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Short communication

An approach of evaluating the effect of vinylene carbonate additive on graphite anode for lithium ion battery at elevated temperature

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ABSTRACT

An approach is proposed to evaluate the VC effect in a $LiFePO_4$/graphite cell at 60 °C through liquid chromatography mass spectrometry (LC-MS) together with direct analysis in real time mass spectrometry (DART-MS). The LC-MS result shows that VC can effectively suppress the formation of phosphate esters as well as carbonate oligomers during the electrochemical cycling. It is also known from DART-MS analysis that VC assists the formation of thermally resistant oligomeric phosphate ester layer on the graphite surface, storing more solvent EC inside the layer. On the other hand, no compounds are observed on the $LiFePO_4$ cathode surface. The formation of the denser oligomeric phosphate ester layer is found to be the reason for the improved cycle stability of the cell cycled at elevated temperature.

1. Introduction

Compared with the portable electronic devices, large-scale ones are relatively often used under a high-temperature environment, thus requiring more thermally stable lithium ion batteries (LIBs) for energy storage. Much efforts are put on the development of the thermally stable active materials, binders, substrates, separators and electrolytes. Among these battery components, electrolyte is generally the most thermally unstable component because most of the electrolytes are composed of $LiPF_6$ salt and organic solvents. Rapid degradation of electrolyte at elevated temperature directly leads to the capacity fade of LIBs during cycling. To improve the cell's thermal stability electrolyte additives are thus developed. Vinylene carbonate (VC) is a commonly used one and several previous researches have demonstrated that it can function for various cathode [1–6] and anode materials [4,7–13] with enhancing the cell's cycle stability.

In a previous research work, VC has been shown to have improved performance for the graphite anode [7]. The highly reactive VC tends to polymerization during cell cycling, favoring the formation of the passivating film on the anode surface, corresponding to the cell performance [10,11]. In addition, VC was experimentally proved to improve the Coulomb efficiency and reduce the charge/discharge endpoint slippage of a Li/Graphite cell at 50 and 60 °C rather than 30 and 40 °C [4]. Furthermore, combination of graphite with lithium iron phosphate ($LiFePO_4$) attracted much attention for LIBs used at elevated temperature because $LiFePO_4$ is well-known as a relatively thermal stable cathode material with low cost. Extensive works have focused on the improvement of the cycle stability of the $LiFePO_4$/graphite cell. Several methods including the modifications of the current collector [14], active material [15] and electrolyte [16] were found to be effective. The effect of VC additive has also been investigated for the $LiFePO_4$/graphite cell cycled at elevated temperature [17]. It was reported that the improved cell performance can be attributed to not only the reduced reaction of electrolyte on the $LiFePO_4$ surface but also the inhibition of solvent consumption from forming thicker solid electrolyte interface (SEI) film on the graphite surface as a result of VC additive. Another study exhibited that the polymerization function of VC additive can improve the properties of the passivating films formed on the electrode surface, thus enhancing the cycle stability [18]. The VC polymerization was found to occur on the anode side in the $LiFePO_4$/graphite cell; while on the other hand, no evidence of the polymerization was found on the cathode side. The polymerization mechanism induced by the VC additive is, so far, not well understood. A study detailing the polymerization layer on the electrodes is thus considered significant.

In this study, we aim to clarify the contribution of VC to the formation the polymerization layer on the electrodes of a $LiFePO_4$/graphite

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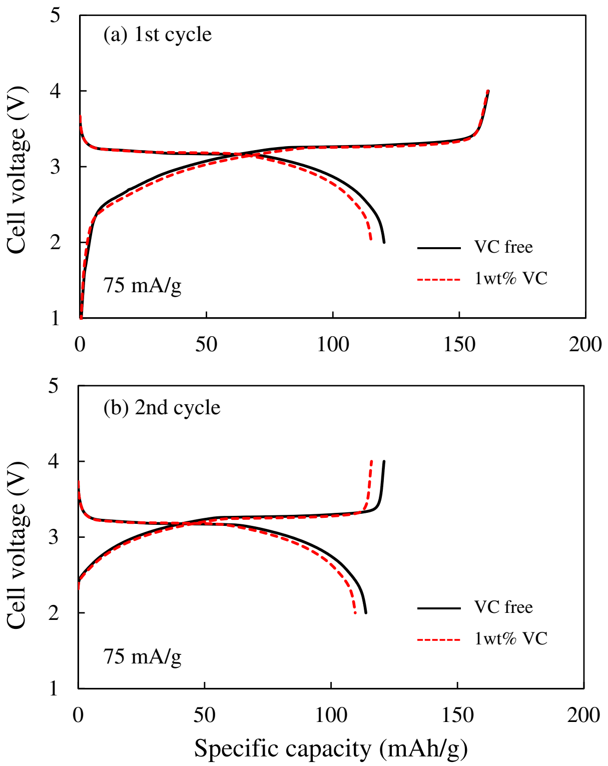

Fig. 1. Charge/discharge curves for $LiFePO_4$/graphite cells with/without VC additive.

cell at 60 °C. In addition to the electrolyte analysis using liquid chromatography mass spectrometry (LC-MS), we used direct analysis in real time mass spectrometry (DART-MS) to analyze the electrode surface for the cycled cells. The DART-MS is a relatively new MS method that can directly and quickly identify intact volatile and nonvolatile polar organic compounds in a variety of matrices without extra sampling procedures [19]. This investigation approach, which, to our best knowledge, has not been proposed.

2. Experimental

To prepare the cathode, $LiFePO_4$ (Sumitomo Osaka Cement Co., Ltd.) powders were mixed with conductive agents including 1.5 wt% vapor growth carbon fiber (VGCF), 1.5 wt% acetylene black (AB) and 3 wt% activated carbon fiber (ACF), together with a 5 wt% water-based acrylic binder. As for the anode, it was prepared by mixing 83.7 wt% graphite (Hitachi Chemical Co., Ltd) powders, 9.3 wt% soft carbon, 1 wt% vapor growth carbon fiber (VGCF), 2 wt% acetylene black (AB) and 4 wt% water-based acrylic binder. The active material loading for the cathode and anode is ca. 6 and 7 mg/cm^2, respectively. The prepared electrodes were assembled into a coin-type test cell (CR2032) with an electrolyte of 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) at the ratio of 1:1 (v/v) (Kishida Chemicals) with/without 1 wt% vinyl carbonate (VC). Also, a glass filter was used as the separator. The electrochemical tests were galvanostatically carried out at 60 °C using a charge/discharge machine (BLS series, Keisokuki Center Co., Ltd.). The current density for the test was controlled at 75 mA/g within a cutoff voltage range of 2.0–4.0 V.

For the analysis, the cycled cells were decomposed in a dry room with an ultra-low humidity environment, followed by collecting the electrolyte and electrodes. The collected electrolyte and electrodes were respectively analyzed by LC-MS (Nexera, Shimadzu Corp. and Esquire 3000 plus, Bruker) and DART-MS (DART-SVP, AMR Inc. and LCMS-8030, Shimadzu Corp.). The electrode surfaces were carefully contacted with the ion beam of the DART apparatus at an angle of approximately 45° without intercepting the beam. Various ion beam

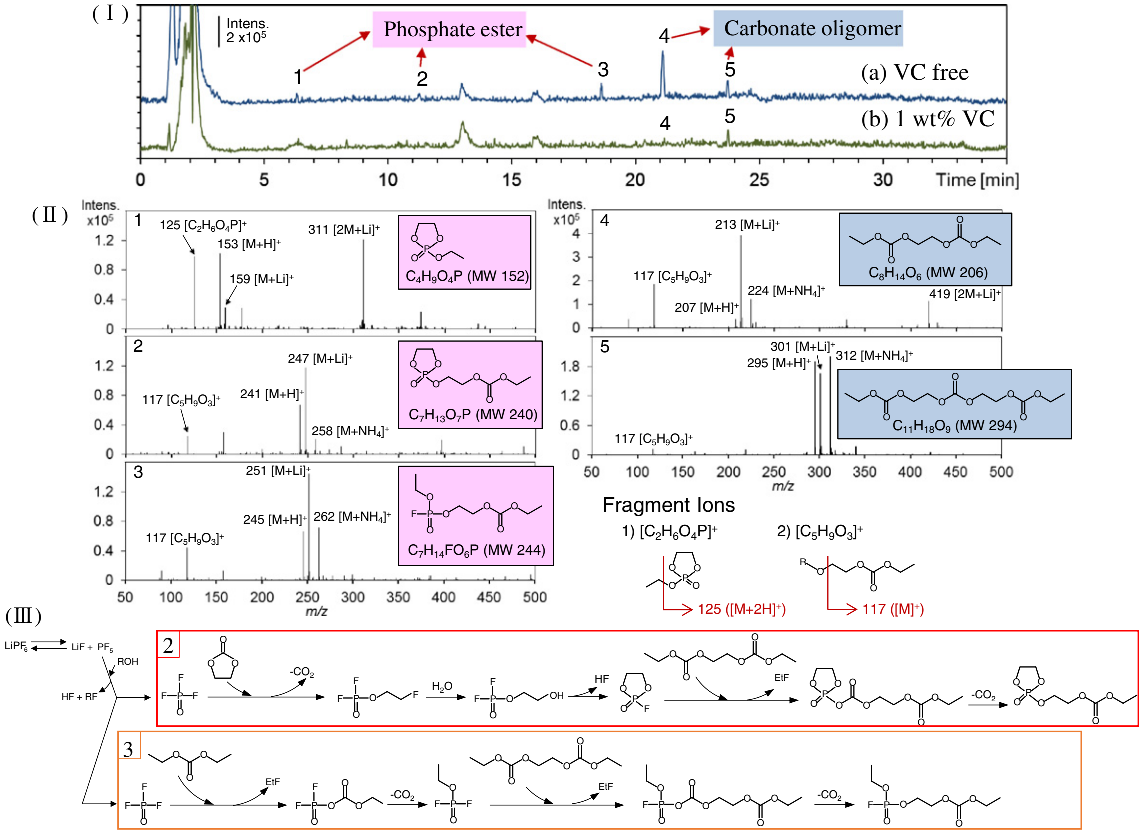

Fig. 2. LC-MS chromatograms (I) and MS spectra (II) of electrolytes after 2 cycle charge/discharge test, and the proposed formation mechanisms for the compounds 2 and 3 (III).