



Facilely solving cathode/electrolyte interfacial issue for high-voltage lithium ion batteries by constructing an effective solid electrolyte interface film



Jingjing Xu^a, Qingbo Xia^{a,b}, Fangyuan Chen^{a,b}, Tao Liu^a, Li Li^{a,b}, Xueyuan Cheng^{a,b}, Wei Lu^a, Xiaodong Wu^{a,*}

^a *i-Lab, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China*

^b *Nano Science and Technology Institute, University of Science and Technology of China, China*

ARTICLE INFO

Article history:

Received 18 November 2015

Received in revised form 16 January 2016

Accepted 19 January 2016

Available online 22 January 2016

Keywords:

High-voltage Lithium ion batteries

Cyclic performance

Solid electrolyte interphase (SEI)

Oxidable additive

Cathode/electrolyte interface

ABSTRACT

The cathode/electrolyte interface stability is the key factor for the cyclic performance and the safety performance of lithium ion batteries. Suppression of consuming key elements in the electrode materials is essential in this concern. In this purpose, we investigate a facile strategy to solve interfacial issue for high-voltage lithium ion batteries by adding an oxidable fluorinated phosphate, Bis(2,2,2-trifluoroethyl) Phosphite (BTfEP), as a sacrificial additive in electrolyte. We demonstrate that BTfEP additive could be oxidized at slightly above 4.28 V which is a relatively lower voltage than that of solvents, and the oxidative products facilitate *in-situ* forming a stable solid electrolyte interphase (SEI) film on the cathode surface. The results manifest the SEI film validly restrains the generation of HF and the interfacial side reaction between high-voltage charged $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) and electrolyte, hence, the dissolution of Mn and Ni is effectively suppressed. Finally, the cyclic performance of LNMO after 200 cycles was remarkably improved from 68.4% in blank electrolyte to 95% in 1 wt% BTfEP-adding electrolyte.

© 2016 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Lithium ion batteries (LIBs) have been widely used as power sources in portable electronic devices and also are promising as power battery for electric vehicles. But the limitation on energy density confines the usage development in electric vehicles. Many efforts have been carried out for developing high-voltage cathode materials to enhance energy density, such as Li-rich cathode materials [1–3] and spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [4–7]. However, their common demerit is the voltage plateau is beyond 4.5 V which is regarded as the top limit voltage of the conventional carbonate-based liquid electrolyte [8,9]. Thus, the high voltage will lead to severe electrolyte oxidization on cathode surface [10,11]. Moreover, interfacial side reaction between high-voltage charged cathode material and the liquid electrolyte is unavoidable, which is even more vigorous at elevated temperatures. As a result, the

unstable cathode/electrolyte interface provokes serious capacity loss during high-voltage charge/discharge cycles.

In order to overcome such shortcoming, one proverbial way is to modify the cathode material surface by coating it with a film layer which is Li-ion-conductive but electron insulating. The coating layer materials are usually aluminium compound or phosphate, such as Al_2O_3 [12,13], AlF_3 [2,14], AlPO_4 [15,16], and Li_3PO_4 [17,18], which have been proved being effective and stable when they endure high-voltage cycles or high-temperature cycles. Unfortunately, the coating processes are often complex and cost-consuming methodologies but difficult to achieve uniform coating.

Numerous studies have proved that using a film-forming chemical additive in electrolyte is a very facile strategy to solve the interfacial issue between negative electrode and liquid electrolyte. In this approach, the additive is reduced and subsequently a SEI layer *in-situ* forms on negative electrodes. Thus, the interfacial side reaction is effectively prevented and the cyclic performance is eventually improved [19–23]. Enlightening by these researches, using a film-forming additive to get over the interfacial issue for high-voltage LIBs has recently drawn considerable attention [24–28]. An excellent film-forming additive for high-voltage LIBs should show the following properties: 1) can be dissolvable and

* Corresponding author at: No. 398 Ruoshui Road, SEID, Suzhou Industrial Park, Suzhou, Jiangsu Province 215123, China. Tel.: +86 051262872763; fax: +8651262603079.

E-mail address: xdwu2011@sinano.ac.cn (X. Wu).

stable in electrolyte; 2) can be preferentially oxidized than solvents and the oxidative products form a SEI film on cathode surface; 3) more importantly, the resulting SEI film should be robust during high-voltage cycles [19–28].

Among many film-forming additives for high-voltage LIBs, phosphite-based additives have been reported they can scavenge HF in electrolyte and subsequently form P-O based compound SEI film on cathode surface [29–31]. In our previous work, we have demonstrated a reductive P-containing compound, triphenylphosphine, was easy to be oxidized forming a SEI film on the cathode [32]. Phosphites are also P-containing compounds with reductive property, so we believe they are oxidizable SEI former. In this study, we proposed a new mechanism of bis (2, 2, 2-trifluoroethyl) phosphite additive (BTfEP, the molecular structure shown in Fig. S1), which not only was as HF scavenger, but also as an oxidizable and self-sacrificial additive. Cyclic voltammetry (CV) demonstrated that BTfEP can be preferentially oxidized than solvents. A SEI film composed of the oxidative products of BTfEP additive was confirmed to be formed on high-voltage $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO) cathode surface by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). More notably, the advantageous influence of SEI film on high-voltage cyclic performance is directly proved to relate with the inhibition of HF generation and the suppression of dissolution of Mn and Ni.

2. EXPERIMENTAL SECTION

2.1. Electrolyte preparation and cells assembling

The electrolyte, 1.0M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethylmethyl carbonate (EMC) (1/1/1, in volume), was purchased from Guangzhou Tinci Materials Technology Co. Ltd., China. The water content of the electrolyte was 13.7 ppm. The additive BTfEP, with a purity over 94%, was a production of J&K Scientific Ltd. The electrolyte and BTfEP were stored in a glove box with high purity argon and a low moisture atmosphere (<10 ppm).

The electrolyte preparation and the cell assembly were performed in a dry glove box filled with high purity argon. The electrolyte with 1.0M LiPF_6 in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1/1/1, in volume) was employed as base electrolyte in this work (defined as BEL). BTfEP was added in base electrolyte and stirred to prepare the functional electrolytes with the concentration of BTfEP as 0.5 wt%, 1 wt% and 2 wt% (defined as $\text{FEL}_{0.5}$, FEL_1 , and FEL_2 , respectively. The subscript numbers represented the weight percentages of BTfEP in the electrolytes).

LNMO electrodes were prepared by coating the mixture of 88 wt% LNMO cathode materials (Production of Xingneng New Material Co. Ltd.), 5 wt% acetylene black (AB) and 7 wt% LA132 binder (a kind of polyacrylate binder) on Al current collector. Deionized water was used as the solvent. Coin cells were fabricated with LNMO electrode as the positive, lithium foil as the negative and Celgard 2400 as the separator. Each coin cell contained 50 μL of electrolyte.

2.2. Material Characterization

The surface morphologies and element analysis of the LNMO cathodes were characterized by SEM and affiliated energy-dispersive spectroscopy (EDS). The samples for analyses were obtained from the cycled cells. The disassembled LNMO electrodes for SEM and EDS measurements were washed with anhydrous DMC solvent for 3 times to remove residual EC and LiPF_6 salt.

The XPS was conducted on AXIS ULTRA DLD and the graphite peak at 284.7 eV was used as a reference for the final adjustment of

the energy scale in the spectra. XPS peak software was used for spectra fitting. The samples were obtained from the cycled cells.

2.3. Electrochemical measurements

Electrochemical performances of LNMO electrodes in all electrolytes were determined using coin cells by cyclic voltammetry (CV) on RST-5200 instrument (Suzhou Ruisite Co. Ltd., China) and the scan rate of CV was 0.05 mV s^{-1} . The cyclic stability of the cells was measured on Neware battery test system at room temperature in the voltage range of 3.5–4.95 V at a constant current density of 147 mA g^{-1} (1C-rate).

2.4. Quantitative characterization of Mn and Ni dissolution from LNMO cathodes

To understand the influence of BTfEP additive on improving cyclic performance, the concentrations of Mn and Ni dissolution were quantitatively characterized. Firstly, LNMO/Li cells using BEL and FEL_1 were experienced 5 cycles to make BTfEP fully oxidized, and then LNMO-BEL cathode and LNMO- FEL_1 cathode were taken from the fully charged cells and washed three times by DMC. The resulting LNMO cathodes (around 8.8 mg LNMO) were stored in the fresh commercial electrolyte (5 mL) at 55°C . In order to avoid the interference of the air, all the experimental processes were completed in a glove box, including taking LNMO cathodes from the cells and washing them for three times by DMC, placing the cathodes into the glass vials with the electrolytes, and finally greasing and sealing the ground stopper. The concentrations of Mn and Ni dissolved into the electrolytes were quantitatively tracked as a function of storage time using inductively coupled plasma optical emission spectroscopy (ICP-OES, OPTIMA 2100 DV, PerkinElmer).

3. RESULTS AND DISCUSSION

3.1. Improved cyclic performance of LNMO/Li cells by using BTfEP adding electrolyte

Fig. 1a presented the cyclic stability of LNMO/Li cells using electrolytes with different concentration of BTfEP. The capacities of the involved cells were normalized to calculate the capacity retention (The actual 1C capacity values were given in Fig. S2.). It can be seen the capacities retention of LNMO after 200 cycles were 68.4% (■, black), 84.0% (●, red), 95.0% (▲, blue) and 89.0% (▼, olive) for BEL, $\text{FEL}_{0.5}$, FEL_1 , and FEL_2 samples, respectively. Apparently, the introduction of BTfEP significantly improved the cyclic performance of LNMO cathode and the performance showed sensitive dependence on the BTfEP concentration, and the optimal concentration of 1 wt% was selected for further experiments. The Coulombic efficiencies of LNMO cathodes during cycling were shown in Fig. 1b. Due to the irreversible oxidation of BTfEP additive, the initial coulombic efficiency with BTfEP is lower than that without BTfEP. After the irreversible oxidation totally completed, all coulombic efficiencies were close to 99%, implying all the cells showing good reversibility.

The first charge/discharge profiles of LNMO/Li cells using electrolytes with different concentration of BTfEP cycled at 147 mA g^{-1} (1C-rate) were shown in Fig. 1c. It can be seen that with the concentration of BTfEP increasing, a voltage plateau around 4.28 V got longer and the first charging capacity increased, which related with the oxidation of BTfEP additive. To further understand the effect of BTfEP, two separate LNMO/Li cells using BEL and FEL_1 were cycled at 14.8 mA g^{-1} (0.1C-rate) to make BTfEP oxidized sufficiently and the first charge/discharge profiles were shown in Fig. 1d. For BEL cell, a voltage plateau appeared at around 4.7 V (■,

Download English Version:

<https://daneshyari.com/en/article/6609262>

Download Persian Version:

<https://daneshyari.com/article/6609262>

[Daneshyari.com](https://daneshyari.com)