Journal of Power Sources 272 (2014) 183–189

Contents lists available at ScienceDirect

Journal of Power Sources

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

Electrochemical performance of 5 V $LiNi_{0.5}Mn_{1.5}O_4$ cathode modified with lithium carbonate addition in electrolyte

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HIGHLIGHTS

- A novel lithium carbonate sand-like electrolyte is prepared.
- Capacity fading rate of the 5 V cathode is reduced by using the electrolyte.
- Li_2CO_3 can consume PF_5 in the electrolyte.
- The oxidizability of Ni^{4+} on the cathode surface is weakened by adding Li_2CO_3.
- Intensive electrolyte oxidation is suppressed during cycling under high voltage.

ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form
15 August 2014
Accepted 20 August 2014
Available online 28 August 2014

Keywords:
Sand-like electrolyte
Lithium carbonate
High voltage cathode
Cycling stability
Precipitates

ABSTRACT

$LiNi_{0.5}Mn_{1.5}O_4$ electrode modification is achieved in this work through adding inorganic lithium carbonate (Li_2CO_3) into carbonate electrolyte. Superior cyclic stability of the cathode in the range of 5–2 V is attained, a capacity of 0.3698 mAh g^{-1} is lost per cycle, which is half of the value in the Li_2CO_3-free condition. The capacity loss above and below 3.5 V are both alleviated in the presence of Li_2CO_3. Its effect on both the electrolyte bulk and the cathode surface is analyzed with SEM, TEM and XPS measurements. The density functional theory (DFT) calculation is carried out to discuss the modification mechanism. It is speculated that $Ni^{4+}\cdots CO_3^{2-}$ coordination may be formed through the interaction between Ni and O, weakening the oxidizability of Ni^{4+} on the electrode surface. In addition, Li_2CO_3 can consume PF_5 in the electrolyte. The interphase film can also maintain thin and steady during the cycling within 5–2 V.

1. Introduction

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) spinel cathode has received special attention for its higher energy density than the layered $LiCoO_2$ oxide material that is widely used in commercial Li-ion batteries (LIB), together with the merits of low cost and toxicity. As the most successful high-voltage cathode [1], it shows an operating voltage above 4.8 V. The high capacity is believed to be due to the oxidation of Ni^{2+} to Ni^{4+} through Ni^{3+}during charge process in which the valence of Mn does not change [2,3].

Theoretically, $LiNi_{0.5}Mn_{1.5}O_4$ can exhibit two plateaus at the voltages of ~4.7 and ~2.7 V when lithium ions are inserted/extracted into/from 8a tetrahedral and 16c octahedral sites of the spinel lattice, respectively [4,5]. The capacity is only ~140 mAh g^{-1} above 3 V [6]. However, the high capacity about 260 mAh g^{-1} can be delivered when it is charged/discharged in a wide voltage range of 5–2 V, which is much closer to its theoretical capacity of 294 mAh g^{-1}. In this case, the spinel cathode suffers severe capacity fading during cycling.

Part of the capacity loss is caused by Jahn-Teller distortion happened near 2.7 V (severe volume change accompanying the transition from cubic phase to tetragonal one) and Mn dissolution due to the existence of high spin Mn^{3+} [7]. Besides, it also may be caused by electrolyte oxidation owing to the instability of presently-used carbonate electrolyte under high voltage. The compatibility is still a tough problem to the application of high voltage cathode [8,9]. It is a challenge to stabilize the electrolyte on the surface of the high-voltage spinel cathode and enhance the cycling stability within 5–2 V.

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http://dx.doi.org/10.1016/j.jpowsour.2014.08.085
0378-7753/

However, there are few reports devoted to the cycling performance enhancement of LNMO electrode under high voltage utilizing electrolyte modification [10]. In this work, inorganic lithium carbonate (Li_2CO_3) was added into carbonate electrolyte to optimize the electrolyte, since it is one of the main products from electrolyte decomposition, and also can act as a good Li^+ conductor with a low energy barrier [11]. The addition of Li_2CO_3 may foster the compatibility of electrode/electrolyte interface. Its role was primarily concerned in modifying the performance of high voltage cathode. Li_2CO_3 was almost insoluble and made the electrolyte sand-like. Some particles would precipitate on the electrode surface from the electrolyte, some of them remained in electrolyte bulk. With this perspective, the effect of the additive on the cathode electrolyte interphase (CEI) [12,13] and the electrolyte was examined in detail, the electrochemical properties of the cathode were studied in the electrolyte with/without Li_2CO_3 as well.

2. Experimental section

Electrolyte preparation was completed in an Ar-filled glove box. The solvents and lithium hexafluorophosphate ($LiPF_6$, Xianghe kunlun chemical products Co., LTD, China) were used without further purification. 1 mol L^{-1} $LiPF_6$/ethylene carbonate (EC)/propylene carbonate (PC)/di-ethyl carbonate (DEC) (1/1/3, wt.) was used as the base electrolyte. 4 wt% Li_2CO_3 (99.9%, Aladdin Chemistry Co. Ltd, China) was added into the electrolyte to make a homogeneous suspension, the soluble quality is about 0.2%, this sample is called as sand-like electrolyte. $LiNi_{0.5}Mn_{1.5}O_4$ (Institute of Nuclear & New Energy Technology, Tsinghua University, China) was prepared using co-precipitates method with detailed procedure illustrated in reference [14], its tap density was about 2.0 g cm^{-3}. The obtained spherical particles were within 10 μm in sizes. 80 wt% $LiNi_{0.5}Mn_{1.5}O_4$, 10 wt% super P. and 10 wt% polyvinylidene fluoride (PVDF) were mixed to make the slurry for electrode preparation. The $LiNi_{0.5}Mn_{1.5}O_4$ electrode (11 mm in diameter) was assembled in CR2025 coin cell with lithium sheet as the counter electrode, celgard 2400 polyethylene membrane as the separator. In the electrolyte-changing experiment, the cell cycled for 3 times was disassembled, the cathode and the anode were washed with DEC for many times to remove the original electrolyte and then reassembled with another electrolyte and seperator.

The cells charged to 5 V were kept in a constant temperature chamber (Wuxi Suoyate Testing Equipment Co., Ltd., China) for 2 h to maintain the desired temperature (−30 °C, −40 °C), then discharged at 0.1 C. The charge/discharge (C/D) tests were proceeded on CT2001A Land tester (Wuhan Jinnuo Electronics Co., Ltd.). The electrochemical properties were examined on CHI660c electrochemical station (Shanghai Chenhua Co. Ltd), including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests (0.1 Hz–0.1 MHz, 5 mV perturbation). Electrodes were disassembled from the cycled cells without any solvent washing to keep the precipitates on the electrode surface, then they were used in the analysis of Scanning Electron Microscope (SEM, FEI, Quanta 200f) coupled with INCA energy-dispersive X-ray spectroscopy (EDX), JEM-2100 high resolution transmission electron microscope (HRTEM). The X-ray photoelectron spectroscopic (XPS) measurement (PHI QUANTERA-II SXM system, Japan/Uivac-PHI, INC) was performed with X-ray power-AlKα 1486.6 eV, pass energy 26.0 eV, chamber pressure 2.0×10^{-7} Pa, take off angle 45°. The graphite peak (284.3 eV) was used as the check chemistry for the binding energy scale and charging effect. The depth profile of the interphase was studied through Ar^+ ion beam sputtering (2 keV). The obtained spectra were analyzed by XPSPEAK software. X-ray diffraction (XRD) was carried out using X-ray diffractometer with a CuKα radiation source from 10° to 90°at a scan rate of 8° min^{-1}.

The density functional theory (DFT) computation was conducted using Becke's three parameters (B3) exchange function along with Lee–Yang–Parr (LYP) non-local correlation function (B3LYP). All complexes were calculated at B3LYP/6-31 + G(d,p) level for full geometry optimization and natural bond orbital (NBO) analysis.

3. Results and discussion

The cyclic voltammetry was investigated for the cells with the sand-like and the base electrolytes in the initial cycle. As shown in Fig. 1, the two pairs of redox peaks around 4.7 V are ascribed to the two-step reactions of Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+}, both of them are cubic/cubic two-phase reactions representing the lithium ions insertion/extraction into/from 8a tetrahedral sites of the cubic spinel structure [3,4,15]. The other pair of strong peaks around 2.7 V is attributed to the redox reactions of Mn^{3+}/Mn^{4+} involving lithium ions insertion/extraction into/from 16c octahedral sites of the spinel structure, which is associated with a cubic/tetragonal phase transition [16]. The unintegrated peak at 2.0 V should be also ascribed to the reduction of Mn^{4+} to Mn^{3+}, which is the same with the one at ~2.7 V [7,17]. A pair of peaks around 4.0 V, corresponding to the redox of Mn^{3+}/Mn^{4+} along with lithium ion insertion/extraction into/from 8a tetrahedral sites are observable in quite low intensity. It is related to the presence of a small amount of Mn^{3+} in the pristine sample [18]. It is found that the intensities of peaks around 4.7 V and 2.7 V increase slightly in the case of the sand-like electrolyte. The redox peak potential differences around 4.7 V and 2.7 V are 80 mV and 30 mV smaller than the ones in the base electrolyte, respectively. Comparatively, electrode polarization is smaller in the initial cycle using the sand-like electrolyte.

As well known, the capacity fade of LNMO electrode can be attributed to Jahn-Teller distortion, Mn dissolution and electrolyte decomposition. The capacity loss caused by Mn dissolution is severe in full cell using graphite as anode, due to the loss of active Li^+ in the repeated SEI formation process [19,20]. But, generally, the Mn dissolution-derived decay is greatly reduced in a half cell with Li anode because Li^+ loss during cycling can be compensated by lithium metal anode [7,20–22]. Thus, the decay of the half cell cycled between 5 and 2 V is primarily ascribed to electrolyte oxidation and Jahn-Teller distortion. Fig. 2a shows the cycling performance of LNMO/Li half cell in the range of 5–2 V. The slope of the linear fitting line is used to illustrate the average fading rate within 5–54 cycles. A value of −0.7332 is obtained for the electrode in the Li_2CO_3-free electrolyte, meaning a capacity of

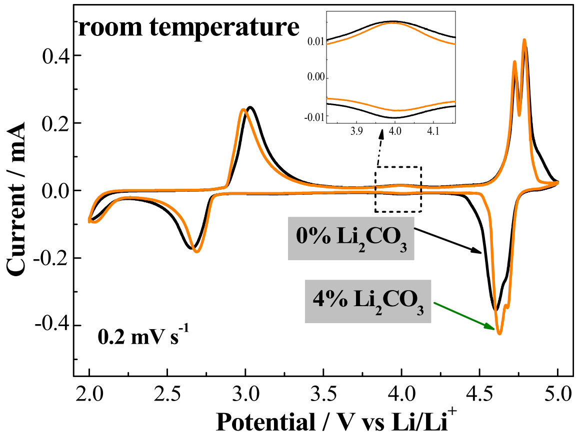

Fig. 1. Cyclic voltammograms of $LiNi_{0.5}Mn_{1.5}O_4$ electrode at room temperature (0.2 mV s^{-1}) in the electrolytes with 0% (black) and 4% Li_2CO_3 (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)