



Triphenyl borate as a bi-functional additive to improve surface stability of Ni-rich cathode material



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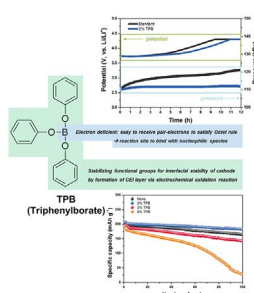
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HIGHLIGHTS

- Residual lithium species remaining on NCM cathode is removed by TPB additive.
- TPB additive reduces internal pressures of NCM electrode.
- Electrochemical reaction of TPB affords borate-based CEI layer on NCM electrode.
- CEI layer allows improved surface stability of NCM cathode.
- Borate-based CEI layer exhibits improved electrochemical performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Nickel-rich cathode material has received marked attention as an advanced cathode material, however, its inferior surface property limits the achievement of high performance in lithium-ion batteries. We propose the use of a bi-functional additive of triphenyl borate (TPB) for improvement of the safety and electrochemical performance of Ni-rich cathode materials. First, TPB removes residual lithium species from the Ni-rich cathode surface via chemical binding with anion part of residual lithium species, and effectively reduces swelling behavior of the cell. Second, TPB creates effective cathode–electrolyte interphase (CEI) layers on the electrode surface by an electrochemical reaction, and greatly enhances the surface stability of the nickel-rich cathode. This work demonstrate that a cell cycled with the TPB additive exhibits a remarkable retention of 88.6% at 60 °C after 100 cycles for an NCM721 cathode material. We suggest a working mechanism for TPB based on systematic analyses, including in-situ and ex-situ experiments.

1. Introduction

Electric vehicles (EVs) have received substantial attention as one form of eco-friendly alternative transportation because of the evolution of the environmental crisis as a global issue. However, the insufficient driving range of EVs is considered a key hurdle that currently limits the

widespread use of EVs. The mileages of EVs are highly associated with the energy density of the cell, so much effort is now directed at the development of advanced electrode materials that can provide high specific capacity with high voltage for lithium-ion batteries (LIBs) [1–3]. Among the many advanced cathode materials, one of the most attractive is layered nickel/cobalt/manganese oxide ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$,

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NCM) because of its high specific capacity when compared with conventional lithium cobalt oxides (LiCoO_2) [4–6]. Notably, the specific capacity of NCM can be improved by increasing the Ni composition in the layered structure [7–9]: a Ni-rich NCM cathode material with 60% Ni can provide more than 170 mA h g^{-1} of specific capacity, whereas a conventional LCO shows almost 150 mA h g^{-1} of specific capacity at the 4.3 V cutoff condition.

Despite its advantage in energy density, Ni-rich NCM cathode material suffers from poor surface stability, which gives rise to continuous fading of the cycling performance. Electrolyte decomposition readily occurs at the Ni-rich surface because unstable Ni^{4+} species tend to revert to more stable Ni^{3+} , triggered by irreversible electrolyte oxidation [10]. This results in the continuous accumulation of electrochemically decomposed adducts on the Ni-rich cathode surface, thereby increasing the resistance of the cell and causing the fading of cycling performance. In addition, many residual lithium species (e.g., lithium hydroxide and lithium carbonate) remain on the Ni-rich cathode surface, having originated from the lithium precursor used in the calcination stage for the synthesis of the Ni-rich NCM cathode material. The problem is that these residual lithium species can be decomposed by the electrochemical reaction in the cell above 4.0 V (vs. Li/Li^+), and this then drives a drastic swelling of the cell by the formation of gaseous adducts, such as oxygen, hydrogen, and carbon dioxide [11,12]. Because these intrinsic surface properties of Ni-rich NCM cathode material give rise to poor electrochemical and safety performances of LIBs, these issues inevitably must be overcome to achieve high performance of LIBs that employ Ni-rich cathode material.

In this work, we propose the use of a functionalized additive, triphenyl borate (TPB), which improves the inferior surface properties of Ni-rich cathode materials (Fig. 1). First, we design a functional additive by focusing on the intrinsic chemistry of the boron (B) element. Note that B has a few valence electrons that do not satisfy the octet rule. This exception to the octet rule allows the neutral B to become more electron deficient: the B readily receives two additional electrons from the electron-rich molecule to fill empty valence 2p orbitals [13–15]. The use of TPB is anticipated to be effective for reducing the residual lithium species in the cell, because the electron-deficient B can bind with hydroxyl (OH^-) and carbonate (CO_3^{2-}) anions, which are counterions of the residual lithium species. In other words, the use of TPB would help to improve the safety performance of Ni-rich NCM cathodes by decreasing the internal pressure in the cell by scavenging of residual lithium species.

Second, additives modified by a borate functional group, $\text{B}(\text{OR})_3$, can improve the cycle life of the cell, because the electrochemical reaction of $\text{B}(\text{OR})_3$ effectively suppresses electrolyte decomposition, as it creates cathode–electrolyte interphase (CEI) layers on the electrode

surface [16–21]. This implies that the proposed TPB, $\text{B}(\text{OPh})_3$, additive would enhance the surface stability of a Ni-rich NCM cathode. We demonstrate the effect of TPB on the safety and electrochemical performance of Ni-rich NCM cathode material and we verify the underlying role of task-specific additive, trivalent B combined with alkoxy substituents, in terms of chemical and electrochemical reactivity using several in-situ and ex-situ experiments.

Lastly, one of the authors (Y.K.H.) and co-workers [22] suggested that TPB is a very promising molecule as powerful CEI-forming additive from their first-principles calculations of oxidation potentials, reduction potentials, F^- binding affinities, and steric hindrance around the boron center for various borate candidate molecules.

2. Experimental

The chemical reactivity of TPB and residual lithium species was estimated by adding 1.0 mmol of LiOH (Aldrich) and Li_2CO_3 (Aldrich) to a dimethyl carbonate (DMC) solution (10 mL) containing with 10.0 mmol dissolved TPB (Aldrich). The mixture was then vigorously stirred for 24 h and filtered to remove insoluble LiOH and Li_2CO_3 . The resulting filtrate was analyzed by nuclear magnetic resonance spectroscopy (NMR, ASCEND 400, Bruker) to confirm the change in the chemical environment of TPB. The real effect of TPB on scavenging residual lithium species was probed by immersing $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ (Ecopro, NCM721) in TPB solution for 24 h and analyzing the residual lithium species of the treated NCM721 on a potentiometric titrator (Metrohm 848 Titrino Plus). For comparison, the same treatment was performed for NCM721 with DMC only.

Chemical reaction enthalpy values were evaluated by first-principles calculations. The ground-state structures were fully optimized using the density functional theory (DFT) with the B3PW91 functional and 6-311G(d,p) basis sets. Vibrational frequency analysis was performed to obtain thermodynamic properties. The relative enthalpy energy was calculated at 298.15 K and 1 atm. We used the conductor-like polarizable continuum model [23], which locates the solute in a molecular-shaped cavity embedded in a continuum dielectric medium. A dielectric constant was adopted as $\epsilon = 3.107$ of DMC. All the DFT calculations were performed using the Gaussian09 program package [24].

The in-situ pressure behavior of the cell during the charging process was observed by preparing the NCM721 electrode as follows: A mixture of NCM721, poly(vinylidene fluoride) (PVdF) (KF1100, Kureha), and carbon black (Super P) was dispersed in *N*-methyl-2-pyrrolidone (NMP, Aldrich) at a ratio of 92:4:4. The mixture was then stirred for 6 h and coated onto Al foil. It was then dried at 120 °C for 12 h under vacuum. The loading density of the NCM721 electrode was fixed at about

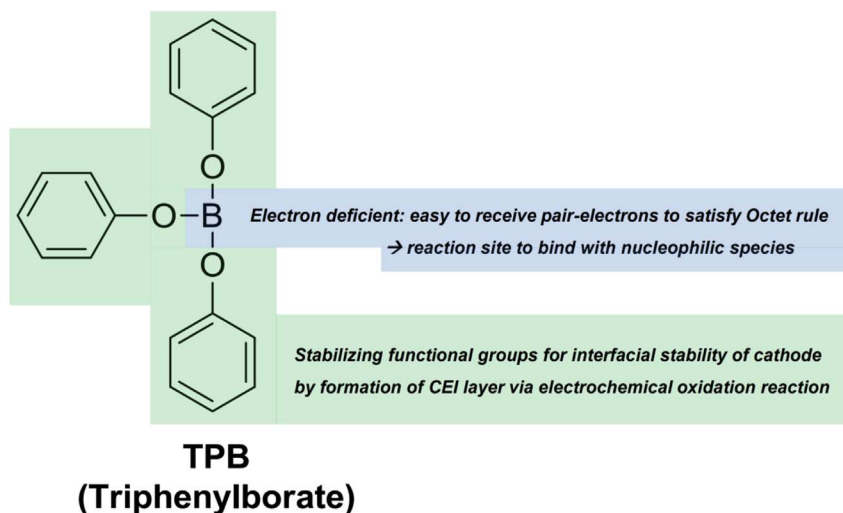


Fig. 1. Molecular structure of TPB and material strategy for use of TPB.

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