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# Insight into self-discharge of layered lithium-rich oxide cathode in carbonate-based electrolytes with and without additive

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## HIGHLIGHTS

- Self-discharge of charged layered lithium-rich oxide cathode is understood.
- Trimethyl borate (TMB) is used as an electrolyte additive to suppress this self-discharge.
- Suppression mechanism involves a cathode film derived from the preferential oxidation of TMB.

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## ABSTRACT

Self-discharge behavior of layered lithium-rich oxide as cathode of lithium ion battery in a carbonated-based electrolyte is understood, and a simple boron-containing compound, trimethyl borate (TMB), is used as an electrolyte additive to suppress this self-discharge. It is found that layered lithium-rich oxide charged under 4.8 V in additive-free electrolyte suffers severe self-discharge and TMB is an effective electrolyte additive for self-discharge suppression. Physical characterizations from XRD, SEM, TEM, XPS and ICP-MS demonstrate that the crystal structure of the layered lithium-rich oxide collapses due to the chemical interaction between the charged oxide and electrolyte. When TMB is applied, the structural integrity of the oxide is maintained due to the protective cathode film generated from the preferential oxidation of TMB.

## 1. Introduction

Lithium ion battery has been widely used as power source for electronic devices due to its high energy density and long cycle life compared with other rechargeable batteries [1–4]. However, the energy density of currently commercialized lithium ion battery cannot meet the demand of electric vehicles, because the specific capacity of cathode materials such as $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$ is low compared to that of graphite anode [5–7]. Layered lithium-rich oxide, composed of $Li_2MnO_3$ and $LiMO_2$ ($M = Mn_{1-x-y}Co_xNi_y$), has drawn much attention recently and are considered as a promising cathode for high energy density lithium ion battery, because it can provide a specific capacity of as high as 300 mAh $g^{-1}$ under high voltage (4.8 V, vs. $Li/Li^+$) [8–12]. In addition, this oxide is cheaper than $LiCoO_2$, the most widely used cathode for lithium ion battery up to date, due to the abundance of manganese.

However, there remain challenges before layered lithium-rich oxide can be put into practical use. To achieve its larger specific capacity, layered lithium-rich oxide cathode needs to be charged over 4.5 V for the activation of $Li_2MnO_3$ [13–18]. Under such high voltage, the electrolyte tends to be oxidized electrochemically on cathode [19,20], which is accompanied with the crystal destruction of layered lithium-rich oxide, leading to the poor cyclic stability [21–29]. Besides, like other high voltage cathode materials such as $LiNi_{0.5}Mn_{1.5}O_4$ [3,30,31], charged layered lithium-rich oxide might fail due to self-discharge when it is kept in storage. The failure mechanism of the cathode due to the self-discharge is different

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from that resulting from charge/discharge cycling, because self-discharge takes place through the chemical interaction between charged cathode and electrolyte [3]. Unfortunately, less attention has been paid to the mechanism on and the solution to the self-discharge of layered lithium-rich oxide.

Surface coating is proven to be an effective way to improve interfacial stability of layered lithium-rich oxide. Many inorganic compounds, such as $Al_2O_3$ [32], MgO [33], $MnO_x$ [34], $AlPO_4$ [35,36], $AlF_3$ [37,38], $Li_4Ti_5O_{12}$ [39], or their composites [40,41], have been used to coat layered lithium-rich oxide. However, coating is not cost-efficient because coating procedure is complicated and introducing inert compounds reduces the specific capacity of layered lithium-rich oxides.

Compared to the coating, using electrolyte additives to modify the electrode-electrolyte interface is easy and economical. Some electrolyte additives have been developed successfully to improve the cyclic stability of layered lithium-rich oxide. These additives include 4-(trifluoromethyl)-1,3-dioxolan-2-one (TFM-EC) [42], tris(hexafluoro-iso-propyl)phosphate (HFip) [43], 3-Hexylthiophene [44], LiDFOB [45], tris(trimethylsilyl)phosphate (TMSP) [46], tris(trimethylsilyl)borate (TMSB) [47]. This cyclic stability improvement is attributed to the formation of cathode film on layered lithium-rich oxide, which suppresses the electrolyte decomposition and prevents the oxide from structural destruction during charge/discharge cycling. The cathode film should also be beneficial for the self-discharge suppression of layered lithium-rich oxide, because it provides a separation layer and avoids the direct contract between the oxide and electrolyte.

In our previous report, a simple and cheap boron-containing compound, trimethyl borate (TMB), was found to be effective for the cyclic stability improvement of a cathode, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, under 4.5 V [48]. This improvement is attributed to the formation of a protective cathode film on $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ particles from preferential oxidation of TMB, which not only suppress the electrolyte decomposition, but also protects cathode from crystal destruction. Boron in the additive is believed to be incorporated into the cathode film, which coordinates with F ions preventing the formation of LiF on one hand, and contributes to the improved ionic conductivity of the resulting films and the improved rate capability of the protected cathodes on the other hand [49–52]. In this work, the self-discharge mechanism of layered lithium-rich oxide in carbonate-based electrolyte was understood and TMB was used as an electrolyte additive to suppress the self-discharge of charged layered lithium-rich oxide.

## 2. Experimental

### 2.1. Theoretical calculation

The energy levels of highest occupied molecular orbital (HOMO) of organic molecules were calculated by the Gaussian 03 program package [11], for the comparison in oxidative possibility of TMB with solvents, ethylene carbonate, ethyl methyl carbonate and diethyl carbonate.

### 2.2. Sample preparations

A representative layered lithium-rich oxide, $Li[Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13}]O_2$, was used in this work. It was prepared by co-precipitation method [53]. Typically, 1 g polyvinyl pyrrolidone was dispersed under magnetic stirring in the mixed solvent of 60 mL distilled water and 20 mL ethylene glycol. 4.875 g lithium acetate ($CH_3COOLi\cdot 2H_2O$), 4.901 g manganese acetate ($Mn(CH_3COO)_2\cdot 4H_2O$), 1.224 g nickel acetate ($Ni(CH_3COO)_2\cdot 4H_2O$), and 1.245 g cobalt acetate ($Co(CH_3COO)_2\cdot 4H_2O$) were added successively under continuous stirring. An oxalic acid solution (120 mL distilled water and 9.331 g oxalic acid) as a precipitating agent was added drop by drop into the solution above under stirring. After complete precipitation, the mixture was evaporated at 90 °C. Finally, the dried powder was pre-heated in air at 450 °C for 5 h and then calcined in air at 900 °C for 12 h. The final product was obtained after uniform grinding.

TMB (>99.5%) was purchased from Aladdin Industrial Inc., China, and used without further purification. Battery-grade carbonate solvents and lithium hexafluorophosphate ($LiPF_6$) were provided by Dongguan Kaixin Materials Technology Co. Ltd, China. The baseline electrolyte was 1.0 M $LiPF_6$ in a mixed solvent of ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/diethyl carbonate (DEC) (3/5/2, in weight). 2 wt% TMB was added to obtain the TMB-containing electrolyte. All the electrolytes were prepared in a highly pure argon-filled glove box (MBRAUN, Germany), in which water and oxygen contents were controlled less than 0.1 ppm. The contents of water and free acid (HF) in the electrolyte were determined by Karl-Fisher 831 Coulometer (Metrohm, Switzerland) and Karl-Fisher 798 GPT Titrino (Metrohm, Switzerland), which were controlled lower than 20 and 50 ppm, respectively.

The cathode was prepared with a slurry of 80 wt% of as-prepared $Li[Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13}]O_2$ powder, 10 wt% polyvinylidenefluoride (PVDF) binder and 10 wt% acetylene black. The slurry was cast on aluminum foil, followed by drying and calendaring. The electrode area was 1.2 $cm^2$ and its thickness was 28 μm. $Li/Li[Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13}]O_2$ 2025-coin cell was assembled with Celgard 2400 separator in the glove box. Transparent V-type cells with lithium as anode and $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ as cathode were also assembled for phenomenological observation.

### 2.3. Electrochemical measurements

Cyclic voltammetry (CV) was performed on a Solartron-1470 instrument (U.K) at a scan rate of 0.1 mV $s^{-1}$ in the coin cell. Self-discharge test of coin cells was performed according to the following protocols. The cells were charged and discharged at 0.1 C for the first 3 cycles and 0.5 C for additional 17 cycles ($1\ C = 250\ mA\ g^{-1}$) in the voltage range of 2–4.8 V with the end-off voltage of 4.8 V on LAND test system (LandCT2001A, China) and then left at open-circuit voltage for 18 days. The cycling performance of $Li/Li[Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13}]O_2$ coin cells after self-discharge test was re-evaluated at 0.5 C rate in the voltage range of 2–4.8 V. Electrochemical impedance spectroscopy was performed on a PGSTAT-30 electrochemical station (Autolab, Metrohm, Netherlands) in a frequency range of $10^5$–0.1 Hz with a potential amplitude of 5 mV.

### 2.4. Physical characterizations

The cycled $Li[Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13}]O_2$ electrodes were rinsed with anhydrous DMC three times to remove residual electrolyte salts precipitated on the surface, and then evacuated overnight at room temperature for physical characterizations [54]. Crystal structure was identified by X-ray diffraction (XRD, BRUKER D8 ADVANCE, Germany) operated at 60 kV and 80 mA using CuKα radiation in the 2θ range of 15–90° with a sweep rate of $0.05^\circ s^{-1}$. Surface morphology was observed by scanning electron microscopy (SEM, JSM-6510) and transmission electron microscopy (TEM, JEM-2100, JOEL, Japan). Surface compositions were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250), using a focused monochromatized Al Kα radiation ($h\upsilon = 1486.6$ eV) under ultra-high vacuum. The obtained spectra were fitted using XPS peak software (version 4.1). Lorentzian and Gaussian functions