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Short communication

Effects of vinylene carbonate on high temperature storage of high voltage Li-ion batteries

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ABSTRACT

The effects of vinylene carbonate (VC) on high temperature storage of high voltage Li-ion batteries are investigated. 1.3 M of $LiPF_6$ dissolved in ethylene carbonate (EC), ethylmethyl carbonate (EMC) and dimethyl carbonate (DMC) of 3:3:4 volume ratio is used as original electrolyte for 18650 cylindrical cells with $LiCoO_2$ cathode and graphite anode. VC is then added to electrolyte. At the initial stage of the high temperature storage, higher open-circuit voltage (OCV) is maintained when increasing the VC concentration. As the storage time increases, OCV of higher VC concentration drops gradually, and then the gas evolution takes place abruptly. Gas analysis shows methane (CH_4) decreases with increase of the VC concentration due to formation of stable solid electrolyte interface (SEI) layer on the graphite. Since the residual VC after formation of the SEI layer decomposes on the cathode surface, carbon dioxide (CO_2) dramatically increases on the cathode with the VC concentration, leaving poly(VC) film at the anode surface, as suggested by XPS test results.

1. Introduction

Rechargeable Li-ion batteries are presently one of the major power sources for portable electronic devices because of their high energy density. Most research performed to advance Li-ion batteries has concentrated on improving the aspects of battery performance such as cycling characteristics, rate characteristics, and high temperature storage.

High voltage charging system over 4.2 V is recently applied to Li-ion batteries for higher energy density. In this system, the electrolyte composition and additives used in lower voltage (like 4.2 V) charging system cannot be applied directly, because many side reactions will take place on the interface between electrodes and electrolyte over 4.2 V. These reactions lead to gas evolution and changes of the interface layer on electrodes, inducing Li-ion battery OCV drop subsequently [1]. Notably, these reactions may occur abruptly under high temperature.

Numerous studies have been done on developing new electrolytes for Li-ion batteries with high ionic conductivity and good chemical and electrochemical stabilities [2–6]. Inorganic compounds [7–11] and organic compounds such as unsaturated carbon bond-containing components [12–16], sulfur-containing components [17–20], halogen-containing components [21–25], and other components [26–28] have been proposed as electrolyte additives for Li-ion batteries. It is considered that these additives could improve the properties of the SEI layer formed on the graphite anode.

VC has also been employed as an electrolyte additive to improve battery performance [12]. The cycling performance and high-temperature storage are enhanced by adding it to the EC-based electrolyte. Thus VC has been recognized as an effective additive for the electrolyte when using the graphite anode.

In this work, the effects of VC concentration on high temperature storage of high voltage Li-ion batteries were investigated. The reaction between electrodes and electrolyte was examined by composition analysis of evolved gas, electrolyte and surface film with different VC concentrations during high temperature storage.

2. Experimental

The cylindrical cells of 18650 size composed of $LiCoO_2$ as a cathode and graphite as an anode were used with 1.3 M of $LiPF_6$ dissolved in 3:3:4 volume ratio of EC, EMC and DMC as electrolyte. VC was added to the electrolyte.

The cells charged to 4.35 V were stored in a chamber at 90 °C for 24 h. OCV was continuously monitored during the high temperature storage. An amount of evolved gas during the high temperature storage was measured using a graduated measuring vial. The gas

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was collected by the paraffin oil bath based method, and then a composition of gathered gas was analyzed with gas chromatography (GC). GC analysis was conducted on an Agilent Technologies 6890 GC with a packed Column and TCD detector. Helium was used as the carrier gas with a flow rate of 3.3 mL min^{-1}. Samples were ramped from 40 to 150 °C at 10 °C min^{-1}. To determine the source of evolved gas elements, after disjointing charged cells to cathode and anode, separately both cathode and anode added an electrolyte in 18650 can were stored in chamber at 90 °C for 24 h, and then the evolved gas on cathode and anode was analyzed respectively.

GC was also used to analyze electrolyte composition changes along with addition of VC. And X-ray photon spectroscopy (XPS) was employed to characterize the element chemical state changes caused by the reaction between electrodes and electrolyte with different VC concentrations during high temperature storage.

3. Results and discussion

Fig. 1 shows that the cycling performance of 18650 cylindrical cells with different VC concentrations. Adding small amount of VC dramatically improved the cycling performance, indicating that the VC derived SEI layer on the graphite anode was very stable in the high voltage charge system. Further increasing VC concentration over 3% did not bring significant improvement of cycling performance.

Fig. 2 shows that the OCV curves of 18650 cylindrical cells with different VC concentrations during high temperature storage. At the initial stage, high OCV was maintained with the addition of VC. The sufficiently formed SEI layer was from reduction of VC on graphite anode before that of EC, and exhibited excellent thermal stability [1]. While in VC free electrolyte, the non VC derived SEI layer is partially destroyed under high temperature. Thus formation of new SEI layers would consume Li ions, leading to decrease of OCV. As the storage time went, OCV of cells with higher VC concentration dropped gradually, and then the current interrupt device (CID) of 18650 cylindrical cells was triggered by the abrupt gas evolution. As the VC concentration increased, the amount of evolved gas during high temperature storage abruptly went up over VC 3%, as shown in Table 1.

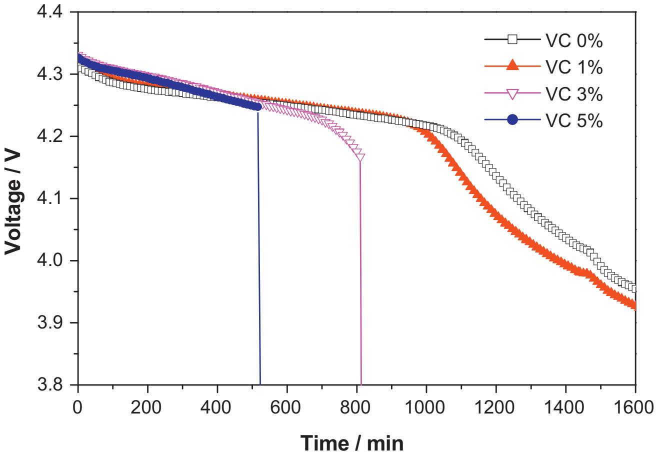

Fig. 2. OCV transition of 18650 cylindrical cells as the VC concentration during storage at 90 °C for 24 h.

Table 1
The amount of evolved gas during storage at 90 °C for 24 h as the VC concentration.

Concentration of VC	Average amount of evolved gas	Remark
VC 0%	2.3 cc	
VC 1%	2.5 cc	CID open of 1/2 cell
VC 3%	2.7 cc	CID open of 2/2 cells
VC 5%	3.3 cc	CID open of 2/2 cells

The composition of evolved gas was analyzed, as shown in Fig. 3. The volume percentage of hydrogen (H_2), carbon monoxide (CO), ethylene (C_2H_4), and ethane (C_2H_6) after being stored at 90 °C for 24 h almost remained the same for different VC concentration. However, those of CH_4 and CO_2 were dramatically changed when increasing VC concentration. To identify the source of evolved gas elements, gas from both cathode and anode was analyzed respectively, as given in Table 2. The evolution on anode could be related to the formation of SEI layer in the following equation:

$$2\mathrm{EC} + 2e^- + 2\mathrm{Li}^+ \rightarrow (\mathrm{CH_2OCO_2Li})_2 + \mathrm{C_2H_4} \tag{1}$$

$$\mathrm{EC} + 2e^- + 2\mathrm{Li}^+ \rightarrow (\mathrm{CH_2OLi})_2 + \mathrm{CO} \tag{2}$$

$$\mathrm{DMC} + e^- + \mathrm{Li}^+ \rightarrow \mathrm{CH_3OCO_2Li} + \mathrm{CH_3}' \tag{3}$$

$$\mathrm{DMC} + 2e^- + 2\mathrm{Li}^+ \rightarrow 2\mathrm{CH_3OLi} + \mathrm{CO} \tag{4}$$

$$\mathrm{CH_3}' + \mathrm{H}' \rightarrow \mathrm{CH_4} \tag{5}$$

CH_4 gas was only detected on the anode side. And no CH_4 could be found in the EC only electrolyte, indicating that CH_4 gas was mainly generated through the reduction of DMC on the surface of graphite anode, since. The explanation could be given in Eqs.

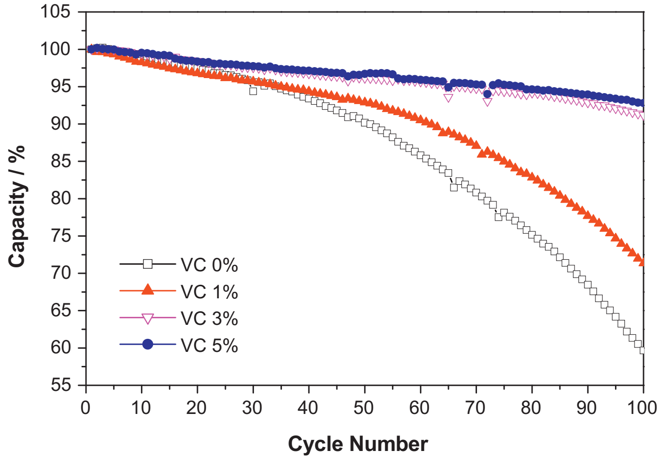

Fig. 1. Cycling performance of 18650 cylindrical cells as the VC concentration. The cells were charged to 4.35 V at 0.8 C-rate on constant current–voltage mode and discharged to 3.0 V at 1.0 C-rate on constant current mode.

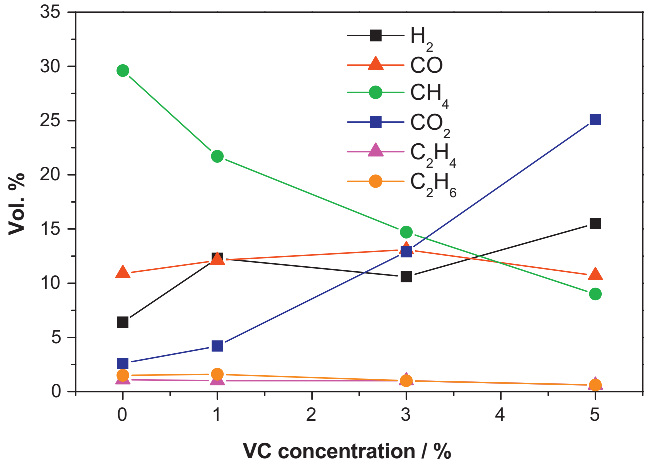

Fig. 3. Composition of evolved gas during storage at 90 °C for 24 h as the VC concentration.

Table 2
The evolved gas on both cathode and anode with electrolyte of VC 1% during storage at 90 °C for 24 h.

Gas elements	Vol. % of evolved gas on cathode	Vol. % of evolved gas on anode
H_2	–	–
CO	2.3	8.2
CH_4	–	6.4
CO_2	45.4	0.4
C_2H_4	13.2	0.8
C_2H_6	1	0.8

(3) and (4), where DMC produced a CH_3 radical, which reacted with the H radical from H_2O in the electrolyte and electrodes. As the VC concentration increased, the evolution of CH_4 gas was decreased continuously during high temperature storage, as shown in Fig. 3. This suggested that the VC suppressed the decomposition of DMC and thus the SEI formation. On the other hand, CO_2 gas was mainly evolved on cathode, although small amount of which was detected on the graphite anode. The amount of CO_2 gas was abruptly increased with increase in the VC concentration, as shown in Fig. 3. It was considered that the evolution of CO_2 gas was due to the decarboxylation of VC [1]. Then residual VC after formation of the SEI layer on the graphite anode would react on the surface of cathode, evolving CO_2 dramatically on the side of cathode in higher VC concentration.

Fig. 4 shows the results of electrolyte analysis after storage at 90 °C for 24 h with different VC concentrations. Its main composition (EC:EMC:DMC) was not changed remarkably after storage with different VC concentrations. However, a new solvent component diethyl carbonate (DEC) appeared, which was from the following reaction during high temperature storage:

$$2\text{EMC} \rightarrow \text{DMC} + \text{DEC} \quad (6)$$

The amount of DEC was greater when VC concentration was lower, indicating that the effect of VC suppressing the decomposition of EMC. At the same time, the residual VC could not be detected, and the remaining VC in electrolyte after storage, which was originally 5% in volume, was also very low. This suggested that the residual VC after formation of the SEI layer on the graphite anode reacted on the surface of cathode continuously, corresponding with the result of gas composition analysis after storage, as previously shown in Fig. 3.

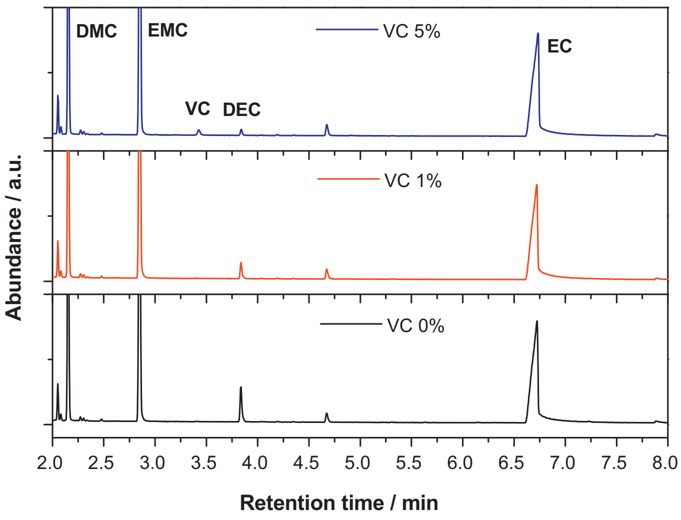

Fig. 4. Residual electrolyte analysis after storage at 90 °C for 24 h as the VC concentration.

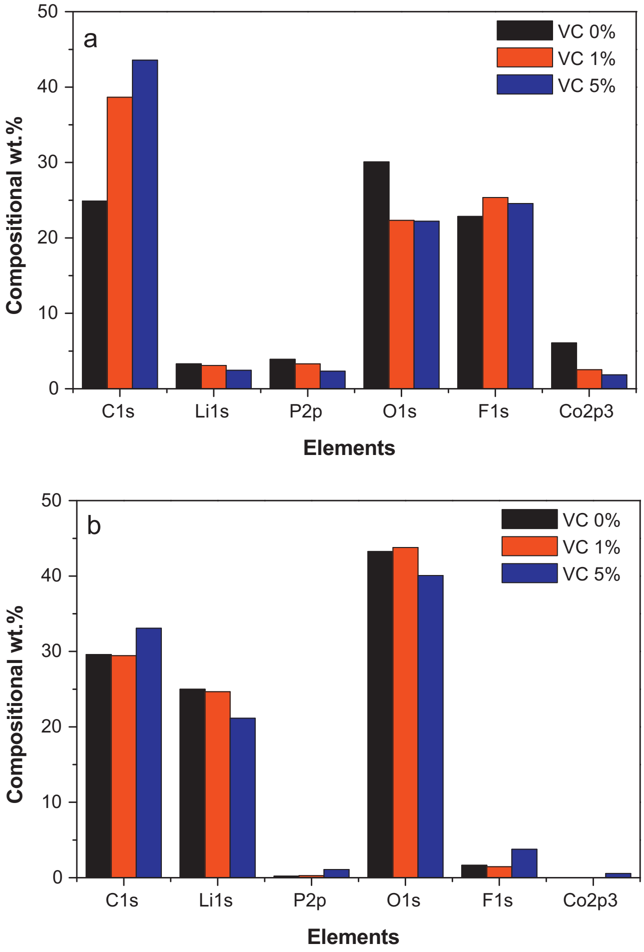

Fig. 5. Composition comparison on the surface of (a) cathode and (b) anode after storage at 90 °C for 24 h as the VC concentration by XPS analysis.

Fig. 5 shows composition comparison of the surface of cathode and anode by XPS analysis. At the cathode surface, the C 1s composition was significantly increased by addition of VC. On the other hand, composition of the anode surface was not changed greatly with different VC concentrations. This suggested that the amount of VC contributing to formation of the SEI layer on the graphite anode remained the same, regardless of total VC concentration, and then the residual VC after formation of the SEI layer reacted on the cathode surface continuously. This reaction resulted in the abrupt gas evolution on the cathode surface. It should be noted in the result of XPS composition that in Co 2p signal on the cathode surface decreased, while that on the anode surface increased with higher VC concentration. It is believed that the residual VC after formation of the SEI layer on the anode surface would react on the cathode surface and lead to the dissolution of metal elements on the cathode surface. These dissolved metal elements were then reduced on the anode surface. These reactions contributed to OCV drop during high temperature storage.

XPS spectra of the surface film formed on cathode and anode is shown in Fig. 6. Changes of the peak position and height on the C 1s and the O 1s spectra were observed after addition of VC, indicating dependence of the composition of SEI layer formed on the cathode and the anode on VC concentration. Considerable changes are shown in the C 1s and the O 1s spectra of the cathode surface. By adding VC, the peak intensity on the C 1s spectrum was increased and the peak on the O 1s spectrum was shifted to higher binding energy position. It was reported that the peak around 286 eV in the C 1s spectrum and around 534 eV in the O 1s spectrum were

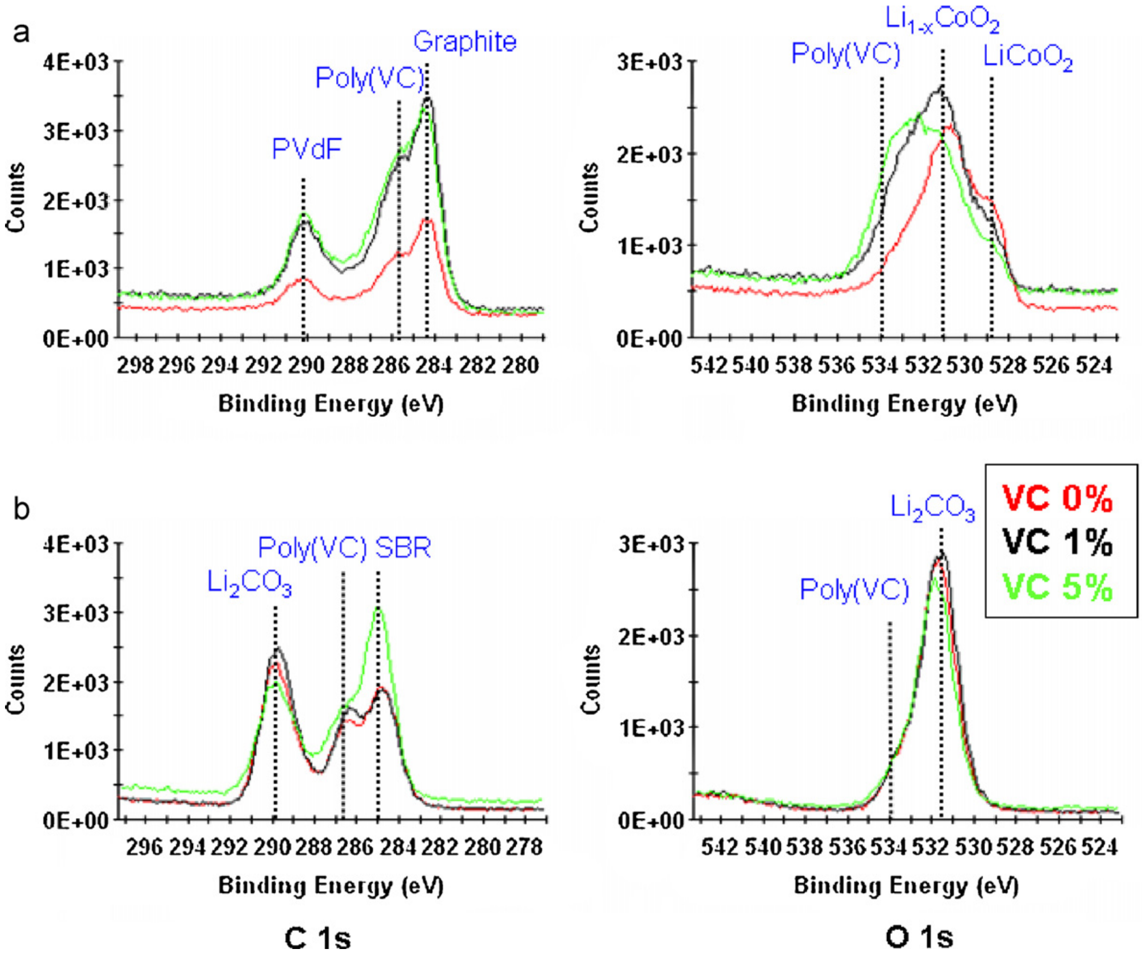

Fig. 6. C 1s and O 1s spectra of (a) cathode and (b) anode after storage at 90 °C for 24 h as the VC concentration by XPS analysis.

related to polymer species [29,30]. These polymer species were from the decomposition of VC. The formation of poly(VC) on the cathode surface was shown more clearly than on the anode surface by the decomposition of VC. Therefore, it was believed that the poly(VC) was formed on the cathode surface continuously by the residual VC after formation of the SEI layer on the anode. This result was in agreement with that of the gas and the electrolyte GC analysis.

4. Conclusions

The effects of VC on the high temperature storage of high voltage Li-ion batteries are investigated. At the initial stage of high temperature storage, higher OCV is maintained with higher VC concentration. As the storage time increases, OCV of higher VC concentration drops gradually, followed by abrupt gas evolution.

The gas analysis result shows CH_4 gas decreases when increasing VC concentration, due to formation of stable SEI layer on the graphite. Since the residual VC after formation of the SEI layer decomposes on the cathode surface, CO_2 gas dramatically increases on the cathode with higher VC concentration. These gas evolutions on the cathode are caused by formation of the surface film through decomposition of VC. The reactions also formed the poly(VC) film on the cathode surface, as suggested by XPS tests.

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