



Stabilizing lithium manganese oxide/organic carbonate electrolyte interface with a simple boron-containing additive



Xuerui Yang^a, Jianhui Li^a, Lidan Xing^{a,b}, Youhao Liao^{a,b}, Mengqing Xu^{a,b},
Qiming Huang^{a,b,*}, Weishan Li^{a,b,*}

^a School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

^b Engineering Research Center of MTEES (Ministry of Education), Research Center of BMET (Guangdong Province), Engineering Lab. of OFMHEB (Guangdong Province), Key Lab. of ETESPG (GHEI), and Innovative Platform for ITBMD (Guangzhou Municipality), South China Normal University, Guangzhou 510006, China

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ABSTRACT

A simple boron-containing molecule, tripropyl borate (TPB), is used as an electrolyte additive to stabilize the interface between spinel lithium manganese oxide (LiMn_2O_4) and carbonate-based electrolyte under elevated temperature. Electrochemical measurements indicate that the cyclic stability of LiMn_2O_4 electrode can be significantly improved by TPB. The capacity retention of LiMn_2O_4 at 1C after 200 cycles under 55 °C is improved from 47% to 74% by adding 3% TPB into a standard electrolyte (1.0 mol L⁻¹ LiPF₆-EC/EMC/DEC (3/5/2, in weight)). Most importantly, the self-discharge of LiMn_2O_4 under 55 °C, which takes place dramatically in the standard electrolyte, is effectively suppressed in 3% TPB-containing electrolyte. Theoretical calculations and physical characterizations demonstrate that a protective cathode electrolyte interface (CEI) film is formed on LiMn_2O_4 from the preferential oxidation of TPB, which suppresses the oxidation decomposition of the standard electrolyte. Due to the incorporation of boron, the CEI film formed from TPB is beneficial to the rate capability of LiMn_2O_4 .

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1. Introduction

Over the past decades, lithium ion battery has dominated the power source market for small portable electronic devices due to its higher energy density, longer cycle and calendar life than other secondary batteries. [1,2]. Nowadays, it is used as an indispensable power source for large-scale electric vehicles [3,4]. However, the cost of lithium ion battery is high compared to its counterparts such as lead-acid and nickel-hydride batteries, when it is used in electric vehicles. It is a challenge to reduce the cost for the fabrication of lithium ion battery.

Traditional cathodes such as layered lithium cobalt oxide (LiCoO_2) and olivine lithium iron phosphate (LiFePO_4) are mainly responsible for the high cost of currently commercialized lithium ion battery, due to the deficient resource of cobalt and the complicate synthesis of LiFePO_4 [4–11]. Comparatively, spinel lithium manganese oxide (LiMn_2O_4) attracts much attention due to

the abundant resource of manganese, the easiness for its synthesis and its environmental friendliness [12,13]. However, the interfacial instability between LiMn_2O_4 and conventional carbonate-based electrolyte, especially under elevated temperature, limits its application in practice [14–17]. The electrolyte tends to decompose on LiMn_2O_4 generating HF that causes the dissolution of manganese ions from LiMn_2O_4 [18–21].

A number of approaches have been developed to improve the interfacial stability between LiMn_2O_4 and electrolyte. Doping elements such as Co, Ni, Cr, or F in LiMn_2O_4 or coating LiMn_2O_4 with inert compounds such as Al_2O_3 and ZrO_2 are found to be effective for the improvement in structural stability of LiMn_2O_4 [22,23]. However, these approaches not only require complicate synthetic processes and add cost into the product LiMn_2O_4 , but also reduce the specific capacity of LiMn_2O_4 due to the introduction of inert components.

Based on the successful application of electrolyte additives from maintaining structural integrity of graphite anode of lithium ion battery, electrolyte additives have also been used to form cathode electrolyte interphase (CEI) films to improve the interfacial stability of various cathodes in carbonate-based electrolyte [24–26]. Similarly to the coating with inert compounds, the CEI

* Corresponding authors at: School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China.

E-mail addresses: huangqm@scnu.edu.cn (Q. Huang), liwsh@scnu.edu.cn (W. Li).

films formed from electrolyte additives separate cathodes from direct contact with electrolyte, and thus suppress the oxidation decomposition of electrolyte and the dissolution of transition metal ions from cathode. Comparatively, the approach by applying an electrolyte additive for the interfacial stability improvement of cathode is simple and cost-efficient.

Several electrolyte additives including prop-1-ene-1,3-sultone (PES) [27], 3,3'-sulfonyldipropionitrile [28] and dimethyl phenylphosphonite (DMPP) [29], have been developed for improving the interfacial stability of LiMn_2O_4 in carbonate-based electrolyte. Unfortunately, these additives yield adverse effect on the electrochemical performance of LiMn_2O_4 when they are used in a higher concentration. For example, the discharge capacity of LiMn_2O_4 is decreased from the 113 mAh g^{-1} in the base electrolyte to 106 mAh g^{-1} and 102 mAh g^{-1} for 0.5% and 1% DMPP-containing electrolytes, respectively [29]. This adverse effect is attributed to the poor ionic conductivity of the CEI film formed from the additives, which is detrimental to the rate capability of LiMn_2O_4 .

Boron-containing compounds are often used as electrolyte additives for the formation of protective films for various cathodes of lithium ion battery [25,30–35]. Differently from other electrolyte additives, boron-containing compounds form CEI films with lower interfacial impedance that is independent of the concentration of the additives. This feature of boron-containing compounds is attributed to the coordination of boron with F^- ions, which reduces the formation of highly resistive LiF [36–39]. However, most of boron-containing additives for the formation of CEI film have complicated molecule structures, such as tris(trimethylsilyl) borate (TMSB) [25], tris(pentafluorophenyl) borane (TPFPB) [37] and tris(2H-hexafluoroisopropyl) borate (THFPB) [40], which may decrease the ionic conductivity of the electrolyte. Boron-containing salts such as lithium bis(oxalate)borate (LiBOB) were also used for the cyclic stability improvement of lithium ion batteries, but their contributions result mainly from the thermal stability improvement of the electrolyte due to their substitutions for the less stable of LiPF_6 [41].

It has been found that some simple boron-containing compounds such as trimethyl borate (TMB) and triethyl borate (TEB) are effective as good as TMSB for improving the interfacial stability of different cathodes but hardly affected the properties of the electrolyte even if they are used in high concentrations [30,42,43]. In this work, we reported a new finding that another simple boron-containing compound, tripropyl borate (TPB), was effective for stabilizing the interface between LiMn_2O_4 and carbonate-based electrolyte under elevated temperature. At 55°C , not only the cyclic stability of LiMn_2O_4 was improved significantly, but also the self-discharge of the charged LiMn_2O_4 was suppressed effectively. The contribution of TPB was understood through electrochemical measurements, theoretical calculations and physical characterizations. The electrochemical measurements and physical characterizations demonstrated that TPB functions like other simple boron-containing electrolyte additives such as the same category TMB and TEB, forming a protective CEI on cathode. However, theoretical calculations indicated that TPB had a lower oxidation potential than TMB and TEB, which is beneficial for the formation of an effectively protective CEI film [31].

2. Experimental

2.1. Preparation

Tripropyl borate (TPB) (99%) was purchased from Aladdin Industrial Inc, China, and used without further purification. The standard (STD) electrolyte (1.0M LiPF_6 in a mixed solvent of ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/diethyl

carbonate (DEC) (3/5/2, in weight)) was provided by Dongguan Kaixin Materials Technology Co. Ltd, China. Various contents of TPB were added into the STD electrolyte in weight percentage to obtain 2.0, 3.0 and 4.0 wt. % TPB-containing electrolytes. All the electrolytes were prepared in a highly pure argon-filled glove box (MBRAUN, Germany), in which water and oxygen contents were controlled to less than 0.1 ppm. The LiMn_2O_4 electrodes were prepared by blending 80 wt. % LiMn_2O_4 (Qingdao Xinzheng Lithium industry Co., Ltd, China), 10 wt. % Acetylene Black and 10 wt. % polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP), coating the slurry on aluminum foil, drying under vacuum, and punching into disks of 1.44 cm^2 . To ensure the consistency of all the electrodes, the loading of LiMn_2O_4 in the electrodes were controlled at the level of $1.81 \pm 0.01 \text{ mg cm}^{-2}$. Based on the electrode area (1.44 cm^2), the loading of LiMn_2O_4 in the electrodes, and the theoretical specific capacity of LiMn_2O_4 (148 mAh g^{-1}), the theoretical discharge capacity of the prepared LiMn_2O_4 electrodes was $0.39 \pm 0.01 \text{ mAh}$. To evaluate the effect of the additive on anode of lithium ion battery, graphite electrodes were prepared by using the mixture of 80 wt. % artificial graphite (provided by Dongguan Kaixin New Energy Technology Co., Ltd, China), 10 wt. % acetylene black and 10 wt. % polyvinylidene fluoride (PVDF). Li/ LiMn_2O_4 or Li/graphite 2025-coin cell for electrochemical measurement was assembled using Celgard 2400 as separator and lithium foil as counter and reference electrode in the glove box mentioned above.

2.2. Electrochemical measurements

The cycle stability and rate capability of LiMn_2O_4 electrode were evaluated via constant current charge/discharge tests in Li/ LiMn_2O_4 coin cell between 3.0 to 4.5 V on LAND test system (CT2001A, China). In the assessment of cycle stability, the cell was charged and discharged at 0.5C ($1\text{C} = 148 \text{ mAh g}^{-1}$) for the first three cycles and then at 1C for the subsequent cycles. In the assessment of rate capability, the cell also was charged and discharged at 0.5C for the first three cycles and then at various currents of 1C, 4C, 6C, and 10C. The Li/graphite cells were charged and discharged with 0.1C ($1\text{C} = 372 \text{ mAh g}^{-1}$) for the first two cycles and 0.3C for the subsequent cycles at room temperature. Self-discharge test was performed after the charging the Li/ LiMn_2O_4 cell to 4.5 V, and then open-circuit voltage (OCV) was traced at 55°C . The electrochemical impedance spectroscopy was performed on an Autolab (PGSTAT302N) electrochemical station in a frequency range from 10^5 to 0.1 Hz with the amplitude of 5 mV. To ensure the accuracy of the data, all electrochemical measurements on each sample were performed with five cells. The reported data are those from the cell whose values are the mean ones among five cells.

2.3. Physical characterizations

For characterizing the cycled LiMn_2O_4 electrodes, the cells were disassembled in the glove box. The cycled LiMn_2O_4 electrodes were rinsed with anhydrous DMC three times to remove residual solvents and LiPF_6 salt on the surface and then dried over night at room temperature. The surface morphology of the cycled electrodes was observed by scanning electron microscopy (SEM, JSM-2100, Japan) and transmission electron microscopy (TEM, JEM-2100HR, JOEL, Japan). The surface compositions of the LiMn_2O_4 electrodes were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, US) by using a focused monochromatized Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) as the X-ray source under ultra-high vacuum.

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