



# Terthiophene as electrolyte additive for stabilizing lithium nickel manganese oxide cathode for high energy density lithium-ion batteries



Wenqiang Tu<sup>a</sup>, Pan Xia<sup>a</sup>, Jianhui Li<sup>a</sup>, Lizhen Zeng<sup>c</sup>, Mengqing Xu<sup>a,b</sup>, Lidan Xing<sup>a,b</sup>, Liping Zhang<sup>d</sup>, Le Yu<sup>d</sup>, Weizhen Fan<sup>d</sup>, Weishan Li<sup>a,b,\*</sup>

<sup>a</sup>School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

<sup>b</sup>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

<sup>c</sup>Research Resources Center, South China Normal University, Guangzhou 510006, China

<sup>d</sup>Guangzhou Tinci Material Technology Co., Ltd., Guangzhou 510760, China

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## ABSTRACT

Terthiophene (3THP) is evaluated as an electrolyte additive for improving cyclic stability of lithium nickel manganese oxide ( $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ) cathode for high energy density lithium-ion batteries. Charge/discharge tests demonstrate that 3THP is effective for improving the cyclic stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . With applying only 0.25% 3THP in a standard (1 M  $\text{LiPF}_6$  in EC and DMC, 1/2 in volume) electrolyte, the capacity retention of  $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cell after 350 cycles at 1C ( $1\text{C} = 147\text{ mA g}^{-1}$ ) under 4.9 V was improved from 50% to 91%, which is among the best that have been reported in literatures although the content of 3THP is far lower than those achieved by applying other additives. The physical characterizations from scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction, indicate that a thin cathode film has been formed on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particles, which suppresses the decomposition of electrolyte and protects  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  from structural destruction.

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## 1. Introduction

Lithium-ion batteries have been widely used in electronic devices due to their high energy density and long cycle life, but their energy density needs to be improved for large-scale applications such as electric vehicles [1–5]. To increase the energy density of lithium-ion batteries, currently commercialized cathodes ( $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$ , etc.) or anodes (e.g. graphite) should be replaced by other cathodes with higher working potential or anodes with larger specific capacity.  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is one of the most promising candidates due to its high work potential ( $\sim 4.7\text{ V}$  vs.  $\text{Li}^+/\text{Li}$ ) [6–13]. However, there are issues that we have to face before  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is used in practice. Like other high potential cathode materials,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  exhibits the poor cyclic stability due to the serious decomposition of electrolytes

under high potential [14–18] and the dissolution of transition-metal ions [9,19].

Coating high potential cathode materials with inert inorganic compounds can improve their cyclic stability to some extent [20–27], but this approach is not cost-efficient because coating procedures are complicated and introducing inert compounds results in the decrease of the specific capacity. Substituting more stable electrolyte for currently used carbonate-based ones in lithium-ion batteries can avoid the electrolyte decomposition. Up to date, however, no suitable substitutes have been found because of their poor compatibility with cathodes or low ionic conductivity compared with carbonate-based electrolyte [28–32].

Comparatively, applying electrolyte additives is cost-efficient for the cyclic stability improvement of high potential cathode materials. Several additives have been used for the cyclic stability improvement of high potential cathode materials [33–37], but the concentration of these additives should be over 0.5% to yield an effective improvement. High additive concentration might cause negative effect on electrolyte properties such as ionic conductivity and compatibility with cathode materials. In this work, terthiophene (3THP), which has been found to be effective for the cyclic

\* Corresponding author at: School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China. Tel.: +86 20 39310256; fax: +86 20 39310256.

E-mail address: [liwsh@scnu.edu.cn](mailto:liwsh@scnu.edu.cn) (W. Li).

stability improvement of LiCoO<sub>2</sub> cathode [38], was first evaluated as an electrolyte additive for improving the cyclic stability of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>. The effect of 3THP was investigated by combining electrochemical measurements with physical characterizations, which indicated that applying a small amount of 3THP (0.25%) can significantly improve the cyclic stability of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>.

## 2. Experimental

### 2.1. Preparation

LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> electrode was prepared by coating a mixture of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> powders (Sichuan Xingneng Co. Ltd., China), acetylene black and polyvinylidene fluoride (PVDF) (8:1:1 by weight) on Al foil. Graphite electrode was prepared by coating a mixture of artificial graphite (Dongguan Kaijin New Energy Technology Co., Ltd, China), Super-p (MMM carbon, Belgium) and polyvinylidene fluoride (PVDF) (9:0.6:0.4 by weight) on copper foil. 1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/2 in volume, provided by Guangzhou Tinci Materials Technology Co. Ltd., China) was used as the standard (STD) electrolyte. 3THP, purchased from Alfa Aesar Technology Co., was used without further treatment. 2025 coin cells, with LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> or graphite as working electrode, Celgard 2025 as separator and lithium foil as counter and reference electrode, were assembled in a dry argon glove box, where the contents of water and oxygen were controlled lower than 0.1 ppm.

### 2.2. Electrochemical measurements

Charge/discharge tests were conducted on a LAND cell test system (Land CT 2001A, China). The Li/LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cells were cycled according to the following protocol: charged to 4.9 V at a constant current, followed by a constant charge potential ( $E = 4.9$  V) for 10 minutes and then discharged to 3 V at the constant current under room temperature (25 °C). The applied constant current is 0.5C ( $1C = 147$  mA g<sup>-1</sup>) for the initial three cycles and then 1C for the subsequent cycles. The Li/graphite cells were charged and discharged at constant current protocol, 0.1C ( $1C = 350$  mA g<sup>-1</sup>) for the first cycle and 0.2C for the subsequent cycles. Cyclic voltammetry, Chronoamperometry were performed on Solartron-1480 instrument (England) with a scan rate of 0.1 mV s<sup>-1</sup>. The electrochemical impedance spectroscopy was carried out on a PGSTAT-302N electrochemical station (Autolab, Metrohm Co., Switzerland) at discharge state ( $\sim 3.0$  V) over the frequency range from 100 KHz to 0.1 Hz with a potential amplitude of 5 mV. The ionic conductivity of the electrolytes was measured on an 856 conductivity module (Metrohm, Switzerland).

### 2.3. Physical characterizations

For structure and composition characterizations, the cells after cycling were disassembled in the glove box and the electrodes were rinsed three times with DMC to remove residual electrolyte and dried in vacuum box overnight at room temperature. The crystal structure was analyzed by XRD (D8 Advance X-ray diffractometer) operated at 60 KV and 80 mA using Cu K $\alpha$  radiation ( $\lambda = 1.5405$  nm) in the  $2\theta$  range of 15–80°. The surface morphology was observed by SEM (JEM-6510, Japan) and TEM (JEM-2100HR, Japan). The surface composition was analyzed by XPS on ESALAB 250 system using a focused monochromatized Al K $\alpha$  radiation ( $h\nu = 1486.6$ ) under ultrahigh vacuum. The final adjustment of the energy scale was made based on the C1s peak of graphite at 284.8 eV. The wettability of the electrolytes were evaluated by measuring the contact angle of electrolyte/glass interface with a contact angle system (JC2000C, China). The contents of Mn and Ni

deposited on the cycled lithium foils were analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, ICAP 6500 Duo, USA). The lithium electrodes taken from cycled Li/LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cells were rinsed with DMC and dissolved in 5 ml 3% HNO<sub>3</sub>, and the solution was diluted to 25 mL for ICP-AES analysis.

## 3. Results and discussion

### 3.1. Electrochemical performance

Fig. 1 presents the cyclic performances of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> at 0.5C for initial three cycles and 1C for the subsequent cycles in the electrolytes with different contents of 3THP. It can be seen from Fig. 1a that LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> suffers serious capacity decaying in STD electrolyte, with a capacity retention of only 50% after 350 cycles. The capacity retention was calculated based on the capacities at the first and the 350<sup>th</sup> cycle at 1C. This poor cyclic stability is ascribed to the oxidation decomposition of electrolyte and the structural destruction of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> under high potential. When 3THP is added in STD electrolyte, the cyclic stability of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> is significantly improved. The capacity retention of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> is improved to 91% by using only 0.25% 3THP. This improvement was among the best that have been reported in literatures, although the content of 3THP is far lower than those achieved by applying other additives. For example, the capacity

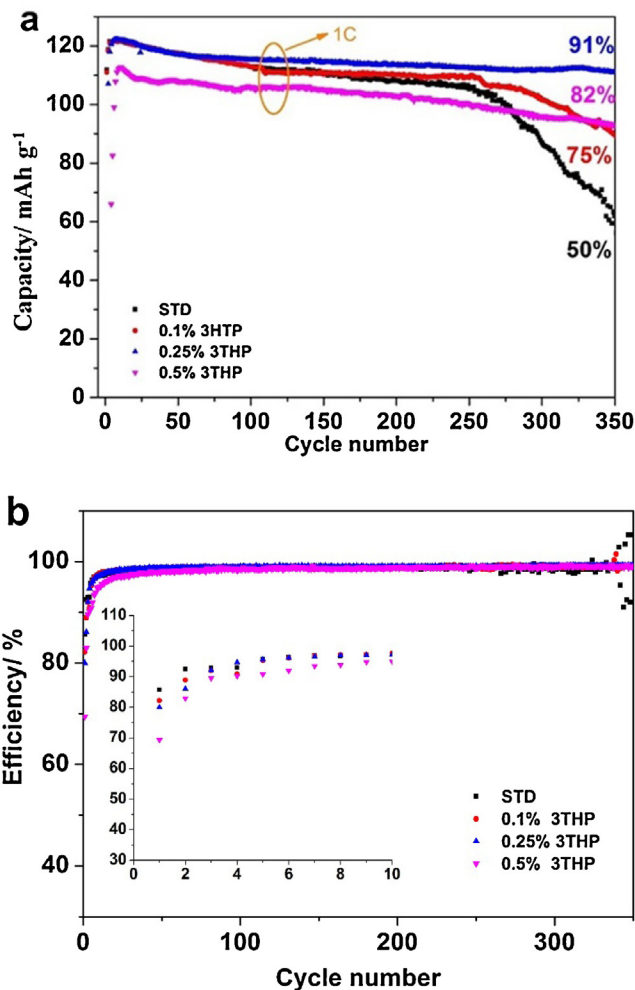


Fig. 1. Cyclic performances of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> in STD and 3THP-containing electrolytes at 0.5C for initial three cycles and 1C rate for the subsequent cycles: cyclic stability (a) and coulombic efficiency (b).

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