



# Improving the electrochemical performance of high voltage spinel cathode at elevated temperature by a novel electrolyte additive



Jiahui Chen, Hui Zhang, Mingliang Wang, Jianhong Liu, Cuihua Li<sup>\*</sup>, Peixin Zhang<sup>\*\*</sup>

Department of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, China

## HIGHLIGHTS

- AMSL is proposed as a novel electrolyte additive for high voltage spinel cathode.
- The cycling performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is dramatically improved by using AMSL.
- A less resistive and high thermal stable SEI film is formed on the cathode surface.
- The AMSL derived SEI film is essential to suppress the electrolyte decomposition.

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## ABSTRACT

In this work, we report a novel electrolyte additive allyloxytrimethylsilane (AMSL) to improve the electrochemical performance of high voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode. In presence of 0.5% AMSL, the discharge capacity retention of  $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cell is improved from 73.1% to 80.2% after 500 cycles at room temperature, and from 52.4% to 92.5% after 100 cycles at 55 °C. Moreover, the  $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cell with AMSL delivers a superior discharge capacity of 95.6 mAh  $\text{g}^{-1}$  at high rate of 3 C, whereas the cell without AMSL only remains 76.8 mAh  $\text{g}^{-1}$ . Theoretical calculation and experimental results reveal that AMSL is oxidized prior to the carbonate solvents during the first charge process and then creates a less resistive and high thermal stable SEI film on the surface of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode. The AMSL derived SEI film, composed of organic silicon-based species, ether moieties and reduced LiF, is responsible for the suppression of serious electrolyte decomposition and dissolution of transition metal ions at high voltage, especially at high temperature.

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## 1. Introduction

Li-ion batteries have been widely used as power sources for portable devices due to their characteristics of high energy and power densities, long cycle life and environmental friendliness [1–3]. However, conventional Li-ion batteries based on layered lithium metal oxides (e.g.  $\text{LiCoO}_2$ ) or olivine phosphates (e.g.  $\text{LiFePO}_4$ ) with poor energy density can hardly satisfy the increasing energy demand for electric vehicles, energy storage systems and other high power applications [4–7]. A high density in Li-ion battery can be obtained by increasing either the operating potential or the reversible capacity of the cathode. As the attempts of increasing

the working potential, spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  was proposed as a high voltage cathode candidate with operating voltage at  $\sim 4.75$  V vs.  $\text{Li}/\text{Li}^+$  and energy density of 650 Wh  $\text{kg}^{-1}$  [8,9]. In this respect,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has been extensively investigated as a promising material for the next generation Li-ion battery.

Although  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode possesses high energy density, its practical application to lithium ion batteries is still quite challenging. Firstly, the conventional electrolyte readily suffers from substantial oxidative decomposition at voltages above 4.5 V vs.  $\text{Li}/\text{Li}^+$  and elevated temperature (for instance, 55 °C), which may result in the formation of resistive and unstable solid/electrolyte interface (SEI) film on the cathode surface [10,11]. In addition, the commonly used  $\text{LiPF}_6$  salt in current commercialized electrolyte is very susceptible to hydrolysis even if trace amounts of water are present in the electrolyte [12], i.e.:  $\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + \text{LiF} + 2\text{HF}$ . The  $\text{PF}_5$ , a thermal decomposition product of  $\text{LiPF}_6$ , can also produce HF via many reaction paths [13]. This resulting HF attacks the

<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author.

E-mail addresses: [licuihuasz@163.com](mailto:licuihuasz@163.com) (C. Li), [pxzhang2000@163.com](mailto:pxzhang2000@163.com) (P. Zhang).

LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode and thus causes Mn and Ni ions dissolution. Moreover, the HF severely consumes active Li<sup>+</sup> to form LiF and promotes useless SEI film growth. These undesired processes significantly scarify battery cycling life, especially at elevated temperature.

To improve the stability of electrolyte, the use of novel electrolyte solvents and electrolyte additives has been extensively investigated. Ionic liquids [14], fluorinated ethers and carbonates [15–17], sulfones [18], and dinitriles [19] with high anodic stability have been explored as high voltage electrolyte solvents. Unfortunately, these solvents still remain problems to be solved, such as, high viscosity, poor compatibility with anodes and difficulties in synthesis. Zhang et al. [20] reported the combination of fluorinated cyclic and linear carbonates together with fluorinated ether as electrolytes to improve the electrochemical performance of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> full cell at elevated temperature. But these fluorinated electrolytes tend to decompose on graphite anode continuously. Dong et al. [21] employed a sulfone/carbonate mixed electrolyte for Li/LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cell and obtained improved capacity retention from 81% to 98% at 5 C rate. According to recent reports, the use of film forming electrolyte additives is an effective and economic way to improve the electrochemical performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode [22]. These additives usually decompose preferentially to form protective film on the cathode surface and thus stabilize the cathode/electrolyte interface and suppress electrolyte decomposition. Yan et al. [23] reported that a stable SEI film can be formed on the LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode through the polymerization of 1-propylphosphonic acid cyclic anhydride (PACA), and consequently suppressed the self-discharge and transition metal ions dissolution, leading to improved cycling stability. By using tris(trimethylsilyl) phosphate (TSP) as an electrolyte additive, Rong et al. [24] improved the capacity retention of Li/LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cell from 70% to 94.9% after 70 cycles at 55 °C (cycled between 3.0 and 4.9 V at 0.5 C). A detailed investigation from Song's group revealed that TSP was capable of eliminating HF from the electrolyte and modifying the surface of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode [25]. Very recently, Huang et al. [26] proposed phenyl trifluoromethyl sulfide (PTS) as additive to enhance the interfacial stability between LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and electrolyte. The Li/LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cell with PTS containing electrolyte exhibited high capacity retention of 95% after 100 cycles at 55 °C (cycled between 3.0 and 4.9 V at 1 C). To date, massive film forming additives have been explored, but the achievement is not satisfying yet. Density functional theory (DFT) calculation provides a more efficient and economic approach for discovering appropriate additives and finding mechanisms of their actions than the experimental trial and error testing.

Bearing this in mind, a novel electrolyte additive, allyloxy-trimethylsilane (AMSL), was screened out through DFT calculation. We expected that it will create a protective SEI film on the LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode surface that can alleviate electrolyte decomposition and transition metal ions dissolution. Based on a comprehensive understanding of the effect of AMSL, electrochemical performances, thermal stability and surface chemistry of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode were systematically investigated.

## 2. Experimental

### 2.1. Calculation methods

All calculations were performed by the Gaussian 09 package [27]. The equilibrium structures were optimized at the DFT/B3LYP level using 6-31 + G (d, p) basis set. Conductor-variant polarized continuum model (CPCM) was employed to investigate the effects of solvents. A dielectric constant of 28.8 was adopted as a volume

average value of the dielectric constants of ethylene carbonate (EC: 89.2), ethyl methyl carbonate (EMC: 2.9) and diethyl carbonate (DEC: 2.8), since EC:EMC:DEC = 3:5:2 (by volume) solution is used as an electrolyte solvent in this study. The frontier molecular orbital energy and Li<sup>+</sup> binding energy were calculated at B3LYP/6-31 + G (d, p) level. The calculated oxidation potential was converted from the free energy cycle for the oxidation reaction [28].

### 2.2. Electrolyte and electrode preparation

Battery grade carbonate solvents and LiPF<sub>6</sub> were kindly provided by Optimum Nano Energy Co. Ltd. AMSL was purchased from Alfa Aesar and used as received. The blank electrolyte was consisted of 1 mol/L LiPF<sub>6</sub> in a solvent mixture of EC, EMC, and DEC in 3:5:2 volume ratio. The additive containing electrolyte was obtained by adding 0.5 wt% AMSL into the blank electrolyte. The HF and water content in these electrolytes were controlled to less than 15 ppm. LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> electrode was prepared with a mixture of 80 wt% LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (Shenzhen Tianjiao Co. Ltd), 10 wt% acetylene carbon black and 10 wt% polyvinylidene (PVDF) binder in N-methylpyrrolidone. The resulting slurry was cast onto an aluminum foil and dried overnight at 70 °C. After drying, the electrode was punched into 14 mm diameter round discs and dried again at 110 °C for 8 h. The active material loading is about 1.6 mg cm<sup>-2</sup>. Graphite electrode was prepared with the same method as LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> electrode, coating a mixture of 80 wt% artificial graphite (Shenzhen Kejing Co. Ltd), 10 wt% acetylene carbon black and 10 wt% PVDF on copper foil. For the electrochemical tests, CR2032 type coin cells were assembled in an Ar-filled glove box (Unilab, Mbraun) with LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode or graphite anode as working electrode, lithium foil as counter electrode, Celgard 2400 polypropylene membrane as separator and prepared electrolyte. Same amount of electrolyte of 50 μL was added for each cell.

### 2.3. Electrochemical measurements

The fabricated Li/LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> coin cells were galvanostatically precycled for three formation cycles at 0.1 C (1 C = 147 mA g<sup>-1</sup>) between 3.5 and 5 V on LAND battery test system (CT2001A, Wuhan Land Electronics Co. Ltd). Thereafter, the cells were cycled at different current densities between 3.5 and 5 V at room (25 °C) and elevated (55 °C) temperature. Rate capability test was conducted at various C rates: 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 3 C. To investigate the impact of AMSL on the graphite anode, Li/graphite cells were galvanostatically cycled at 0.5 C (1 C = 372 mA g<sup>-1</sup>) between 0.01 and 3 V at 25 °C after three formation cycles at 0.1 C. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a potentiostat (1470E, Solartron) coupled with a frequency response analyzer (FRA 1260, Solartron) in frequency range from 10<sup>6</sup> Hz to 0.01 Hz with an amplitude of 10 mV. Cyclic voltammetry was also performed on the Solartron 1470E potentiostat between 0.01 and 2 V with a scan rate of 0.1 mV s<sup>-1</sup>.

### 2.4. Material characterization

After cycling at elevated temperature, the cells were disassembled in Ar-filled glove box. The cathodes were rinsed with anhydrous dimethyl carbonate (DMC) three times to remove residual electrolyte components followed by vacuum drying at 40 °C for surface characterization and thermal stability test. Surface morphology of the cathodes was observed by field emission scanning electron microscopy (FE-SEM, S3400N, Hitachi). X-ray photoelectron spectroscopy system (XPS, Quantera-II, Ulvac-Phi) was used to analyze the surface compositions, using a focused monochromated Al K $\alpha$  radiation under ultra-high vacuum. All XPS

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