Vinylene carbonate (VC) is widely adopted as an electrolyte additive molecule in lithium–ion batteries.\textsuperscript{1–4} The function of VC was explained as the formation of a solid electrolyte interphase (SEI) via reductive decomposition of VC molecules at the surface of anode. The SEI is supposed to prevent the further degradation of electrolytes resulting in preferable cycle characteristic or successful battery lifetime.\textsuperscript{5,6} Figure 1 indicates the HOMO-LUMO levels of carbonate esters concerning electrolyte solvents. The LUMO level of VC is the lowest among those of the other carbonate esters such as ethylene carbonate (EC) and ethylmethyl carbonate (EMC) exhibiting that VC is reductively decomposed prior to others. So far poor attention experimental results. VC also has the highest HOMO level expecting those of the other carbonate esters such as ethylene carbonate (EC) and 1,4-dioxolane (DOL) could be attributed to the reductive decomposition of EC.\textsuperscript{11,12} The peak at ca. 2.95 V in these two figures for VC0 could be attributed to the reductive decomposition of EC and VC and these values were plotted toward lower potential is also indicative of the increase in the molar number of decomposed VC over EC and the VC decomposition took place prior to EC. This indicates that both EC and VC were reductively decomposed at the surface of anode presumably forming SEI.\textsuperscript{9} The peak shift toward lower potential is also indicative of the increase in the molar number of decomposed VC over EC and the VC decomposition took place prior to EC. This is also corresponding to the theoretical results discussed with theoretically calculated free energy changes in which the following mechanism is proposed that EC preliminarily suffered oxidatively decomposition at the cathode and then the electrolyte was centrifugally extracted from the cell for VC1. The electrolytes were also extracted from the cells for VC0-VC5 after charge-discharge tests. 1H-NMR spectroscopy and gas chromatography (GC) of extracted electrolytes were measured with a JEOL 500-MHz NMR spectrometer and a HITACHI G5000 GC to provide quantitative analyses of carbonate esters including VC. Theoretical calculations to obtain the orbital coefficients and most stable conformations have been done by density functional theory (DFT) with the B3LYP hybrid functional and the 6–31+G(d,p) basis set. These calculations were carried out with the Gaussian 09 suite of programs.\textsuperscript{10}

Results and Discussion

The charge-discharge curves at the first cycle for electrolyte V0-V5 were illustrated in Figure 2. The inset in the figure was an expanded drawing of the charge curves. All cells showed good reversibility with charge-discharge capacities at 1,600 and 1,400 mA respectively at the first cycle where the capacities were broadly independent from the initial VC concentrations. Table I summarizes charge-discharge capacities and Columbic efficiencies at the first cycle. Columbic efficiencies slightly decreased by increasing VC concentration in electrolytes. The reason of the decrease of the efficiencies will be discussed below.

The differential type of Figure 2 was shown in Figure 3 as the \(\frac{dQ}{dV}\) curves. The peak at ca. 2.95 V in these two figures for VC0 could be attributed to the reductive decomposition of EC.\textsuperscript{11,12} This peak was shifted lower potential as the VC concentration increased. This indicates that both EC and VC were reductively decomposed at the surface of anode presumably forming SEI.\textsuperscript{9} The peak shift toward lower potential is also indicative of the increase in the molar number of decomposed VC over EC and the VC decomposition took place prior to EC. This is also corresponding to the theoretical results in Figure 1, the LUMO level of VC being lower than that of EC. These experimental observations conflict with the previous report discussed with theoretically calculated free energy changes in which the following mechanism is proposed that EC preliminarily suffered the one-electron reduction providing the EC anion radical and then the anion radical reacted with VC to form SEI.\textsuperscript{7}

The values of integral of these peaks in Figure 3 are equivalent to the electric capacity (= electric power, mAh) consumed during the reductive decomposition of EC and VC and these values were plotted in Figure 4. We have repeated the measurements with independent three cells for V0-V5 to secure the reproducibility. An intriguing phenomenon is that the electric capacity is nearly constant at ca. 20 mAh irrespective of initial VC concentrations (Figure 4). These data exhibit that the total molar numbers of EC and VC decomposed at the graphite anode is constant during a single charging process so long as the one-electron reduction reaction mechanism were presupposed for both EC and VC.

The consumption via oxidative and reductive decompositions of vinylene carbonate (VC) molecules as an electrolyte additive at the anode and cathode in a 18650 lithium-ion battery was quantitatively analyzed with charge-discharge tests, NMR spectroscopy, and gas chromatography. It was unambiguously concluded that the molar number of VC reductively decomposed at the anode has the upper limit whereas that of VC oxidatively decomposed at the cathode depended highly upon the initial VC concentration. The excess amount of VC molecules causes the increase in oxidative decomposition at the cathode surface eventually reducing the Columbic efficiency at the first cycle.

The theoretical calculations to obtain the orbital coefficients and most stable conformations have been done by density functional theory (DFT) with the B3LYP hybrid functional and the 6–31+G(d,p) basis set. These calculations were carried out with the Gaussian 09 suite of programs.\textsuperscript{10}

\[\text{Charge-Discharge Cycle}\]

\[\text{Electrolyte Additive in an 18650 Lithium-Ion Battery at the First Charge-Discharge Cycle}\]

\[\text{Accurate Consumption Analysis of Vinylene Carbonate as an Electrolyte Additive in a 18650 Lithium-Ion Battery at the First Charge-Discharge Cycle}\]
LUMO levels
HOMO levels
(a) (b)

HOMO-LUMO levels (a) and chemical structures of carbonate esters (b), theoretical levels were obtained with DFT calculations (B3LYP/6-311+G(d,p)), DMC, DEC, and PC denote dimethyl, diethyl, and propylene carbonates.

Figure 2. Charge(left)-discharge(right) curves of 18650-type battery cells at the first cycle, the inset is an expanded drawing of the charge curves.

Table I. Charge-discharge capacities and Columbic efficiencies of 18650-type cells for respective electrolytes with voltage range of 3.0-4.2 V at the rate C/60.

| Electrolyte | Charge capacity (mAh) | Discharge capacity (mAh) | Columbic efficiency (%) |
|-------------|-----------------------|--------------------------|-------------------------|
| VC0         | 1603                  | 1418                     | 88.4                    |
| VC1         | 1575                  | 1404                     | 89.1                    |
| VC2         | 1576                  | 1400                     | 88.8                    |
| VC3         | 1571                  | 1391                     | 88.5                    |
| VC5         | 1556                  | 1381                     | 88.1                    |

The quantitative analyses of carbonate esters involving EC, EMC, and VC for VC1 were conducted with $^1$H-NMR spectroscopy. The NMR’s were measured for the extracted electrolytes from the cells before and after charge-discharge as well as after reductive decompositions of EC and VC at charging (Figure 5). The inset in the figure was an expanded drawing of the area including VC signals at 6.6 ppm.

Electric capacities (mAh)

VC concentrations in electrolytes (wt%)
The signals in the figure were connected with protons marked in red via dotted lines as signal assignments. The values of integral derived from EMC signals were adopted as standard for quantitative analyses since the EMC molecules were supposed to be hardly involved in the electrochemical reactions.

When comparing the two spectra of before charge-discharge and after reductive decompositions of EC and VC in Figure 5 (a) the VC concentration decreased to roughly half and thus the molar number decomposed could be calculated to be approximately 0.35 mmol. The calculations to obtain the molar numbers of VC are as follows; thus the molar number of VC in the 18650 battery cell for VC1 before first charge is equal to 0.7 mmol (6.1 g × 1.0 wt%/86.04) where the weight of electrolyte in the battery cell and molecular weight of VC are 6.1 g and 86.04 g/mol respectively. 1H-NMR spectra showed the VC concentration halved after reductive decompositions of EC and VC. Therefore the molar number of VC reductively decomposed is equal to 0.35 mmol (= 0.7 mmol/2). This number is equivalent to the electric capacity of 20 mAh for VC1 in Figure 4. When comparing the two spectra of after the reductive decomposition of EC and VC and after charge-discharge in Figure 5 (b) the VC concentration further decreased to ca. 0.07 wt%. Therefore ca. 43 wt% (0.30 mmol) of VC seems to be oxidatively decomposed at the cathode for VC1 right after the VC consumption at the anode.

The VC decrease via electrochemical decomposition was also confirmed by gas chromatography analyses and these quantitative analyses with NMR and GC is consistent, VC concentration after charge-discharge for VC1 being at ca. 0.08 wt% (Table II). Table II also indicated that the oxidative decomposition of VC during first discharge largely increased when the initial VC concentration increased while the reductive decomposition of VC at the anode is limited by a ceiling whereas that of VC oxidatively decomposed at the cathode depended highly upon the initial concentration of VC in a 18650 battery. The excess amount of VC molecules causes the increase in oxidative decomposition at the cathode surface eventually giving rise to the high interfacial resistance. The origin of an appropriate concentration of VC that is commonly referred as an electrolyte additive was derived to form characteristics of cathodic and anodic reactions above.

### Table II. VC concentrations and molar numbers before charge as well as VC concentrations and molar numbers after charge-discharge for respective electrolytes provided by gas chromatography analyses.

| Electrolyte | VC Concentration before charge (wt%) | VC Molar number before charge (mmol) | VC Concentration after charge-discharge (wt%) | VC Molar number after charge-discharge (mmol) |
|-------------|--------------------------------------|--------------------------------------|----------------------------------------------|----------------------------------------------|
| VC0         | 0.0                                  | -                                    | -                                            | -                                            |
| VC1         | 1.0                                  | 0.71                                 | 0.08                                         | 0.057                                        |
| VC2         | 2.0                                  | 1.42                                 | 0.34                                         | 0.24                                         |
| VC3         | 3.0                                  | 2.13                                 | 1.10                                         | 0.78                                         |
| VC5         | 5.0                                  | 3.55                                 | 2.48                                         | 1.76                                         |

**Conclusions**

We have found that the molar number of VC reductively decomposed at the anode is limited by a ceiling whereas that of VC oxidatively decomposed at the cathode depended highly upon the initial concentration of VC in a 18650 battery. The excess amount of VC molecules causes the increase in oxidative decomposition at the cathode surface eventually giving rise to the high interfacial resistance.

The origin of an appropriate concentration of VC that is commonly referred as an electrolyte additive was derived to form characteristics of cathodic and anodic reactions above.

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