of 2 wt.% addition, oxidative decomposition of the additives progresses as the cycle proceeds, leading to the battery capacity fading because of the grown thick cathode film with high Li$^+$ resistance.

Our design concepts to develop the cathode additive are: (1) the additive is chemically stable in electrolyte, (2) the additive has lower oxidation potential than those of elec-

trolyte solvents and (3) the additive is decomposed on cathode to form ECM. Concerning about the electrochemical nature, (4) the additive is required to show no harmful influence on anode in charge–discharge cycles and (5) the resulting ECM has electron conductivity. We expect these results help progress of formerly unknown cathode additives to improve the LIB performance.

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