

# Tris(trimethylsilyl)phosphite as electrolyte additive for high voltage layered lithium nickel cobalt manganese oxide cathode of lithium ion battery



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## ABSTRACT

Tris(trimethylsilyl) phosphite (TMSPi) is reported as an effective electrolyte additive for high voltage layered lithium nickel cobalt manganese oxide cathode of lithium ion battery. Charge/discharge tests demonstrate that the cyclic stability and rate capability of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  can be improved significantly by adding 0.5wt% TMSPi into a standard electrolyte, 1.0M  $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate (1/2, in volume). The capacity retention of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  is improved from 75.2% to 91.2% after 100 cycles at 0.5 C rate ( $1\text{C}=160\text{mA g}^{-1}$ ), while its discharge capacity at 5 C is enhanced from  $122.4\text{mAh g}^{-1}$  to  $134.4\text{mAh g}^{-1}$ . This improvement can be ascribed to the suppression of electrolyte decomposition and transition metal ion dissolution by TMSPi, due to the preferential oxidation of TMSPi to electrolyte and the formation of a protective solid electrolyte interphase on  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , which are confirmed by electrochemical measurements and surface characterizations.

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## 1. Introduction

Lithium ion battery has been extensively used for the applications in portable electronic devices, while its energy density needs to be improved for large-scale applications [1–3]. One of the approaches for improving the energy density of lithium ion battery is to enhance its working voltage [4]. Layered  $\text{LiMO}_2$  ( $\text{M}=\text{Ni}$ ,  $\text{Co}$  and  $\text{Mn}$ ) cathodes such as  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  are attractive, because they deliver a specific capacity of over  $160\text{mAh g}^{-1}$  under a working voltage of 4.5 V [5]. Under such a high voltage, however, these cathodes suffer serious capacity decaying [6,7]. This is because the electrolyte is unstable thermodynamically at the voltage of over 4.2 V [8,9] and the electrolyte decomposition is usually accompanied by the cathode destruction. Currently, commercial layered oxides are usually used under 4.2 V. The electrolyte decomposition is not so serious under this voltage but will become significant when the voltage is improved to 4.5 V. Therefore, the suppression of the electrolyte decomposition is

important to the electrochemical performance of the layered oxides used under high voltage.

Several methods have been proposed to suppress the electrolyte decomposition on the high voltage cathode materials and the consequent cathode destruction, including surface coating, solvent substitution and electrolyte gelation. Coating layered oxide cathode materials with more stable inorganic compounds, such as  $\text{Sb}_2\text{O}_3$  [6],  $\text{ZrF}_4$  [10] and  $\text{TiO}_2$  [11], can improve the cyclic stability of the cathode, but this approach is too complicated for material preparation and at the expense of specific capacity loss. Some solvents like sulfone have been reported to be stable at 5 V (vs.  $\text{Li/Li}^+$ ) [12–14], but these solvents have high viscosity and exhibit poor compatibility with the cathode materials. The gelation of liquid carbonate-based electrolyte by polymer has been shown to be able to improve the cyclic stability of high voltage layered oxide cathode [15], but the ionic conductivity of gel polymer electrolytes is low, about one decade lower than that of liquid electrolyte.

Recently, motivated by the protection of graphite anode from electrolyte additives, researchers have used electrolyte additives to improve cyclic stability of cathodes in lithium ion battery [16–18]. Accordingly, several electrolyte additives have been developed to

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improve the cyclic stability of layered oxide cathodes. 1,3-Propane sulfone (PS), an effective electrolyte additive for graphite anode [19], has been found to be also able to improve the cyclic stability of  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$  cathode [20]. Zuo et al. [7] reported that the cyclic stability of  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2/\text{graphite}$  cell (3.0–4.4 V) could be improved by introducing tris(trimethylsilyl) borate (TMSB) into electrolyte and ascribed this improvement to the thinner film on  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  formed by TMSB. Yan et al. [21] reported that tris(trimethylsilyl) phosphate (TMSP) could be used as a film-forming additive for  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cathode. With using 1% TMSP in electrolyte, the capacity retention of the cathode was improved from 77% to 90.9% after 100 cycles at 1 C.

Apparently, using electrolyte additives to improve cyclic stability of layered oxide cathode is easy and economical, compared to the other approaches mentioned above. Similarly to those for the graphite anode, the electrolyte additives for cathode contribute to the formation of a protective solid electrolyte interphase (SEI) film on cathode, which suppresses the electrolyte decomposition and transition metal dissolution [22]. The oxidation decomposition potential and the molecular structure of the electrolyte additives are important for the formation of a protective SEI film for anode or cathode, because the additives should react preferentially to the electrolyte to avoid the interfering with the SEI formation from electrolyte decomposition and to provide the SEI with stable components from their decomposition products [23].

With the knowledge that TMSP can provide protection for layered oxide and the expectation that Tris(trimethylsilyl) phosphite (TMSPi) might be more effective than TMSP due to its possibly preferential oxidation, we use TMSPi as an electrolyte additive to improve the cyclic stability of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  in this work. The suppression of electrolyte decomposition and the protection of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  by TMSPi are understood with electrochemical measurements and surface characterizations. TMSPi has been used as electrolyte additive for spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  [24], but never be considered for layered oxide cathodes.

## 2. Experimental

### 2.1. Preparation of electrolyte and electrode

Battery-grade carbonate solvents and lithium hexa-fluorophosphate ( $\text{LiPF}_6$ ) were provided by Guangzhou Tinci Materials Technology Co., Ltd. TMSPi and TMSP were purchased from Alfa Aesar Technology Co. All these chemicals were used without further treatment. 1.0 mol  $\text{dm}^{-3}$   $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/2, in volume) was prepared as a standard (STD) electrolyte. TMSPi or TMSP was added into the standard electrolyte to prepare additive-containing electrolytes.  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  electrode was prepared by coating a mixture, 80 wt%  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (Qingdao Xinzheng Lithium Co., China), 10 wt% acetylene black and 10 wt% PVDF, on Al foil.

### 2.2. Electrochemical measurements

The linear sweep voltammetry (LSV), cyclic voltammetry (CV) were performed on Solartron-1480 instrument (England). LSV was carried out on a three-electrode cell using Pt electrode (100  $\mu\text{m}$  diameter) as working electrode with a lithium foil as counter and reference electrodes with a scan rate of 5  $\text{mV s}^{-1}$ . CV was performed in  $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  coin cell, which was setup in an Ar-filled glove box with prepared electrolytes and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  electrode. Celgard 2400 was used as the separator. Charge/discharge test was performed on LAND test system (CT2001A, China) with the  $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  coin cell. Cyclic

stability was obtained by cycling the cell for the first two formation cycles at 0.1 C ( $1\text{C} = 160\text{ mA g}^{-1}$ ) and then at 0.5 C for the remaining cycles. Rate capability was obtained by cycling the cell for the two formation cycles of 0.2 C for charge and discharge, and then at 0.5 C for charge and at different current rates for discharge for remaining cycles. The electrochemical impedance spectroscopy (EIS) measurements were carried out at fully discharged state, the AC perturbation was  $\pm 10\text{ mV}$ , and the frequency range was from  $10^5\text{ Hz}$  to  $10^{-1}\text{ Hz}$  on a PGSTAT-302N electrochemical station (Autolab, Metrohm Co., Switzerland). Storage test was performed after the first charging of the  $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cell to 4.5 V, and the open-circuit voltage (OCV) was traced at room temperature.

### 2.3. Surface characterizations

The cells after cycling were disassembled in the glove box, and the electrodes were rinsed with anhydrous DMC to remove residual EC and  $\text{LiPF}_6$  salt, followed by vacuum drying overnight at room temperature. The surface morphology of the cycled  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  electrodes was observed by SEM (JSM-6510, JEOL Co., Japan). The surface composition was analyzed with X-ray photoelectron spectroscopy (XPS) on ESCALAB 250 using a focused monochromatized Al  $K\alpha$  radiation ( $h\nu = 1486.6\text{ eV}$ ) under ultra high vacuum. The final adjustment of the energy scale was made based on the C 1s peak of graphite at 284.3 eV. The spectra obtained were fitted using XPSPeak 4.1. Lorentzian and Gaussian functions were used for the least-square curve fitting procedure.

## 3. Results and Discussion

The reason for the selection of TMSPi as the electrolyte additive is the possibly preferential oxidation of TMSPi to TMSP, due to the lower oxidation state of phosphorus in TMSPi than in TMSP. To confirm this assumption, LSV is performed in the electrolytes with and without TMSPi and TMSP. Fig. 1 presents the voltammograms of Pt microelectrode in various electrolytes. In the standard electrolyte, the oxidation current appears at about 4.2 V (vs.  $\text{Li}/\text{Li}^+$ ) and then increases slowly from that potential. This slowly increased current demonstrates that the standard electrolyte is unstable under such high potentials. The oxidation decomposition of the standard electrolyte becomes serious from 4.8 V, as indicated by the quick increase of the oxidation current. It should be noted that the electrolyte decomposition might take place earlier and more seriously on layered oxides because of the catalysis from transition metals in the oxides. When adding TMSP into the

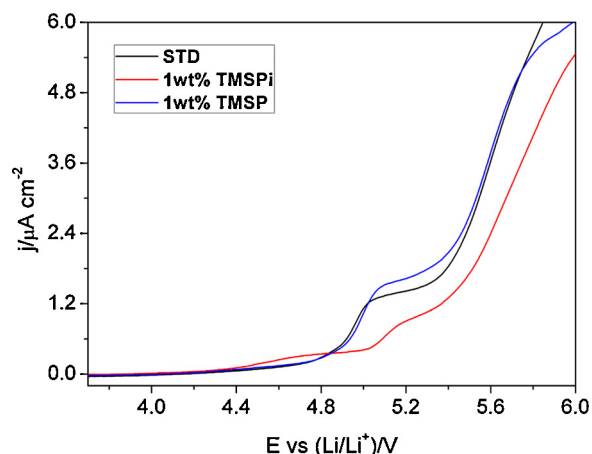


Fig. 1. Linear sweep voltammograms of platinum electrode in standard, TMSP- and TMSPi-containing electrolytes at a scan rate of 5  $\text{mV s}^{-1}$ .

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