



Functional electrolytes: Synergetic effect of electrolyte additives for lithium-ion battery

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ABSTRACT

We have found that certain combinations of specific additives show a very interesting behavior in Li-ion batteries. During the course of investigating further improvements in the performance of the triple-bonded compounds, which we very recently reported, a novel and unique effect of an additive combination was observed. The combination of the triple-bonded compounds and the double-bonded compounds has proven to show a much improved battery performance, especially in cycleability and gas evolution than the case when they are singly used. Especially, the synergetic effect of propargyl methanesulfonate and vinylene carbonate is remarkable. To clarify the synergetic effect, the electrochemical properties of the additives and the electrode analyses were investigated. It is assumed that the higher battery performance of the combination effect resulted not only from the thin and dense SEI on the negative electrode but also from the positive electrode surface co-polymerized film produced by the synergetic decomposition of the additives. We suggest that the keys for producing the synergetic functions are (1) a structural difference in the unsaturated moiety, and (2) a greater difference in the reduction potential.

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1. Introduction

Since 1991, when the lithium-ion battery (LIB) appeared on the market, the use of small-sized electronic devices such as portable phones and notebook PCs has quickly expanded. Presently, the use of the LIB is spreading to power tools, HEVs and EVs. The energy density of the LIB has improved three times in capacity since 1991. However, a capacity increase is still required for future uses. It is obvious that the capacity increase of the LIB is due not only to the improvement of the battery manufacturing technology and the electrode material, but also to the development of its electrolyte technology.

As the electrolyte development technology, old examples, such as the additions of CO₂ [1–3], SO₂ [4,5], N₂O [6] and 12-crown-4-ether [7,8] are known. In contrast to the conventional technology, we have proposed the concept of “Functional Electrolytes”, based on a highly purified electrolyte to which only a slight amount of electrolyte additives is introduced [9,10]. Due to the high purity of the electrolyte, electrolyte decomposition itself is inhibited. Consequently, a slight amount of the electrolyte additives is deliberately decomposed on the negative electrode surface to produce the solid

electrolyte interphase (SEI), which improves the battery performance. In 1997, we commercialized the “Functional Electrolytes”, and several kinds of additives for negative electrode surface modification have been reported, such as conjugated double-bonded compounds like cathecol carbonate [11,12], imide compounds [13] and double-bonded compounds like vinyl acetate [14–20]. Since the emergence of “Functional Electrolytes”, the study of electrolyte additives has become the key to electrolyte research and has contributed to the rapid increase in the LIB market. Various chemical compounds are now reported as electrolyte additives, a positive electrode modifying agent [21–23], an overcharge inhibitor [24,25], a wettability additive [26–28], etc., as well as an additive for negative electrode surface modification. As described above, the electrolyte containing additives, which improve the specific performance of the batteries, has been the key to electrolyte research in recent years and is now widely called “Functional Electrolytes”. The basic concept of the “Functional Electrolytes” is now generally utilized as one of the necessary technical elements of the LIB. As one such example, “Role-Assigned Electrolytes” emerged in 2003 [29,30].

Recently, the performance demand for the LIB has been increasing, i.e., an electrolyte able to be utilized at a higher working voltage and over a wider working temperature is required. Especially, at a higher working voltage or a higher temperature, the LIB has an inherent problem of property degradation or gas

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evolution. Recently, we reported a novel type of negative electrode additive containing a triple-bonded moiety, which produces a thin and dense SEI, affording improved battery cycleability [31]. In this study, we investigated the further improvement of the performance of such triple-bonded compounds. Our strategy is to determine the combination effect of the triple-bonded compounds and the specific structured compounds for negative electrode surface modification. Therefore, we have focused on the combination effect of the triple-bonded compounds and the double-bonded compounds. For the double-bonded compounds, we selected vinylene carbonate (VC), which is known to form a stable SEI on the graphite negative electrode, however, the effect of decreasing the gas evolution is not sufficient as the increased amounts of CO, CO₂, CH₄ and C₂H₄ resulting from the solvent decomposition, are still high [32,33]. Very interestingly, we found that the combination of the triple-bonded compounds and VC resulted in unique characteristics related to the synergetic effect in the battery performance. We now discuss the battery performance, gas evolution and the resulting SEI analyses due to the synergism of the negative electrode additives and propose a mechanism for the synergetic effect by the additives.

2. Experimental

The preparation of the positive electrode and negative electrode, and the assembly of a coin cell and 18650 cylindrical cell were described in previous reports [21–23]. As the electrode active materials, LiCoO₂ supplied from Nihon Kagaku Kogyo Co. and the artificial graphite (MAG) supplied from Hitachi Chemical Co. were used. Battery grade electrolyte solvents, such as propylene carbonate (PC), ethylene carbonate (EC) and methyl ethyl carbonate (MEC), were used. The base electrolytes, 1M-LiPF₆ [PC:MEC (3:7 by vol.)] and 1M-LiPF₆ [EC:MEC (3:7 by vol.)] were prepared (Powerlyte, UBE Industries, Ltd.). The additives used in this study were synthesized according to prior methods [34–36] and were further purified by distillation. In general, every additive was distilled or recrystallized to remove impurities and moisture as the purified additives improve battery performance.

As for the gas analysis, the 18650 cylindrical cells were used right after one charge–discharge cycle between 4.2 and 3.0 V with 1C rate at 45 °C. Total volume of the evolved gas from the cell was measured using Archimedes' principle. The collected gas was analyzed by gas chromatography (Shimadzu, GC2014) using a standard gas.

An ALS model 608A was used to measure the cyclic voltammetry (CV), the linear sweep voltammetry (LSV) and the AC impedance in a three-electrode glass cell. The oxidation potential measurement by LSV using platinum wire as the working electrode and the reduction potential measurement by CV using graphite as the working electrode are described in a previous report [31]. After carrying out the CV measurement from 0 to 2 V vs. Li/Li⁺ at 1 mV s⁻¹, the AC impedance was immediately measured in the frequency range of 100 kHz to 10 mHz. The impedance of the SEI was estimated from the diameter of the semicircle in the Cole–Cole plot according to a known method [37].

SEI analyses of the negative electrode used in the coin-cell that underwent a 50-cycle charge–discharge test were done. The negative electrode was removed from the coin-cell in an argon glove box and washed with dimethyl carbonate (DMC), then dried at room temperature in vacuo. The surface of the SEI was observed using a scanning electron microscope (SEM) (Nihon Denshi Co., JSM-7000F) and the composition of the SEI was determined by X-ray photoelectron spectroscopy (XPS) (PHI, 1600S) using focused monochromatized Mg K α radiation (400 W). The SEI thickness was measured by auger electron spectroscopy (AES) (PHI, SAM670Xi). The depth profile was obtained by argon ion sputtering at the sput-

tering rate based on a SiO₂/Si sample. After measuring the depth profile, the thickness of the SEI was defined as the depth where the carbon atom concentration reached 95%. As the negative electrode surface is not flat, it is very difficult to uniformly etch the surface. Therefore, the rate of the carbon concentration change would decrease around the border of the SEI and negative electrode. This is the reason why we defined 95% as the threshold value of the border between SEI and negative electrode surface.

As for the thickness measurement of the positive electrode surface film, we used AES as in the case for the negative electrode. The thickness of the positive electrode surface film was defined as the 95% atomic concentration of the sum of cobalt and oxygen because the sensitivity of lithium is relatively weak.

3. Results and discussion

3.1. Selection of additive

We investigated the combination effect of propargyl methanesulfonate (PMS) or propargyl methyl carbonate (PMC), which were previously reported as triple-bonded compounds with a superior performance. For its combined use, we selected VC, a commonly known negative electrode additive. For the comparative experiment, we also examined the combination effect of the double-bonded compounds of allyl methanesulfonate (AMS) or vinyl acetate (VA) and VC. We focused on the structure of the unsaturated moiety and the functional groups of the sulfonate or ester.

3.2. Charge–discharge cycles

As a fundamental solvent for the LIB, PC has superior characteristics that include a lower melting point than EC and sufficiently high dielectric constant, however, the PC solvent cannot be used in a battery with a graphite negative electrode which is now generally utilized, since the charge–discharge is limited [38,39]. We have focused on this phenomenon and applied the PC-based electrolyte system as the basis for the electrolyte additive evaluation. Accordingly, when the additive is deliberately decomposed on the graphite negative electrode as we expected, the SEI can be produced on the graphite surface, leading to an effective charge–discharge even in PC. Our design concepts of an additive for the negative electrode are as follows: (1) The additive should be chemically stable in an electrolyte. (2) The additive should have an oxidation potential similar to the main solvents in order to exert no influence on the positive electrode. (3) The additive should have a higher reduction potential in order to be reduced prior to the main solvents in order to produce the alternative SEI. On the basis of such a design concept of the electrolyte additives, we conducted charge–discharge cycle tests of the LiCoO₂–graphite coin cell with a PC-based electrolyte. When the additives are singly used, the amount added to the electrolyte is 1 wt.% based on the total amount of the electrolyte. In the case of the combined use, each amount of the additive is 0.5 wt.%. Fig. 1 shows the results of the 50-cycle charge–discharge tests of the electrolyte containing the combined triple-bonded compounds (Fig. 1a) or the double-bonded compounds (Fig. 1b) and VC. As we have previously reported, in the case of the single use, PMS [31] and VA [14–20] show higher discharge capacities than VC. Very interestingly, when the triple-bonded compounds are used in combination with VC, a higher discharge capacity is obtained than when they are singly used. Especially, in the case of PMS and VC, the effect of the cycleability improvement is remarkable. On the other hand, the double-bonded compounds have proven to show no combined effect. That is, such a unique synergetic effect is peculiar to the triple-bonded compounds.

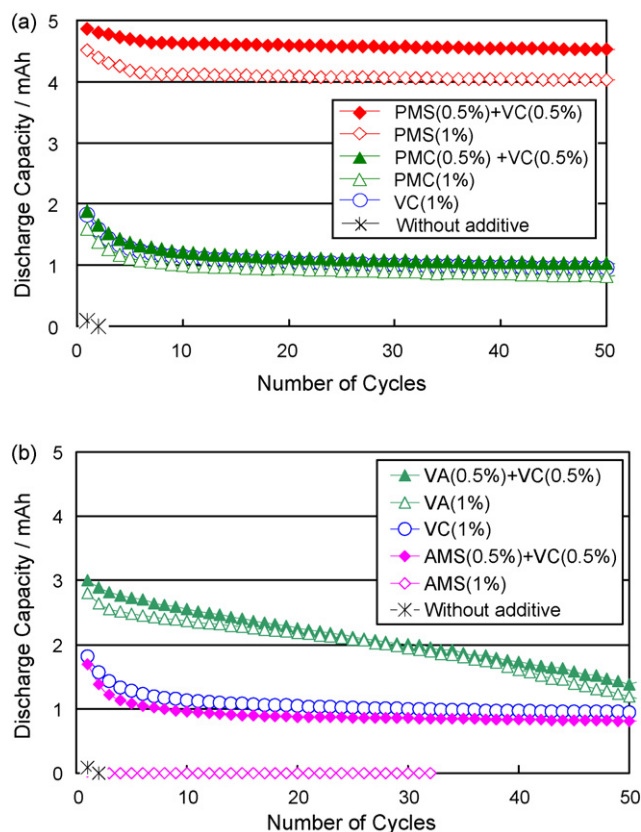


Fig. 1. Cycle performance of LiCoO₂/graphite coin cells in 1M-LiPF₆ [PC:MEC (3:7 by vol.)] between 4.2 and 3.0 V (0.3C) at 25 °C with (a) 1 wt.% of PMC, PMS, VC, combined use, and without additive, and (b) 1 wt.% of VA, AMS, VC, combined use and without additive.

3.3. Gas evolution

During the initial charging of the cell, gas evolution occurs by the decomposition of the solvent or the electrolyte additive

when they produce the SEI on the bare graphite negative electrode surface. Therefore, investigation of the initial gas evolution is an appropriate method to study the synergetic effect of suppressing the gas evolution by the combined use of the additives. We used the LiCoO₂-graphite 18650 cylindrical cell with a commonly used EC-based electrolyte containing PMS, PMC and/or VC. When the additives are singly used, the amount added to the electrolyte is 3 wt.% based on the total amount of the electrolyte. In the case of the combined use, 2 wt.% of the triple-bonded compounds and 1 wt.% of VC are used. The amount and the composition of the evolved gas after one charge–discharge cycle at 45 °C were investigated.

The results are summarized in Fig. 2. When the triple-bonded compounds are used with VC, the total amount of gas evolution is highly suppressed when compared to the single use of the additives, though the double-bonded compounds have no synergetic effect with VC. C₂H₄, CH₄ and CO are known to be produced by the reductive decomposition of the solvent like EC or MEC [33]. When VC is present, CO₂ is known to evolve by both the reductive and oxidative decomposition of VC [32,33]. Accordingly, we suggest that the combination of the triple-bonded compounds and VC stops the electrolyte decomposition on both the negative electrode and positive electrode.

Based on the results of the cycling test and the gas evolution, we have two questions: (1) Why does only the combination of PMS and VC improve the cycleability?, and (2) why does only the combination of the triple-bonded compounds and VC suppress the gas evolution? In order to clarify these questions, we conducted surface film analyses of the electrode from the viewpoint of the difference in the reduction potentials of the additives and the structural difference in the unsaturated moiety.

3.4. Electrochemical evaluation

We investigated the reduction potentials of the additives using a three-electrode cell containing the EC-based electrolyte. When the additives are singly used, the amount added to the electrolyte is 1 wt.% based on the total amount of the electrolyte. For the combined use, each amount of the additive is 0.5 wt.%. The reduction potential was defined by the first reductive curve of

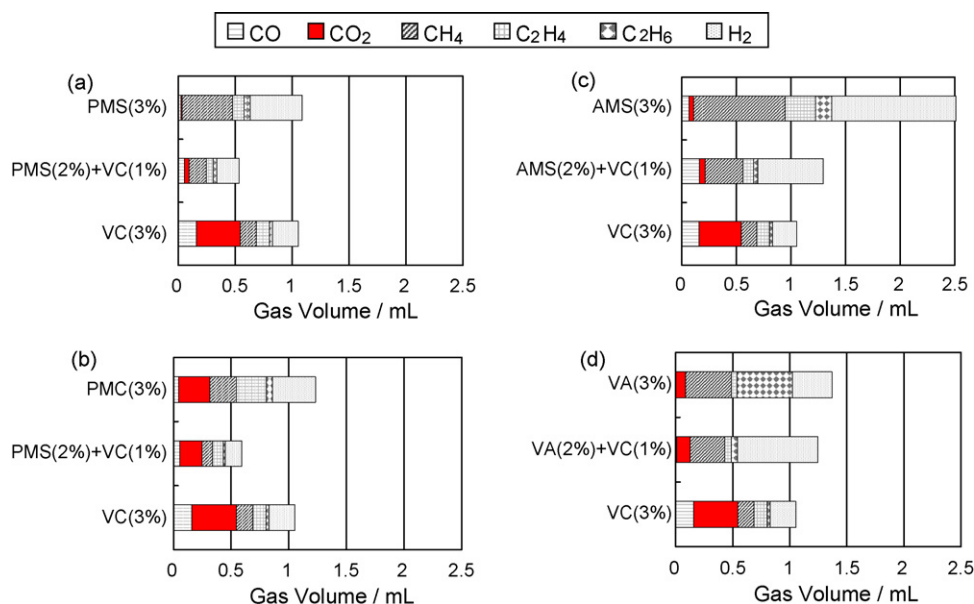
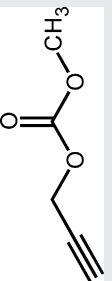
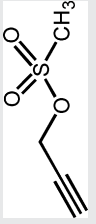
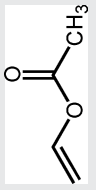
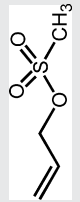
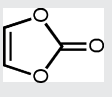
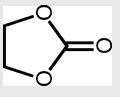


Fig. 2. Evolved gas analysis during the initial charging of the LiCoO₂/graphite 18650 cylindrical cells in 1M-LiPF₆ [EC:MEC (3:7 by vol.)] between 4.2 and 3.0 V (1C) at 45 °C. The results of (a) PMS and VC, (b) PMC and VC, (c) AMS and VC, and (d) VA and VC are summarized. In the case of AMS single use, 1.7 mL of H₂ gas evolved, which cannot be fully drawn at this frame.

Table 1
Structures of the studied additives and EC are listed, together with the reduction and oxidation potentials

Additives	Reduction pot. V vs. Li/Li ⁺	Oxidation pot. V vs. Li/Li ⁺
	0.83	6.20
	1.24	6.21
	0.88	5.20
	1.31	5.65
	0.84	5.03
	0.75	6.00

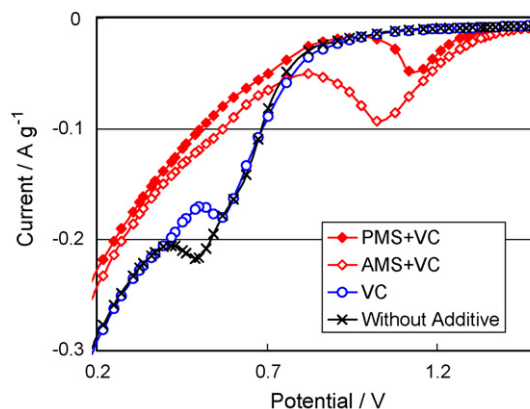


Fig. 3. The reduction potential measurement using CVs of a graphite electrode at 1 mV s^{-1} and 25°C in 1M-LiPF_6 [EC:MEC (3:7 by vol.)] with PMS (0.5%)+VC (0.5%), AMS (0.5%)+VC (0.5%), VC (1%), and without additive.

the cyclic voltammograms, in which the reductive current reached -0.03 A g^{-1} . These results are summarized in Table 1. The cyclic voltammograms of PMC, PMS and AMS are shown in a previous report. [40] PMS and AMS, the sulfonates, have higher reduction potentials than the PMC, VA and VC with the ester structure. This result indicates that the greater difference in the reduction potentials of the combined additives is favored for the battery performance when the triple-bonded compounds and VC are used together. However, the difference in the reduction potentials appears to have no effect on the battery performance for the combined use of the double-bonded compounds and VC. That is, it is clear that the difference in the reduction potentials is not the only factor that determines the synergetic effect by the additives. Fig. 3 shows the reduction curves of the CV for the electrolyte containing both PMS and VC together with the singly used PMS and VC, respectively. When PMS and VC are used together, the original reduction peak at 0.6 V , which is observed when VC is only used, disappeared. This result shows that the SEI produced by PMS, which has a reduction potential higher than VC, inhibits the electrochemical decomposition of VC.

After the CV measurement of the graphite electrode to determine the reduction potentials, we measured the AC impedance, which expresses the capability of the Li ion mobility over the electrode interface. Table 2 shows the results of the SEI impedance analysis. All the additives and all the combinations show lower impedances than the EC-based solvents without any additive. However, when the additives are co-used with VC, the impedance becomes slightly higher than when VC is only used. As the battery performance is influenced not only by the impedance of the initially produced SEI, but by the SEI characteristics, we examined how the SEI characteristics exert an influence on the battery performance.

Table 2
The impedance value and the SEI thickness derived from the additive decomposition

Additives	SEI thickness/(Å)	Impedance/(Ω)
PMC	–	43
PMS	–	28
VA	–	58
AMS	–	77
Without additive		31
–	VC	32
PMC	VC	18
PMS	VC	17
VA	VC	20
AMS	VC	36

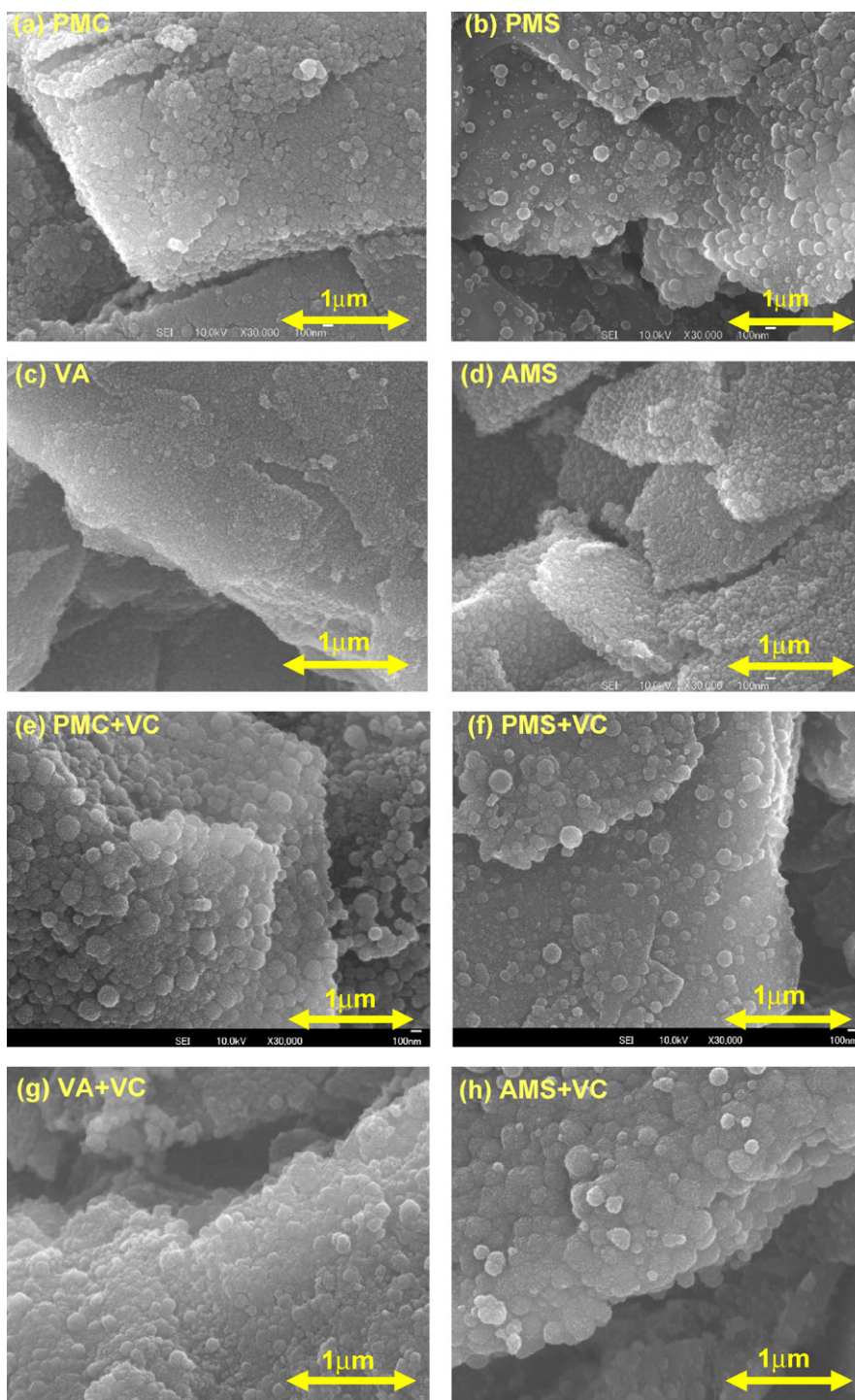


Fig. 4. SEM images of the graphite electrode after the 50-cycle charge–discharge tests in the PC-based electrolyte: (a) PMC (1%), (b) PMS (1%), (c) VA (1%), (d) AMS (1%), (e) PMC (0.5%) + VC (0.5%), (f) PMS (0.5%) + VC (0.5%), (g) VA (0.5%) + VC (0.5%), and (h) AMS (0.5%) + VC (0.5%).

3.5. SEI analysis

SEI analyses were performed on the negative electrode used for the 50-cycle charge–discharge tests of the coin cells with the PC-based electrolytes as described in Fig. 1. The analyses included (1) the surface observation by scanning electron microscopy (SEM), (2) the thickness measurement by auger electron spectroscopy (AES), and (3) the composition detection by X-ray photoelectron spectroscopy (XPS).

Fig. 4 shows a series of SEM images of the graphite electrode for the singly used and co-used additives. In every image of the triple-bonded compounds and the double-bonded compounds, there is no significant difference in the surface morphology of the uniformly covered film. As we cannot determine the difference in the surface morphology, we measured the depth profile of the SEI using AES for the graphite negative electrode in the coin-cell after 50 cycles. The SEI thickness, estimated from the results of the AES depth profiles, is summarized in Table 2. It is noted that our

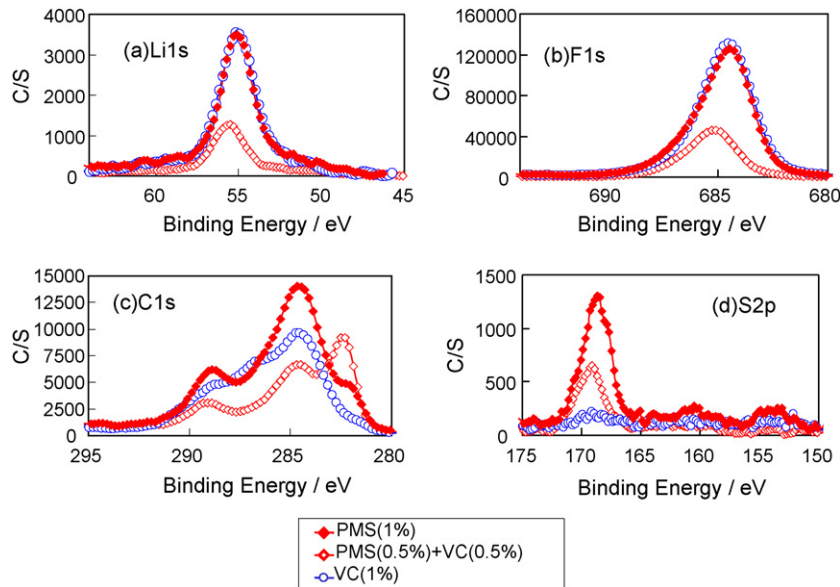


Fig. 5. The graphite surface film components analyzed using XPS after the 50-cycle charge–discharge tests in the PC-based electrolyte: (a) L 1s, (b) F 1s, (c) C 1s, and (d) S 2p.

measured SEI thickness may not indicate the absolute value. However, we think this procedure is appropriate since our purpose is to compare the relative SEI thicknesses among the various additives. It is important to note that each of the combined additive cases has a thinner SEI than that of the single use. Especially, the thickness of the SEI derived from the decomposed products of the triple-bonded compounds and VC is extremely thin. The reason for this should be considered to be due to the fact that the additive decomposition is protected by a co-polymer surface film resulting from the electrochemically decomposed products of the triple-bonded compounds or the double-bonded compounds and VC. As described before, the electrolyte with the triple-bonded compounds and VC shows a lower impedance increase than does the electrolyte with the double-bonded compounds and VC. Accordingly, when the triple-bonded compounds are used with VC, though the Li-ion permeability of SEI slightly decreases, a dense SEI is produced during the charge–discharge cycles, which improves the cycleability and suppresses the gas evolution.

The XPS data of L 1s, F 1s, C 1s, S 2p when PMS and VC are co-used are summarized in Fig. 5. In this measurement, charge-up shifts occurred in the different regions of the negative electrode, where the electric conductivities differed. Concerning the way of correct-

ing this shift, we assigned the peaks of C–C and C–H as 284.6 eV considering the validity of the bonding state of every element [40]. Judging from the L 1s and F 1s spectra, LiF is incorporated into the SEI. In the C 1s spectra, carbonates, such as ROCO_2Li , are present. These components of the SEI are very similar to the one derived from VC. This fact does not correspond with the result of inhibiting the VC decomposition during the first cycle of the CV measurement in Fig. 3. We think VC should be chemically decomposed, i.e., induced by the reductive decomposition of PMS, which has a higher reduction potential. When it comes to the C 1s spectra, the existence of a polymeric hydrocarbon species derived from the unsaturated moiety is suggested, because the C–C and C–H bond intensities remarkably increased by the combination of PMS and VC. In the S 2p spectra, sulfonates, such as RSO_3Li , are present in the SEI. A higher signal intensity than for the single use of PMS implies that a denser SEI is produced when VC is co-used.

3.6. Positive electrode surface film analysis

To understand the mechanism for the synergetic effect of suppressing the gas evolution, we further investigated the positive electrode surface, as CO_2 is produced by the decomposition of VC

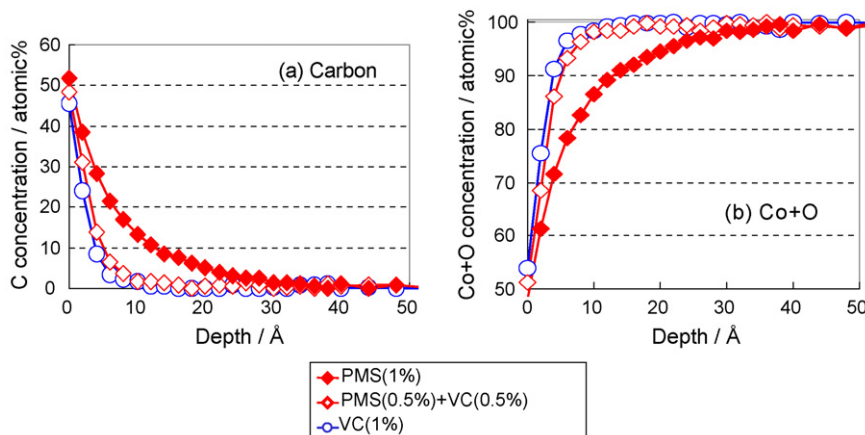


Fig. 6. The LiCoO_2 surface film thickness measured using AES after the 50-cycle charge–discharge tests in the PC-based electrolyte: (a) carbon atomic concentration, and (b) the sum of cobalt and oxygen atomic concentration.

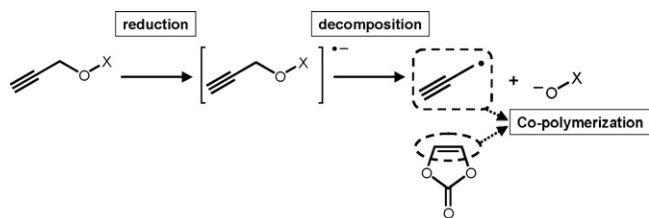


Fig. 7. The assumed mechanism for the additive decomposition of the surface film formation.

on the positive electrode [33]. We measured the depth profile of the positive electrode surface using AES from the coin cell containing LiCoO₂ after 50 cycles in the PC-based electrolyte with both the combination of PMS and VC, and the single use of PMS or VC. The AES depth profiles of carbon are summarized in Fig. 6a, and the cobalt and oxygen profiles are summarized in Fig. 6b. We found only that the combination of PMS and VC affords the 20 Å thin positive electrode surface film, mainly composed of the carbon species. On the other hand, in the case of the single use of PMS or VC, the positive electrode surface film is too thin to efficiently perform as a protective layer. We expect this positive electrode surface film results from the decomposed species of the unsaturated moiety, triggered by the reductive decomposition on the negative electrode as both PMS and VC are highly resistant to oxidative decomposition. We confirmed that the oxidation potentials of PMS and VC are as high as 6.2 and 5.0 V, respectively, showing much higher potentials than the battery operating potential [31,41]. Such a thin surface film would work as protective layer just like the SEI to prevent solvent decomposition and limit the gas evolution on the positive electrode.

Fig. 7 shows the assumed mechanism for the additive decomposition of the surface film formation on the both negative electrode and positive electrode. First, the triple-bonded compound reductively decomposes on the negative electrode to produce the propynyl radical. The electrochemically produced propynyl radical chemically reacts with the double-bonded moiety of VC to gradually form the co-polymer surface film both on the negative electrode and positive electrode.

4. Conclusions

The novel concept of a synergetic effect of negative electrode additives is shown to be useful for the improvement of cycleability and gas evolution. Very interestingly, the combined use of the triple-bonded compounds and the double-bonded compounds, especially propargyl methanesulfonate (PMS) and vinylene carbonate (VC), was proven to show a better battery performance than the case when the additives are singly used. The key point is not just the combined use of each additive effect, but the synergism of a new additives effect. According to the SEI analyses, the synergetic SEI is thinner than the ones derived from the single use by several tens of Å. Furthermore, the positive electrode is covered by a very thin protective 20 Å film, derived from the decomposition of the triple-bonded compounds and the double-bonded compounds. These surface films would work as protective layers and prevent further solvent decomposition, which improves the cycleability and suppresses the gas evolution.

We determined two key factors for the emergence of the synergetic effect: (1) the combination of the triple-bonded moiety and

the double-bonded moiety, and (2) the greater difference in the reduction potential of the two additives are essential. These newly obtained results for the synergetic effect of the negative electrode additives are expected to contribute to the efficient improvement of future LIBs, and this knowledge will allow the development of a unique procedure for modifying the surface film modification.

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