



Improving cyclic stability of lithium nickel manganese oxide cathode for high voltage lithium ion battery by modifying electrode/electrolyte interface with electrolyte additive



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ABSTRACT

We report a new approach to improve the cyclic stability of lithium nickel manganese oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) cathode, in which the cathode/electrolyte interface is modified by using prop-1-ene-1, 3-sultone (PES) as an electrolyte additive. The interfacial properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode in PES-containing electrolyte have been investigated by scanning electron spectroscopy (SEM), transmission electron microscopy (TEM), thermal gravimetry (TG), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), cyclic voltammometry (CV), chronoamperometry (CA), and constant current charge/discharge test. It is found that the application of PES improves significantly the cyclic stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. After 400 cycles at 1C rate ($1\text{C}=147\text{ mA g}^{-1}$), the capacity retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is 90% for the cell using 1.0 wt% PES, while only 49% for the cell without the additive. The characterizations from SEM, TEM, TG, XRD, and XPS confirm that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /electrolyte interface is modified and a protective solid electrolyte interface film is formed on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles, which prevents $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ from destruction and suppresses the electrolyte decomposition.

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1. Introduction

Although lithium ion battery is superior to other secondary batteries in terms of energy density and cycle life [1–3], the energy density of currently commercialized lithium ion battery cannot meet the demands of large-scale applications such as in electric vehicles. One of the ways to improve the energy density of lithium ion battery is to apply new cathodes with high working potential. Recently, spinel-structured lithium nickel manganese oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) has received much attention, because it provides a working potential as high as 4.7 V, vs Li/Li^+ [4–6]. However, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ suffers serious capacity fading when it is cycled due to the instability of cathode/electrolyte interface, which results from the oxidation decomposition of the conventional electrolyte

under high operating potential [7,8] and the destruction of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [5,9,10]. It remains a challenge to overcome the interfacial instability between $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode and electrolyte.

Surface coating of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with various inorganic oxides [11–15] and substitution of new electrolytes for current carbonate-based electrolyte [16–18] have been proposed to improve the stability of electrode/electrolyte interface. The surface coating with inorganic oxide is usually at the expense of capacity loss and increases the manufacturing cost, while the new electrolytes, such as lactone- or sulfone-based electrolytes, exhibit poorer compatibility with the electrode and lower ionic conductivity than the carbonate-based electrolyte.

Applying various inorganic and organic additives to the electrolyte is an economic and effective approach for the improvement of lithium ion battery performance. Since the inactive surface films were observed on the cathodes of lithium ion batteries [19–21], the idea on the application of electrolyte additives for the formation of solid electrolyte interface

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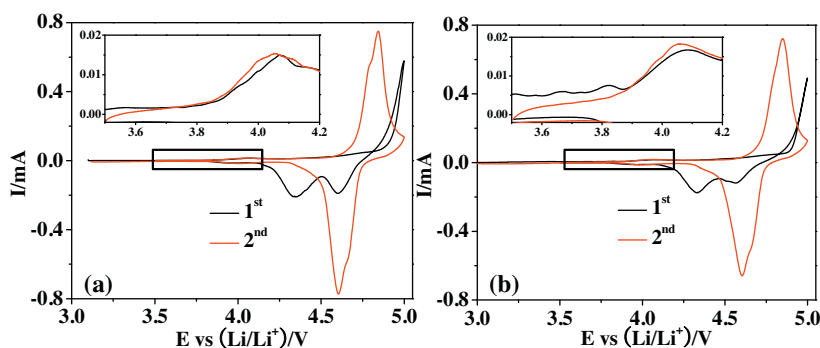


Fig. 1. Cyclic voltammograms of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes in 1.0 mol dm^{-3} $\text{LiPF}_6/\text{EC-EMC}$ (1:2) electrolyte without (a) and with 1.0 wt% PES (b). Scan rate: 0.1 mV s^{-1} .

(SEI) has been adopted for the protection of cathodes and the prevention of electrolyte decomposition on the cathode [22]. Some additives have been developed to improve the performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode, including lithium bis(oxalato) borate [23,24], dimethyl methyl phosphonate [25], tris (pentafluorophenyl) phosphine [26], tris (trimethylsilyl) phosphate [27], 2,5-dihydrofuran and γ -butyrolactone [28].

We previously reported that prop-1-ene-1, 3-sultone (PES) was an effective SEI-forming additive for graphite anode, especially in propylene carbonate based electrolytes [29,30]. Interestingly, PES was also found to be able to form protective film on LiMn_2O_4 cathode and subsequently to improve battery performance at elevated temperature (60°C) [31]. In this work, PES was newly evaluated as an electrolyte additive to improve the cyclic stability of high potential $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. The interfacial properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode in PES-containing electrolyte were understood, in terms of the preferential oxidation of PES, the morphology and structure of the cycled electrode and the composition of the formed SEI film.

2. Experimental

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode was prepared by coating a mixture of 80.0 wt% $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Sichuan Xingneng Co. Ltd, China), 10.0 wt % super-p, and 10.0 wt% poly (vinylidene difluoride) (PVdF) binder onto an Al current collector. 2025-type coin cells of Li/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were set up by using $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes, lithium foil as the counter electrodes and microporous membrane (Celgard 2400) as the separator. Each coin cell contained $30 \mu\text{L}$ of electrolyte. The base electrolyte in this work was 1.0 mol dm^{-3} LiPF_6 in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1:2 in weight, Guangzhou Tinci Materials Technology Co. Ltd, China). PES was purchased from Lianchuang Company (Anhui Lianchuang Medicinal Chemistry Co. Ltd, China). The cells assembling and electrolyte preparation were conducted in a glove box (Mbraun Unilab MB20) under a dry argon atmosphere (the contents of water and oxygen were controlled to lower than 0.1 ppm).

Cyclic voltammetry and chronoamperometry were performed on Solartron-1470 instrument (England) with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode as working electrode and lithium as reference and counter electrode. Charge/discharge test was performed with 1C rate ($1\text{C}=147 \text{ mA g}^{-1}$) over the range of 3.50–4.95 V (vs Li/Li^+) on a LAND cell test system (Land CT 2001A) at room temperature (25°C).

The cycled electrodes for structure and composition characterizations were washed three times with anhydrous dimethyl carbonate to remove residual LiPF_6 salt, and then evacuated overnight at room temperature. The surface morphology was observed with scanning electron spectroscopy (SEM, JEOL-5900)

and high-resolution transmission electron microscopy (TEM, JEM-2100h). Thermal behaviors were analyzed on Perkin-Elmer TGA7 ramping the temperature from room temperature to 600°C . The crystal structure was determined by X-ray diffraction (XRD, D8 Advance X-ray diffractometer) operated at 60 kV and 80 mA using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ nm}$) in the 2θ range of $15\text{--}80^\circ$. The surface composition was analyzed with X-ray photoelectron spectroscopy (XPS) on ESCALAB 250 using a focused monochromatized $\text{Al K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) under ultra high vacuum. The final adjustment of the energy scale was made based on the C 1s peak of graphite at 284.3 eV. The spectra obtained were fitted using XPSPeak 4.1. Lorentzian and Gaussian functions were used for the least-square curve fitting procedure.

3. Results and discussion

The preferential oxidation of PES on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was evaluated with cyclic voltammetry. Fig. 1 presents the cyclic voltammograms of the first two cycles of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes in electrolytes with and without PES. The profiles of the first and the second cycles do not overlap due to the incomplete impregnation of the electrolyte into the electrode. Two redox peaks can be identified in the second cycle. One at about 4.1 V (vs Li/Li^+) is ascribed to $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple and the other at about 4.8 V (vs Li/Li^+) is related to the two-step oxidation/reduction between Ni^{2+} and Ni^{4+} [9]. The latter mainly accounts for the lithium ion insertion/extraction capacity of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In the electrolyte with PES, oxidation current can be observed at the lower potential than that for lithium extraction from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by comparing the insets of Fig. 1a and 1b. This oxidation current can be explained by the adsorption and the oxidation of PES in the

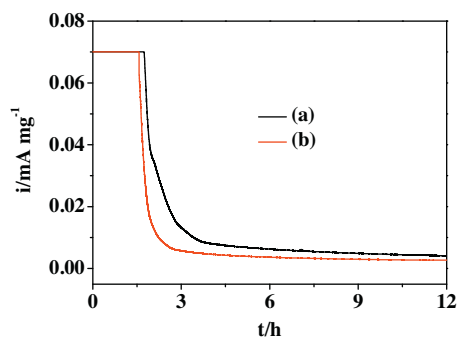


Fig. 2. Chronoamperometric responses of Li/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells in 1.0 mol dm^{-3} $\text{LiPF}_6/\text{EC-EMC}$ (1:2) electrolyte without (a) and with 1.0 wt% PES (b).

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