



Understanding the effects of a multi-functionalized additive on the cathode–electrolyte interfacial stability of Ni-rich materials



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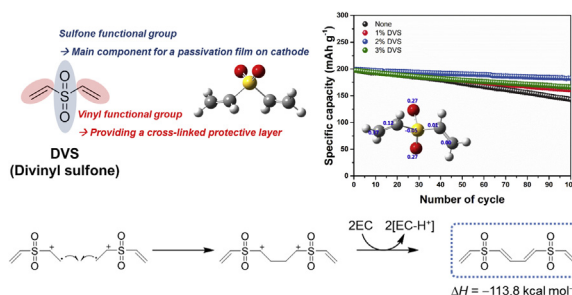
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HIGHLIGHTS

- We suggest an additive composed of sulfone and vinyl groups, divinyl sulfone (DVS).
- DVS affords excellent cycle performance even at elevated temperature.
- DVS enhances the cathode–electrolyte interfacial stability for Ni-rich cathode.
- Sulfone groups are main components of passivation film on the cathode surface.
- Vinyl groups form a cross-linked protection layer on the cathode surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Nickel-rich lithium nickel cobalt manganese oxides have received considerable attention as a promising cathode material, however, they have suffered from poor interfacial stability, especially at high temperature. Here, we suggest a bi-functionalized divinyl sulfone that enhances the applicability of a nickel-rich cathode via stabilization of the electrolyte–electrode interface. The divinyl sulfone forms a protective layer on the cathode surface by electrochemical oxidation reactions and this greatly decreases the internal pressure of the cell via stabilization of the Ni-rich cathode–electrolyte interface. The cell controlled with divinyl sulfone shows remarkable cycling performance with 91.9% capacity retention at elevated temperature even after 100 cycles. Additional electrode analyses and first-principles calculations provide critical spectroscopic evidences to demonstrate the combined effects of the sulfone and vinyl functional groups. Once the divinyl sulfone is electrochemically oxidized, the vinyl functional groups readily participate in further stabilizing sulfone-based solid electrolyte interphase intermediates and afford a durable protective layer on the nickel-rich electrode surface.

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1. Introduction

Since lithium-ion batteries (LIBs) were commercialized, they have been widely used in portable electronic devices such as cell-phones and notebooks because of their excellent cycle performance and moderate rate capability [1–4]. Nevertheless, further opportunities still remain to expand their applications. For example, a large increase in the energy density of current LIBs is required to meet the increasing demands of large-scale devices including hybrid electric vehicles (HEVs), electric vehicles (EVs), and energy storage systems (ESSs) [5–7]. In this respect, alternative cathode materials with higher specific capacities have been extensively investigated. One attractive positive electrode candidate is the layered lithium nickel-cobalt-manganese oxide ($\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$, NCM), which has unique electrochemical characteristics. The first NCM developed was $\text{Li}[\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}]\text{O}_2$ (NCM333), which has equivalent transition metal content. The most significant short-coming of NCM333 is that its specific capacity (155 mAh g^{-1}) is not sufficient for dramatically enhancing the energy density of LIBs. The specific capacity of NCM333 is similar to that of lithium cobalt oxide (LiCoO_2), currently the most popular cathode material in the battery community [8–12]. To overcome the problem of low capacity, layered oxide composites with higher Ni content ($x \geq 60\%$) such as $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$ (NCM622) and $\text{Li}[\text{Ni}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}]\text{O}_2$ (NCM721) have been widely investigated, because the specific capacity of NCM is mainly determined by the Ni content and thus NCM cathode with higher Ni-content can enhance the overall energy density in LIBs [13–23].

Interestingly, the high-Ni NCM cathode shows quite different electrochemical aspects depending on the cycling temperature. There is severe capacity fading at the elevated temperature even though the Ni-rich NCM still exhibit a moderate room temperature performance [22,24–28]. This indicates that ensuring a certain level of high temperature performance is significant as it allows a high-Ni NCM cathode to be attractive. The poor performance at an elevated temperature of a high-Ni NCM cathode material can be attributed to the poor interfacial stability between the cathode and the electrolyte: continuous electrolyte decomposition on the cathode surface occurs and the decomposed adducts accumulate on the electrode surface together with gas evolution, which rapidly deteriorates the overall electrochemical performance of cells due to increasing internal resistance and pressure [14,25,29–31]. In addition, irreversible metal dissolution leads to not only electrochemical fading of the NCM cathode through loss of active metal species but also drastic capacity fading of the anode. In particular, residual metal species in the electrolyte are easily reduced on the anode surface and this destroys the solid electrolyte interphase (SEI) layer that originally developed on the anode [32–36]. Therefore, a fundamental approach to stabilize the interfacial chemistry of the cathode is mandatory to achieve high performance of LIBs employing high-Ni-content NCM as a cathode.

Herein, we focus on stabilizing the interfacial stability of a Ni-rich cathode via incorporation of multi-functional additives in the electrolyte. In detail, we first pay attention to the sulfone functional group ($-\text{SO}_2-$) as a main chemical component on the additive structure owing to its desirable electrochemical aspect on the surface chemistry. It has been recognized that the sulfone functional group affords a reliable protection layer on the electrode surface, which greatly reduces electrolyte decomposition at electrolyte/electrode interfaces even at a high potential [37–43]. We also notice intrinsic chemical reactivity of the vinyl ($-\text{C}=\text{C}-$) functional group to maximize the effectiveness of the additive. Note that vinyl-based organic compounds are a widely used crosslinking agent in polymer science because the vinyl functional group readily participates in the formation of the three-dimensional chemical

network via a cascade-type polymerization reaction, allowing better mechanical properties [44–48]. Therefore, we chose divinyl sulfone (DVS) as an additive, which is functionalized with the sulfone ($-\text{SO}_2-$) and vinyl ($-\text{C}=\text{C}-$) chemical groups (see Fig. 1). We find that DVS greatly improves the interfacial stability, effectively mitigates the main solvent decomposition, and remarkably reduces the dissolution of the transition metal components from the Ni-rich electrode, according to our systematic analyses. Note that, to the best of our knowledge, this is the first attempt to demonstrate the direct effects of additives on the cathode–electrolyte interfacial stability, especially for Ni-rich NCM, on the basis of fundamental understanding attained by combining experimental methods and theoretical calculations. We believe understanding the effects of individual functional group on electrochemical behaviors will provide valuable insight into control of the surface chemistry on the cathode, which is responsible for determining the cycle performance.

2. Experimental details

2.1. In situ measurements of the internal pressure

To simulate the effects of the additives on the internal pressure of the cell at elevated temperature, each cathode charged to 4.3 V vs. Li/Li^+ (100% state of charge) was placed in an in situ pressure monitoring instrument (homemade, with a GE pressure/temperature sensor) with a fresh electrolyte (10 μl). While they were heated to 100 °C for 24 h, the internal pressure of the cells was recorded as a function of time in order to monitor the cathode deterioration.

2.2. Evaluation of the electrochemical performances

To determine the anodic behavior depending on the additive, linear sweep voltammetry (LSV) of the electrolyte was performed with an electrochemical workstation (Biologic, SP-300) at a scan rate of 1 mV s^{-1} in a range of 3.0–5.0 V vs. Li/Li^+ . A glassy carbon electrode ($7.07 \times 10^{-2} \text{ cm}^2$) was used as the working electrode, and lithium foil was used for the counter and reference electrodes. For the CV test, a three-electrode cell was fabricated by carbon-coated aluminum ($7.07 \times 10^{-2} \text{ cm}^2$) as the working electrode, and lithium foil as the counter and reference electrodes. The CV test was performed with an electrochemical workstation (Biologic, SP-300) at a scan rate of 0.5 mV s^{-1} in a range of 3.0–4.3 V vs. Li/Li^+ for three cycles. Further monitoring of the electrochemical behavior of the DVS on a NCM721 electrode was performed using the potentiostatic intermittent titration technique (PITT) with an electrochemical workstation (SERIES4000, MACCOR). Three-electrode beaker cells assembled with the NCM721 electrode as a working electrode and lithium foil as the counter and reference electrodes cells were charged polarized at 3.5 V vs. Li/Li^+ until a low steady-state current was attained. The potential was increased to 4.3 V vs. Li/Li^+ by a potential step of 10 mV.

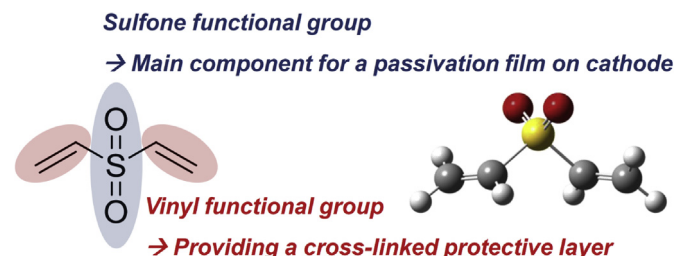


Fig. 1. 2D and 3D molecular structures of DVS.

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