



Triphenyl phosphite as an electrolyte additive to improve the cyclic stability of lithium-rich layered oxide cathode for lithium-ion batteries



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ARTICLE INFO

Article history:

Received 17 June 2016

Received in revised form 2 September 2016

Accepted 2 September 2016

Available online 4 September 2016

Keywords:

Lithium-ion battery

Electrolyte additive

Triphenyl phosphite

Lithium-rich layered oxide cathode materials

High voltage

ABSTRACT

Triphenyl phosphite (TPPi) was investigated as an electrolyte additive for high-voltage lithium-ion batteries using lithium-rich layered oxide cathode in this paper. The cyclic stability of $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ was improved significantly with the adoption of 0.2 wt. % TPPi. The capacity retention of $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ was improved significantly, especially at elevated temperature, from 69.0% to 89.6% after 90 cycles. Electrochemical and physical characterizations indicated that TPPi was oxidized at 4.2 V (vs. Li/Li^+), which was lower than that of the solvents and lithium extraction from $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$, and the oxidization resulting in an artificial cathode interface film, which effectively inhibited the decomposition of traditional electrolyte and protected $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ material from destruction.

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1. Introduction

In recent years, lithium-rich layered oxide cathode materials, represented by the chemical formula $z\text{Li}_2\text{MnO}_3 \cdot (1-z)\text{LiMO}_2$ ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{etc.}$), have attracted a substantial amount of attention as promising cathode materials of high-energy lithium-ion batteries owing to their high working potential, high specific capacity ($\sim 250\text{ mAh g}^{-1}$), low cost, and good safety performance [1–3]. However, there are still some tough problems, such as poor cyclic stability, hindering their practical application in lithium ion batteries [4,5]. Since the cut-off voltage of this material is as high as 4.6–4.8 V, oxidative decomposition of LiPF_6 /carbonate-based electrolytes accompanied by the formation of a resistive and unstable surface film on the cathode during cycling, will accelerate the dramatically fading of capacity and the deterioration of polarization [6–10]. More importantly, for lithium-rich layered oxide cathode materials, the active oxygen radicals generate from oxygen molecule evolves in the first charging step, which leads to further decomposition of electrolytes and worsens the electrochemical performance of the cathode materials [11–13].

Researchers have preceded a large number of studies to overcome these difficulties, including surface modification of cathode materials with inorganics and optimization of electrolytes [8,14–17]. Among these, electrolyte additive is flexible and effective to stabilize the electrode/electrolyte interface [18–20]. A variety of electrolyte additives with different molecular structure were proposed [7,21,22]. Phosphite-based additives with a trivalent phosphorus atom have been reported as electrolyte additives for high-voltage cathode materials [23]. Xiang et al. [24] investigated the effect of trimethyl phosphite (TMPi) on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ and suggested that the TMPi derived SEI could effectively deactivate the catalyzing effect of some transition metal species on the cathode surface. Tris (trimethylsilyl) phosphite (TMSPi) was reported as an oxygen scavenger that remarkably reduced the internal pressure of lithium-rich oxide/graphite full cell owing to its trivalent phosphorus atom and a more stable passivation layer was formed on the cathode using TMSPi as an electrolyte additive [8]. TMSPi was also proposed as a film-forming additive for 5 V-class $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes that alleviates not only the severe electrolyte decomposition, but also the decomposition of LiPF_6 by hydrolysis [25].

Triphenyl phosphite (TPPi) has been investigated as a flame retardant additive for lithium ion battery that can depress the flammability of electrolyte in our previous report [26]. And it is found that a passivation layer derived from TPPi formed on the surface of the LiFePO_4 electrode at high voltage. In this paper, based on the previous work, we proposed TPPi as an electrolyte additive

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to improve the cyclic stability of $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ cathode for the first time. The effect of TPPI on the electrochemical performance and surface chemistry of the cathode material are investigated by electrochemical and physical characterizations.

2. Experimental

2.1. Preparation

Triphenyl phosphite (TPPI) was purchased from Sigma-Aldrich Co., Ltd. and adopted without further purification. Battery-grade ethylene carbonate (EC), ethyl methyl carbonate (EMC) and lithium hexa-fluorophosphate (LiPF_6) were provided by Guangzhou Tianci Materials Technology Co., Ltd. After carbonate solvents dewatered by adding 4A molecular sieve, EC/EMC = 1:2 (volume ratio) with 1 mol/L LiPF_6 was prepared as the blank electrolyte. A certain amount of TPPI was added to the blank electrolyte as the comparative electrolyte.

$\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ was provided by Harbin Coslight Power Co., Ltd and $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ electrode was prepared by coating the slurry of 80 wt. % active materials, 10 wt. % Super-P and 10 wt. % polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone (NMP) solvent onto Al foil current collector. Afterwards, the slice was dried under vacuum and punched into disks, which was compressed subsequently to make materials more compact. Finally, CR2025-type coin cells were assembled with as-prepared electrodes, metallic lithium foil (as the counter electrode and the reference electrode), separator (Celgard2500) and different kinds of as-prepared electrolytes in the argon-filled glove box (<1 ppm H_2O , <10 ppm O_2).

2.2. Characterization

The electrochemical performance of $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2/\text{Li}$ coin cells using Neware BTS Test Control was galvanostatically tested over the range of 2.0–4.8 V at 0.5C ($1\text{C} = 250\text{ mA g}^{-1}$) after three formation cycles at 0.1C at room temperature (25 °C) and elevated temperature (55 °C), respectively.

Linear sweep voltammetry (LSV) was performed with a three-electrode system, in which Pt electrode is used as the working electrode and lithium tablet as both reference electrode and counter electrode from 3 V to 6.5 V at a scan rate of 0.1 mV s^{-1} . After the $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2/\text{Li}$ coin cells were charged to 4.3 V and then rest for 10 h, electrochemical workstation (PARSTAT2273) was adopted to measure the electrochemical impedances spectroscopy (EIS) in a frequency ranging from 100 KHz to 10 mHz with an amplitude of 10 mV.

The cycled $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2/\text{Li}$ coin cells in different electrolytes were disassembled in an argon-filled glove box and the cathodes were taken out and rinsed with anhydrous DMC for three times to remove away residual solvents and salts. After that, the electrodes were dried in a vacuum chamber at room temperature before testing. The surface morphology was observed with scanning electron microscope (SEM, VEGA 3 SBH). The compositions of surface film on $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ cathodes were measured by X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA system) adopting Al $\text{K}\alpha$ radiation ($h\nu = 1486.6\text{ eV}$) as the X-ray light source. The energy scale was calibrated by the C 1s peak at 284.6 eV, and fitted by XPS peak software. The crystal structures of the pristine and cycled $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ electrodes were characterized by X-ray diffraction (XRD, Empyrean) using Cu $\text{K}\alpha$ radiation.

3. Result and discussion

The majority of electrolyte additives for the cathode protection are based on its preferential oxidation compared to the base electrolyte [27–31]. Therefore, oxidation potential is very important to understand the mechanism of additives on electrochemical performance. To evaluate the oxidation potential of Triphenyl phosphite (TPPI), linear sweep voltammetry (LSV) was adopted at platinum foil with a three-electrode system. As shown in Fig. 1a, TPPI was oxidized over 4.2 V (vs. Li/Li^+) with a significant increase of oxidation current in the LSV curve. By contrast, the electrolyte without additive was stable until 4.5 V, which demonstrates that TPPI will oxidative decompose before solvents of electrolyte. Fig. 1b shows the first charge-discharge curves of $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2/\text{Li}$ coin cells between 2.0 and 4.8 V. The charge capacity is increased after adding TPPI, indirectly indicating the electrochemical oxidation caused by TPPI during the first charging step. It is noted that the polarization of the first cycle increased slightly by TPPI, which may due to the artificial interface film derived from TPPI.

Fig. 2 shows the cycling performance of $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2/\text{Li}$ coin cells at 0.5C between 2.0V and 4.8 V at room temperature after three activation cycles. After activation, the discharge capacity of $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2$ in blank electrolyte dropped from 204.3 mAh g^{-1} to 177.5 mAh g^{-1} after 90 cycles, with the capacity retention of 86.3%. This capacity decay results from the unstable electrode/electrolyte interface at high voltages and irreversible phase transition during cycling [32,33]. When 0.2 wt. % TPPI was introduced into the electrolyte, the capacity retention after 90 cycles has been improved to 91.2%, which was ascribed to alternative cathode interface film derived from TPPI. It should be note that the discharge capacity and coulombic

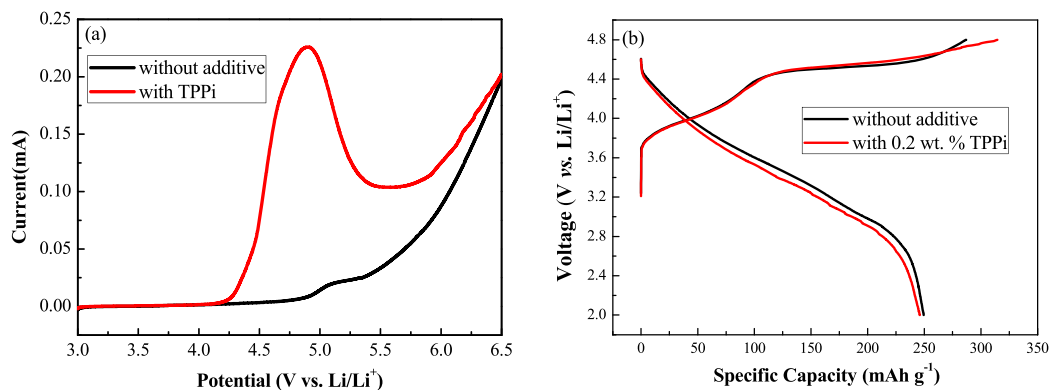


Fig. 1. (a) Linear sweep voltammograms of Pt electrodes in blank electrolyte and 0.2 wt. % TPPI containing electrolyte at a scan rate of 1 mV s^{-1} , (b) first charge-discharge curves of $\text{Li}_{1.16}\text{Ni}_{0.2}\text{Co}_{0.1}\text{Mn}_{0.54}\text{O}_2/\text{Li}$ coin cells between 2.0 and 4.8 V.

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