Improving rate capability and decelerating voltage decay of Li-rich layered oxide cathodes *via* selenium doping to stabilize oxygen

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HIGHLIGHTS

- $Li_{1.2}[Mn_{0.7}Ni_{0.2}Co_{0.1}]_{0.8-x}Se_xO_2$ was synthesized through a facile route.
- Se doping can decelerate the voltage decay process.
- Se doping also can curb a layered-to-spinel phase transformation during cycling.
- LLMO-$Se_{0.14}$ exhibits superior electrochemical properties.

ARTICLE INFO

ABSTRACT

To improve the rate performance and decelerate the voltage decay of Li-rich layered oxide cathode materials, a series of cathode materials $Li_{1.2}[Mn_{0.7}Ni_{0.2}Co_{0.1}]_{0.8-x}Se_xO_2$ (x = 0, 0.07, 0.14 and 0.21) was synthesized *via* co-precipitation. Based on the characterization results, it can be concluded that uniform Se^{6+} doping can improve the degree of crystallinity of Li_2MnO_3, resulting in a better ordering of atoms in the transition metal layer of this type of cathode materials. In the electrochemical experiments, compared to un-doped samples, one of the Se doped samples (LLMO-$Se_{0.14}$) exhibited a longer sloping region and shorter potential plateau in the initial charge curves, a larger first coulombic efficiency (*ca.* 77%), better rate capability (178 mAhm g^{-1} at 10 C) and higher mid-point voltage (MPV) retention (*ca.* 95%) after 100 cycles. These results prove that Se doping can effectively improve the rate capability and decelerate the voltage decay process of these cathode materials during cycling *via* suppressing the oxidation process of O^{2-} to O_2 and curbing a layered-to-spinel phase transformation. The above-mentioned functions of Se doping are probably due to the higher bonding energy of Se–O than that of Mn–O.

1. Introduction

Li-rich layered oxides with a common notation of xLi_2MnO_3 $(1-x)LiMO_2$ (LLMO) have recently received much attention as a type of cathode materials for lithium ion batteries (LIB) because of the their high discharge capacities, low cost, and low toxicity [1–3]. Wide use of this type of materials has been limited, however, due to their poor rate performance, low first coulombic efficiency and voltage degradation during extended cycling [4–6]. These drawbacks have been attributed to a unique electrochemical mechanism of LLMO materials. LLMO materials exhibit a specific first charge profile that is different from those for other LIB cathode materials.

In general, the first charge curve of a Li/LLMO cell exhibits an initial sloping region corresponding to the oxidation of transition-metal (TM) ions, which is followed by a plateau region caused by the loss of oxygen from the lattice [7,8]. Additionally, although the plateau region has a relatively high charge capacity, the first discharge suffers a large irreversible capacity loss due to a structural rearrangement from a layered one to a spinel-like one [9,10]. This transformation leads to cation mixing that is sufficiently large to destroy the structural integrity of the material, which may cause poor rate performance and voltage degradation of LLMO materials during extended cycling [11,12].

To improve the electrochemical properties of LLMO materials, Zr [13,14], Mo [15,16], Ti [17,18], Ru [19,20] and Sn [21] were used to substitute for transition metal. Park et al. [15] investigated the electrochemical performances of Mo-doped Li excess transition

metal oxides synthesized by a co-precipitation method. They showed that Mo doping could enhance the structural stability and electrochemical performance of LLMO cathode materials because strong Mo−O hybridization could induce weak Ni−O hybridization, which may reduce O_2 evolution. According to Yang et al. [17], the substitution of Ti for Mn in $Li_{1.2}Mn_{0.54-x}Ti_xNi_{0.13}Co_{0.13}O_2$ ($x = 0.04$, 0.08, and 0.15) suppressed the layered/spinel phase transformation owing to the introduction of strong Ti−O bonds in the framework. Qiao et al. [21] reported that Mn replacement by Sn in $Li_{1.5}Ni_{0.25}Mn_{0.75}O_{2.5}$ stabilized the host lattice in Li-rich layered oxides because the bonding energy of Sn−O is higher than that of Mn−O. The influence of these cationic substitutions is considered to be a result of enhancement in the covalent bonds, metal−oxygen binding, and electron delocalization of the metal−oxygen bonds [22,23]. Although the above-mentioned cationic substitutions improved the rate performance and restrained the voltage decay of LLMO cathode materials during cycling to a certain degree, greater improvement in the rate performance and further decrease in the voltage decay are still desired.

$Li_{1.2}[Mn_{0.7}Ni_{0.2}Co_{0.1}]_{0.8-x}Se_xO_2$ materials (Hereafter those samples are represented by LLMO, LLMO-Se$_{0.07}$, LLMO-Se$_{0.14}$ and LLMO-Se$_{0.21}$, with $x = 0$, 0.07, 0.14, 0.21, respectively.) presented in this paper were synthesized by the co-precipitation method in order to obtain more homogeneous materials. The resulting LLMO-Se$_{0.14}$ cathode material showed excellent rate capability and higher discharge voltages. The electrochemical properties are discussed in relation to chemistry and structural data. Supporting data are provided with this paper.

2. Experimental

2.1. Preparation of $Li_{1.2}[Mn_{0.7}Ni_{0.2}Co_{0.1}]_{0.8-x}Se_xO_2$

$Li_{1.2}[Mn_{0.7}Ni_{0.2}Co_{0.1}]_{0.8-x}Se_xO_2$ materials were prepared by a solid-state reaction from lithium hydroxide (LiOH·H$_2$O) and manganese-nickel-cobalt-selenium hydroxide $(Mn_{0.7}Ni_{0.2}Co_{0.1})_{1-y}Se_y(OH)_2$ ($y = 0$, 0.1, 0.2, 0.3). Manganese-nickel-cobalt-selenium hydroxide was firstly prepared by co-precipitation from an aqueous mixture of $MnCl_2·4H_2O$, $NiSO_4·7H_2O$, and $CoCl_2·6H_2O$ (Mn:Ni:Co = 7:2:1, molar ratio; the combined concentration was 2 mol L^{-1}) and a mixture of 2.0 mol L^{-1} NaOH and Na_2SeO_3 (NaOH:Na$_2$SeO$_3$ = 2:y, molar ratio) aqueous solutions with a desired amount of NH$_3$·H$_2$O. The solutions were mixed slowly in a nitrogen filled reactor and the pH of the mixed solution was kept in the range of 9.8−10.2 during the precipitation process. Finally, the precipitated $(Mn_{0.7}Ni_{0.2}Co_{0.1})_{1-y}Se_y(OH)_2$ particles were filtered, washed using deionized water, and then dried in a vacuum at 120 °C for 24 h. The obtained $(Mn_{0.7}Ni_{0.2}Co_{0.1})_{1-y}Se_y(OH)_2$ and LiOH·H$_2$O were then mixed for 5 h at a molar ratio of 1.00:1.55 by using a ball mill with absolute ethyl alcohol, and then the mixture was pressed into pellets. To the mixture 5% excess lithium was added to compensate for the lithium evaporation during the calcination process at a high temperature. The pellets were heated at 850 °C for 20 h in air and then quenched to room temperature. The final products LLMO, LLMO-Se$_{0.07}$, LLMO-Se$_{0.14}$ and LLMO-Se$_{0.21}$ were then obtained.

2.2. Characterization

The stoichiometric molar compositions of the prepared samples were accurately analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 5300DV, PerkinElmer, Waltham, Ma, USA). The morphologies of the as-prepared samples were observed with a scanning electron microscope (SEM, HITACHI, S-4700). The crystal structures of the

synthesized samples were determined by X-ray diffraction (XRD) using a D/max−γβ X′ pert diffractometer (Rigaku, Japan) with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was used to analyze the samples on a PHI 5700 ESCA System (USA) using monochromatized Al Kα radiation at 1486.6 eV. The binding energy scale was calibrated from the carbon contamination using the C 1s peak at 284.8 eV. Core peaks were analyzed using a nonlinear Shirley-type background, and then Mn^{3+} (641.6 ev) and Mn^{4+} (642.8 ev) peaks were added. The analysis of XPS data was performed using the XPS Peak Fitting Program version 4.1 [24]. The atomic ratios of Mn^{3+} and Mn^{4+} were derived by calculating the peak areas. The microstructural characteristics of the synthesized samples were observed using a high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010) working at an accelerating voltage of 200 kV. The lattice structure was identified by the selected area electron diffraction (SAED) technique. Scanning transmission electron microscope (STEM, Tecnai F30) was used for the elemental mapping. IR spectra were collected on a Perkin Elmer Spectrum One FT-IR spectrometer (Waltham, MA, USA) equipped with a KBr crystal in the absorbance mode range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. All ss-NMR (Solid State Nuclear Magnetic Resonance) experiments were performed in a 9.4 T magnetic field with a Bruker Avance III 400 spectrometer, operating at a ^{7}Li resonance frequency of 155.5 MHz, using 1.3 mm probe-heads at magic angle spinning (MAS) frequencies of 50 kHz and 60 kHz. A recycle delay of 0.02 s and a 90° pulse length of 1.2 μs were used for ^{7}Li. The ^{7}Li spectra were obtained with a stepwise spin-echo pulse sequence. The irradiation frequency of ^{7}Li was varied with a step size of 0.18 MHz. The chemical shift of ^{7}Li were referenced to LiCl solution (0 ppm).

2.3. Electrochemical evaluation

Two-electrode CR2032-type coin cells were assembled with LLMO, LLMO-Se$_{0.07}$, LLMO-Se$_{0.14}$ and LLMO-Se$_{0.21}$ as the cathodes, respectively, metallic lithium foil as the anode and Celgard-2320 membrane as the separator. The electrolyte used comprised 1 M LiPF$_6$ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) at a volumetric ratio of 1:1:1. The average mass loading of each electrode was ca. 0.91 mg cm^{-2} for LLMO, 1.39 mg cm^{-2} for LLMO-Se0.07, 1.31 mg cm^{-2} for LLMO-Se0.14 and 1.22 mg cm^{-2} for LLMO-Se0.21, respectively. Galvanostatic charge and discharge were performed at different current densities in a voltage range of 2.5−4.6 V using an 8-channel battery analyzer (Neware, China). Theoretical capacities of all cathode materials were set to 200 mAh g^{-1}, i.e., a current density of 200 mA g^{-1} corresponding to 1.0 C. Electrochemical storage capacities of the working electrodes were calculated based on the mass of active cathode materials. Cyclic voltammograms (CV) of different cathodes were recorded at a scanning rate of 0.1 mV s^{-1} between 2.5 and 4.6 V using an electrochemical analyzer CHI630e (Chenhua, China). A PARSTAT 2273 potentiostat/galvanostat (AMETEK, USA) was used in the electrochemical impedance spectroscopy test with a frequency range from 0.1 to 100 kHz. All experiments were carried out at a temperature of 25 ± 0.5 °C.

3. Results and discussion

3.1. Structure and morphology

ICP analyses confirmed that the synthesized materials were close to their nominal compositions with the Li content of all samples at 1.50 ± 0.01 (Shown in Table 1). Using the ICP analysis data the pristine LLMO can be described with a notation of $Li_{1.5}Mn_{0.7}Ni_{0.2}Co_{0.1}O_{2.5}$, which is equivalent to