



# Tris(trimethylsilyl)borate as an electrolyte additive for improving interfacial stability of high voltage layered lithium-rich oxide cathode/carbonate-based electrolyte



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## HIGHLIGHTS

- TMSB can improve the cyclic stability of layered lithium-rich oxides significantly.
- TMSB oxidizes preferentially to carbonate electrolyte and forms a protective film on the oxides.
- Interfacial stability of oxide/electrolyte is improved.
- Electrolyte decomposition and oxide structure destruction are inhibited effectively.

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## ABSTRACT

Tris(trimethylsilyl)borate (TMSB) is used as an electrolyte additive for high voltage lithium-rich oxide cathode of lithium ion battery. The interfacial natures of  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ /carbonate-based electrolyte are investigated with a combination of electrochemical measurements and physical characterizations. Charge/discharge tests show that the cyclic performance of  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  in a mixed carbonate electrolyte is significantly improved by using TMSB. After 200 cycles between 2 V and 4.8 V (vs.  $\text{Li}/\text{Li}^+$ ) at 0.5 C rate, the capacity retention of  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  is only 19% in the blank electrolyte, while it is improved to 74% when 0.5% TMSB is applied. The results from physical characterizations demonstrate that this excellent cyclic performance is attributed to the improved interfacial stability of  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ /electrolyte due to the thin and protective film generated by TMSB.

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## 1. Introduction

Cathode materials with high specific capacity and high working voltage have attracted extensive attention for high energy lithium-ion batteries [1,2]. Compared to the traditional cathodes such as spinel  $\text{LiMn}_2\text{O}_4$  and layered  $\text{LiCoO}_2$ , layered lithium-rich oxides with chemical formulation of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  ( $M = \text{Co}, \text{Ni}$  and  $\text{Mn}$ ) have been widely investigated due to their large reversible

capacity ( $250 \text{ mAh g}^{-1}$ ), high voltage, environmental friendliness, and low cost [3–5]. However, the application of layered lithium-rich oxides is limited by their poor cyclic performance under high voltage, which is mainly caused by the instability of the interface between layered lithium-rich oxide and carbonated-based electrolyte. Carbonate-based electrolyte is necessary for lithium ion batteries due to its highly ionic conductivity, but it tends to decompose under high voltage ( $>4.2 \text{ V vs. Li}/\text{Li}^+$ ), generating gas and polymer products on the electrode surface. On the other hand, metal ions in layered lithium-rich oxides might dissolve in the carbonate-based electrolyte during cycling, resulting in structure destruction and capacity fade of the oxides [3,6–9]. Various

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methods have been proposed to improve the instability of oxide/electrolyte interface [10–22]. To solve these issues, one of the most economic and effective methods is to use electrolyte additives to create a protective film on the surface of layered lithium-rich oxide to prevent the direct contact with electrolyte [23–25]. Tan et al. reported that a highly fluorinated phosphate ester, tris(hexafluoroisopropyl)phosphate, improved the capacity retention of a layered lithium-rich oxide,  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ , from 64.5% to 73.3% after 130 charge–discharge cycles between 2.0 and 4.6 V (vs.  $\text{Li}^+/\text{Li}$ ) at a current of  $180 \text{ mA g}^{-1}$  [20]. Recently, Zhang and co-authors found that the capacity retention of  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}]\text{O}_2$  could be improved from 83.6% to 90.8% after 50 charge/discharge cycles between 2.0 and 4.8 V at a current of  $20 \text{ mA g}^{-1}$  by using tris(trimethylsilyl) phosphate as an electrolyte additive [24]. Obviously, the application of electrolyte additives can improve the cyclic performance of layered lithium-rich oxides. However, the improvements that have been reported are not significant. Furthermore, the detailed mechanism on these improvements remains unclear.

Tris(trimethylsilyl)borate (TMSB) has been found to be an effective electrolyte additive that can significantly improve cyclic performance of several high voltage cathodes including  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  [26],  $\text{LiMn}_2\text{O}_4$  [27] and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  [28] and suppress the self-discharge of fully-charged  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  [29], but has never been evaluated for large capacity and high voltage layered lithium-rich oxide. In this work, TMSB was used as an electrolyte additive to improve cyclic performance of layered lithium-rich oxides for the first time and the improvement mechanism was understood via physical characterizations including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD).

## 2. Experimental

### 2.1. Sample preparation

A representative of layered lithium-rich oxides,  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}]\text{O}_2$ , was used in this work. It was prepared by co-precipitation method [30]. Typically, 1 g polyvinyl pyrrolidone dispersed under magnetic stirring in the mixed solvent of 60 mL distilled water and 20 mL ethylene glycol. 4.875 g lithium acetate ( $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ ), 4.901 g manganese acetate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ), 1.224 g nickel acetate ( $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) and 1.245 g cobalt acetate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) 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  $90^\circ\text{C}$ . Finally, the dried powder was pre-heated in air at  $450^\circ\text{C}$  for 5 h and then calcined in air at  $900^\circ\text{C}$  for 12 h. The final product was obtained after uniform grinding.

Tris(trimethylsilyl)borate (TMSB) (>99.5%) was purchased from Fujian Chuangxin Technology Co. Ltd, China. Battery-grade carbonate solvents and lithium hexafluorophosphate ( $\text{LiPF}_6$ ) were provided by Dongguan Kaixin Materials Technology Co. Ltd, China. The base electrolyte (STD) was 1.0 M  $\text{LiPF}_6$  in a mixed solvent of ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC) (3/5/2, in weight). 0.5 wt.% TMSB was added to obtain the TMSB-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 831Coulometer (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  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}]\text{O}_2$  powder, 10 wt.% polyvinylidene fluoride (PVDF) binder and 10 wt.% acetylene black. The slurry was cast on aluminum foil, followed by drying and calendaring. Lithium foil was used as anode. And the  $\text{Li}/\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}]\text{O}_2$  2025-coin cell was assembled with Celgard 2400 separator in the glove box.

### 2.2. Electrochemical measurements

The cyclic and rate performances of  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}]\text{O}_2$  were evaluated via constant current charge/discharge tests in  $\text{Li}/\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}]\text{O}_2$  coin cell at room ( $25^\circ\text{C}$ ) temperature between 2 V and 4.8 V on LAND test system (CT2001A, China). In the evaluation of cyclic performance, the cell was charged and discharged at 0.1 C ( $1 \text{ C} = 250 \text{ mA g}^{-1}$ ) for the first three cycles and then at 0.5 C for the subsequent cycles. In the evaluation of rate performance, the cell was charged and discharged at various currents of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, and 4 C. Electrochemical impedance measurements were 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.

### 2.3. Physical characterizations

The cycled  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}]\text{O}_2$  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. Crystal structure was identified by X-ray diffraction (XRD, BRUKER D8 ADVANCE, Germany) operated at 60 kV and 80 mA using  $\text{CuK}\alpha$  radiation in the  $2\theta$  range of  $15$ – $90^\circ$ . 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 measurement (XPS, ESCALAB 250), using a focused monochromatized  $\text{AlK}\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ) under ultra-high vacuum. The obtained spectra were fitted using XPS peak software (version 4.1). Lorentzian and Gaussian functions were used for the least-square curve fitting procedure. The cycled lithium electrodes were rinsed with anhydrous DMC and dissolved in 10 mL 2%  $\text{HNO}_3$ . The solution was diluted to 25 mL for Inductively Coupled Plasma (ICP) analysis, which was performed on an IRIS Intrepid II XSP.

## 3. Results and discussion

### 3.1. Electrochemical performance of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$

The cyclic performances and the initial charge/discharge curves of  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  in STD and TMSB-containing electrolytes are shown in Fig. 1. It is obvious that the presence of TMSB significantly improves the cyclic stability of  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ , as shown in Fig. 1A. Under 0.5 C rate, the  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  electrode cycled in the TMSB-containing electrolyte delivers an initial capacity of  $213 \text{ mAh g}^{-1}$  with a capacity retention of 73.6% after 220 cycles, compared to  $201 \text{ mAh g}^{-1}$  and 19.1% for the electrode in the STD electrolyte.

To understand the effect of TMSB, the charge/discharge performance of  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  is analyzed in detail. As seen from Fig. 1B,  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  has similar charge behavior in the STD and TMSB-containing electrolyte: a slope potential increase below 4.5 V and a long voltage plateau around 4.5 V. The former corresponds to the lithium extraction from  $\text{LiMn}_{1/}$

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