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Artificially-built solid electrolyte interphase via surface-bonded vinylene carbonate derivative on graphite by molecular layer deposition

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HIGHLIGHTS

- Ring-opened VC is chemically bonded on graphite surface through MLD method.
- The attached VC copies reduction behavior of VC as additives generating SEI via C=C.
- VC-attached graphite outperforms the pristine graphite in both half cell and full cell.
- VC molecules added in electrolyte generate acid when oxidized.
- The acid generated by VC oxidation accelerates transition metal dissolution from LNMO.

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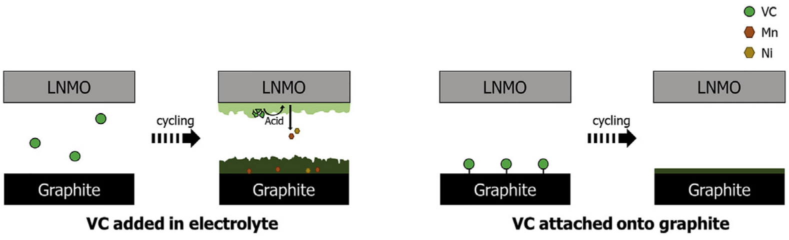
GRAPHICAL ABSTRACT



ABSTRACT

Vinylene carbonate (VC) is attached in a ring-opened form on a graphite surface by molecular layer deposition (MLD) method, and its role as a solid electrolyte interphase (SEI) former is studied. When VC is added into the electrolyte solution of a graphite/$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) full-cell, it is reductively decomposed to form an effective SEI on the graphite electrode. However, VC in the electrolyte solution has serious adverse effects due to its poor stability against electrochemical oxidation on the LNMO positive electrode. A excessive acid generation as a result of VC oxidation is observed, causing metal dissolution from the LNMO electrode. The dissolved metal ions are plated on the graphite electrode to destroy the SEI layer, eventually causing serious capacity fading and poor Coulombic efficiency. The VC derivative on the graphite surface also forms an effective SEI layer on the graphite negative electrode via reductive decomposition. The detrimental effects on the LNMO positive electrode, however, can be avoided because the bonded VC derivative on the graphite surface cannot move to the LNMO electrode. Consequently, the graphite/LNMO full-cell fabricated with the VC-attached graphite outperforms the cells without VC or with VC in the electrolyte, in terms of Coulombic efficiency and capacity retention.

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1. Introduction

Reductive electrolyte decomposition on graphite negative electrodes is unavoidable, because the working voltage of these electrodes is beyond the thermodynamic stability window of commonly used carbonate-based electrolytes. Fortunately, however, the decomposition products are deposited on the graphite surface and once the film grows to a certain thickness, additional electrolyte decomposition is greatly suppressed, as the electrode is now passivated by the surface films (i.e., protected from the reductive electrolyte decomposition). This beneficial feature of surface films is a result of their electronically insulating property. Namely, electron tunneling from graphite to the electrolyte solutions, which is required for the reductive electrolyte decomposition, becomes extremely sluggish if the insulating surface films are sufficiently thick. On the other hand, unlike the electrons, the surface films allow ion transport and prevent concentration polarization for the electrode reactions. Hence, these surface films are referred to as solid electrolyte interphase (SEI).

In order to deposit effective SEI layers with high passivating ability, some SEI formers can be added into electrolyte solutions to be reductively decomposed prior to the electrolytes. Vinylene carbonate (VC) is the most widely used SEI former for negative electrodes such as graphite and Si [1–6]. The unique feature of VC as SEI former is its polymerization assisted by carbon-carbon double bond. The SEI layer generated after VC decomposition contains dense organic layers that include poly (vinylene carbonate), which exhibit excellent passivating ability [2,7,8].

VC is also an effective film former for some 3–4 V positive electrodes (e.g. $LiCoO_2$, $LiFePO_4$, and $LiMn_2O_4$) [9–11]. The effectiveness of VC as a film former can be demonstrated in a graphite/$LiMn_2O_4$ full-cell. In this cell, Mn dissolution from the manganese spinel positive electrode ($LiMn_2O_4$) is appreciable. The critical effects of Mn dissolution are not on the positive electrode. Instead, the dissolved Mn^{2+} ions are plated on the graphite electrode to reduce the passivating ability of the SEI layers thereof. Electrolyte decomposes on the newly plated metallic Mn surface by taking Li^+ ions and electrons from the positive electrode [12–15]. The net result is the loss of cell capacity. The addition of VC in the electrolyte solution can suppress the Mn deposition, due to the high passivating ability of VC-derived surface films on graphite negative electrode, so that the series of undesired events can be avoided from the beginning [16].

Recently, the Ni-doped manganese spinel ($LiNi_{0.5}Mn_{1.5}O_4$, LNMO) has been developed as a 5 V positive electrode. The merit of graphite/LNMO full-cell is its higher energy density than that fabricated with 4 V positive electrodes (e.g. $LiCoO_2$ and $LiMn_2O_4$). For optimal performance, both electrodes in graphite/LNMO full-cells should be passivated by effective surface films. However, while VC is still effective for the graphite negative electrode, it is known to negatively impact the LNMO positive electrode. Namely, VC is not stable against electrochemical oxidation under highly oxidizing condition of LNMO electrodes (4.7–4.8 V vs. Li/Li^+). Serious side effects, such as gas evolution, organic by-product generation, and self-discharge are reported [17–19]. In short, the use of VC is necessary for graphite negative electrodes, while it should be avoided for LNMO positive electrodes. Therefore, the common simple practice to add SEI formers into electrolyte solutions cannot be applied for VC in graphite/LNMO full-cells. Namely, although VC in the electrolyte solution can produce a stable SEI layer on the graphite electrode, it has critically harmful effects on the LNMO electrode.

This work was motivated by the hypothesis that, if VC is fixed on the graphite surface by chemical bonding, its crossover to the LNMO electrode can be avoided. In that case, the undesirable oxidative decomposition of VC on the LNMO electrode is prevented, while an effective SEI layer can still be obtained on the graphite electrode. As a way to attach VC on the graphite surface, molecular layer deposition (MLD) is performed in this work, which is a vapor-phase deposition method and known to give uniform coating [20]. The following objectives have been identified in this work: (a) whether VC can be attached on graphite surface by MLD technique, (b) whether the VC derivative on the graphite still serves as an SEI former, just like VC molecules in electrolyte solutions, (c) whether the surface-attached VC migrate to produce adverse effects on the LNMO positive electrode, and (d) how the VC in the electrolyte solution deteriorates the graphite/LNMO full-cells.

2. Experimental

2.1. MLD of APS and VC on graphite surface

The surface modification was performed on natural graphite (DAG87, Sodiff Co., Ltd.) according to the procedure shown in Scheme 1. Before the MLD, the graphite surface was enriched by hydroxyl groups simply by exposing it to hydrogen peroxide at 60°C for 12 h. After washing with distilled water and vacuum drying, the graphite powder was placed inside a home-made chamber and contacted (3-aminopropyl)triethoxysilane (APS, Sigma-Aldrich) at 100°C for 5 h, followed by washing with toluene and vacuum drying at 80°C. The MLD of VC (Soulbrain) was performed at 100°C for 12 h, by contacting VC to the APS-treated graphite sample. Finally, the surface-modified graphite powder was washed with toluene and vacuum dried at 80°C.

2.2. Surface characterizations

The surface-modified graphite powder was analyzed with X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The surface analysis of LNMO electrodes was also performed using XPS. For this, the graphite/LNMO full-cells were cycled 5 times and then dismantled in an argon-filled dry box. The LNMO electrodes were collected and washed with ethyl methyl carbonate (EMC). A hermetic vessel was used to transfer the samples from the dry box to the instrument chamber to prevent any exposure to air. The XPS data were collected in an ultra-high vacuum multipurpose surface analysis system (Sigma probe, Thermo, UK) that operates at a base pressure of $<10^{-10}$ mbar. The photoelectrons were excited by Al Kα (1486.6 eV) radiation at a constant power of 150 W (15 kV and 10 mA), and the X-ray spot size was 400 μm^2. During data acquisition, a constant-analyzer-energy mode was used at a pass energy of 30 eV and a step of 0.1 eV. TEM measurements were performed using a JEM-2100F (JEOL Ltd, Japan) system operated at 120 kV. The bright-field scanning TEM (BF-STEM) and elemental mapping with energy dispersive X-ray spectroscopy (EDS) were performed with the samples prepared by dropping the graphite powder onto a lacey carbon-coated Cu grid and drying overnight under vacuum.

2.3. Electrochemical characterizations

The graphite composite electrodes were fabricated by mixing the graphite powder, Super P (as a conductive carbon), and poly (vinylidenefluoride) (PVdF, Kureha, KF-1300) (90:5:5 in wt. ratio). The mixture was dispersed in *N*-methyl pyrrolidone (NMP), and the resulting slurry was coated on copper foil, and dried at 120°C for 12 h under vacuum. The standard electrolyte was 1.0 *M* $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and EMC (3:7 in vol. ratio). Three Li/graphite half-cells were fabricated with the graphite composite electrode, PP-PE-PP (PE = polyethylene,