



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.

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