Journal of Power Sources 344 (2017) 111–118

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Stabilizing interface layer of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials under high voltage using *p*-toluenesulfonyl isocyanate as film forming additive

Peng Dong [a], Ding Wang [a, *], Yao Yao [a], Xue Li [a], Yingjie Zhang [a, b], Juanjian Ru [b], Ting Ren [b]

[a] National and Local Joint Engineering Laboratory for Lithium-ion Batteries and Materials Preparation Technology, Key Laboratory of Advanced Battery Materials of Yunnan Province, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China
[b] Faculty of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

HIGHLIGHTS

- PTSI is proposed as film forming additive for layered cathode for the first time.
- The cyclic stability and rate capability are obviously enhanced with PTSI additive.
- PTSI additive tends to be oxidized before the carbonate solvents.
- The electrolyte decomposition is suppressed by PTSI derived passivation film.

ARTICLE INFO

Article history:
Received 18 October 2016
Received in revised form
7 December 2016
Accepted 27 January 2017

Keywords:
p-Toluenesulfonyl isocyanate
High voltage
Lithium ion battery
Electrolyte additive
Solid electrolyte interphase
Surface passivation

ABSTRACT

p-Toluenesulfonyl isocyanate (PTSI) is introduced as electrolyte additive in a bid to enhance the electrochemical performances of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials under high voltage. A less resistive and stable film on the cathode surface derived from PTSI oxidation which taken place prior to the carbonate solvents is formed. As a result, the discharge capacity retention of $Li/LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cell is elevated from 71.4% to 86.2% after 100 cycles at room temperature, and from 32.3% to 54.5% after 100 cycles at 55 °C. In addition, the $Li/LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ half cell with PTSI exhibits superior rate capability compared to that in baseline electrolyte. The improved performance is not only ascribed to the thin protective layer originated from PTSI decomposition which prevent the successive breakdown of the electrolyte on cathode surface, but it is also attributed to the $-S{=}O$ group in PTSI serves as the weak base site to restrain the reactivity of PF_5, resulting in the suppression of LiF formation and HF generation.

1. Introduction

To meet the demand for the development of high energy density lithium ion batteries (LIBs), positively widening the working voltage window of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials has been confirmed a feasible strategy to attain this goal [1–3]. However, the high voltage operation (>4.3 V vs. Li/Li^+) of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials required for high capacity is inevitably accompanied by the collapse of bulk layered structure and the oxidative decomposition of the conventional electrolyte leads to the formation of growing amount of a resistive film on the surface of cathode [4–6]. These are vital bottlenecks must be addressed before its large-scale applications. Fortunately, the former issue can be resolved by coating with inorganic compounds on the cathode surface such as Al_2O_3, Li_2ZrO_3, and V_2O_5, which could protect cathode from structure transformation to some extent [7–10]. However, the electrolyte trend to lose electrons due to the relatively large highest occupied molecular orbital (HOMO) energies of electrolyte components [11–15]. Accordingly, the electrolyte oxidation cannot be alleviated by surface modification during the repeated high voltage operation.

Current strategies to circumvent the challenges of electrolyte oxidation include the design and synthesis of inherently stable electrolytes that possess a high anodic stability and the

---

* Corresponding author.
E-mail addresses: wangding@kmust.edu.cn, wangdingliverpool@foxmail.com (D. Wang).

http://dx.doi.org/10.1016/j.jpowsour.2017.01.116
0378-7753/

development of suitable electrolyte additives to stabilize the interphase between electrode/electrolyte [16–18]. From the tech-economic point of view, the latter approach is more practical and promising. In the course of the past several years, numerous efforts have been made to explore suitable electrolyte additives for $LiNi_{1-x-y}Co_xMn_yO_2$ cathode materials under high voltage [12,13,15,19–27]. Zuo et al. pointed out that the capacity retention of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite full cells is greatly enhanced by adopting tris(trimethylsilyl)borate and lithium tetrafluoroborate as additives [19,20]. Yan et al. reported that tris(trimethylsilyl)phosphate can form a stable solid electrolyte interface (SEI) film at the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode surface to improve the cycle capability and coulombic efficiency of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ at 3.0–4.5 V [22]. Lee et al. found that the striking performance improvements are fulfilled through interfacial stabilization using methyl(2,2,2-trifluoroethyl) carbonate as a novel additive [21]. Moreover, dopamine, tris(2,2,2-trifluoroethyl)phosphite, and 1,1'-sulfonyldiimidazole have also been evaluated as electrolyte additives for high voltage LIBs [25,26,28].

Generally, the additive acts as a sacrificial substance that is decomposed at a lower potential than the baseline electrolyte or electrochemically oxidized to polymer on cathode surface. The formed protective and conductive film originated from the oxidation products plays a dominant role in ameliorating high voltage performances of cathode materials, and it is easy to implement practical application. Recently, *p*-toluenesulfonyl isocyanate (PTSI) is employed as film-forming additive both for $LiMn_2O_4$ cathode at conventional voltage range and $Li_4Ti_5O_{12}$ anode [29,30]. And the outstanding improvement results are obtained on account of the stable passive film derived from PTSI oxidation, the suppression of HF generation, and the inhibition of LiF formation. However, the possible mechanism of the reduction of PTSI on cathode surface is not provided in detail. To the best of our knowledge, the promising performance of PTSI as layered cathode film-forming additive under high voltage has not been proposed in literature. Hence, inspired by the excellent property of PTSI, the influence of PTSI additive on the electrochemical performances in layered structure $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials both at high voltage and elevated temperature is evaluated in current work. Also, the effects of PTSI on the SEI composition and formation mechanism on the surface of cathode are investigated in depth.

2. Experimental

2.1. Preparation of electrolyte and electrode

A mixture of ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 in wt. ratio) containing 1 M $LiPF_6$ (Jiangxi Youli New Materials Co., Ltd) was used as the reference electrolyte (marked as RE). The desired amount of PTSI (SIGMA-ALDRICH, assay $\geq$ 98%) was dissolved into the RE to final PTSI wt.% of 0.5% without further purification in an argon filled glove box.

The commercial $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (Hunan Shanshan Toda Advanced Materials Co., Ltd) material was used to prepare the cathode without further treatment. The electrodes were fabricated by blending 80 wt% $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, 10 wt% Super P carbon and 10 wt% poly(vinylidene fluoride) thoroughly followed by being dispersed in *N*-methylpyrrolidinone (NMP), and then coating on aluminum foil. After dried under vacuum for 12 h at 120 °C, the disc-like electrodes with a diameter of 14 mm and an active mass loading of about 1.8 mg cm^{-2} were punched out for assembling 2025-coin type cells using Celgard 2400 as separator and lithium foil as the counter and reference electrode.

2.2. Electrochemical measurements

The linear sweep voltammetry (LSV) experiments were conducted on Electrochemical Workstation (CHI604E, Chenhua, China) with a three-electrode system incorporating platinum working electrode or $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ working electrode and lithium foil as counter and reference electrodes at a scan rate of 0.1 mV s^{-1}. Electrochemical charge-discharge tests were evaluated with as-prepared 2025-coin type cells employing Neware battery circler between 3.0 and 4.5 V (vs. Li/Li^+) with a desired C rate (1 C corresponds to 160 mA g^{-1}) at room (25 °C) and elevated (55 °C) temperatures. Electrochemical impedance spectroscopy (EIS) measurements of the cells were also carried out at 100% state of charge (SOC) after different cycle numbers in a frequency range from 0.01 to 100 kHz, and the perturbation amplitude was 5 mV.

2.3. Morphological and compositional characterizations

The cycled cells were disassembled in the glove box filled with argon gas. The cathode was rinsed with high purity dimethyl carbonate (DMC) three times to remove the residual electrolyte, and then was dried in a vacuum chamber at 60 °C for 12 h prior to analysis. The detailed morphologies of the fresh cathode and cycled cathode were measured by scanning electron microscope (JEOL, JSM-5612LV) and transmission electron microscope (TEM, Titan, G2 60–300). The crystal structure of the electrodes was analyzed by X-ray powder diffraction (XRD, Rint-2000, Rigaku) using Cu-Ka radiation under the incidence angle range of 10° to 80° at a scanning rate of 5° min^{-1}. X-ray photoelectron spectroscopy (XPS, Perkin-Elmer, PHI 5600) was used to identify the elements composition on the cathode surface.

3. Results and discussion

In order to identify possibility for the use of PTSI as a cathode additive, LSV experiments were conducted with a three-electrode cell. As shown in Fig. 1(a), the RE decomposes until 4.55 V (vs. Li/Li^+), while the start oxidation potential of the PTSI-containing electrolyte is around 4.0 V (vs. Li/Li^+). As expected, the PTSI possesses lower oxidation potential than RE, which indicates that PTSI decomposes preferentially. As a consequence of the PTSI oxidation, a protective film on the cathode surface could effectively prevent the continuous decomposition of solvents under high voltage condition.

Fig. 1(b) presents the LSV curves of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ working electrode with a three-electrode cell at different electrolytes. As can be seen in Fig. 1(b), the oxidation current of the PTSI-containing electrolyte emerges slightly earlier than the RE, and again demonstrating that PTSI is decomposed preferentially to the RE. Furthermore, PTSI-containing electrolyte does not influence the electrochemical performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ electrode, which reveals the well electrochemical compatibility is existed between PTSI and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ electrode.

Fig. 2(a) displays the initial charge-discharge curves at 0.1 C of the $Li/LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ half cells in RE and PTSI-containing electrolytes. It can be seen that the discharge capacity and coulombic efficiency of the cell in RE are 197.2 mAh g^{-1} and 84.3%, while those of the cell in PTSI-containing electrolyte are 200.4 mAh g^{-1} and 86.5%, indicating that PTSI could enhance the capacity and coulombic efficiency of the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material at high voltage state.

The influences of PTSI additive on cyclic performances of $Li/LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ half cells at room (25 °C) and elevated (55 °C) temperatures at 1 C are shown in Fig. 2(b) and (c). As illustrated in Fig. 2(b), the capacity retention of the $Li/LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ half