



Enhanced electrochemical properties of the Cd-modified $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials at high cut-off voltage

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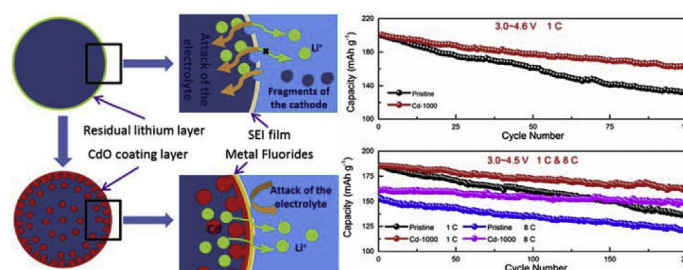
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HIGHLIGHTS

- Cd-modified NCM622 cathode is prepared by chemical precipitated-calcination routine.
- Cadmium oxide covers on the surface and diffuses with gradient distribution.
- Interfacial and crystal structure stabilities are improved after Cd modification.
- High voltage properties have been enhanced significantly after Cd modification.

GRAPHICAL ABSTRACT



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ABSTRACT

High voltage property applied in cells is one of the critical directions for high energy density lithium-ion battery. In this work, cadmium oxides are used as the modifying material on the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials by a facile chemical precipitation method followed by post-calcination. The cadmium oxides not only cover on the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ particles surface homogeneously, but also diffuse into the crystal lattice of the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ with gradient distribution. The formed cadmium oxide and metal fluorides mixed-layer during cycling on the surface makes the interfacial stability significantly improved. Therefore, the side-reactions are suppressed effectively. The gradient doping of the cadmium in the crystal lattice enhances the structural stability of the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ and facilitates the Li^+ and electron transportation in the bulk material. Moreover, the residual lithium components ($\text{Li}_2\text{CO}_3/\text{LiOH}$) also decrease significantly. As a result, the obtained Cd-modified $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathodes rise 16.60 (100 cycles, 3.0–4.6 V) and 13.87 (200 cycles, 3.0–4.5 V) percentage points at 1 C rate, respectively. The initial capacity of cadmium-modified $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ is 160.8 mAh g^{-1} at 8 C rate over 3.0–4.5 V. The proposed cadmium oxide modification may be also potentially applied in other active cathode materials, especially for the high voltage performance.

1. Introduction

Lithium ion batteries (LIBs) have been considered as the most popular candidates for energy storage device of electric vehicles, energy

storage systems and portable electronics owing to their high energy density, long cycle life and better safety [1–3]. Despite the increasing utilization of the LIBs, the share of the electric vehicles in the world's automotive market has been growing at a slower rate than expected due

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to its limited energy and power densities [2]. To meet these requirements, Ni-rich/Li-rich electrode materials are considered as the promising competitors to other counterparts since they can deliver enhanced reversible capacity ($> 200 \text{ mAh g}^{-1}$) at relatively higher operating voltages [4,5]. However, the dramatic capacity and voltage plateau fading upon cycling greatly limit its commercial application for Li-rich cathode material [5,6]. As for Ni-rich cathode material, a large degree of Li/Ni mixing and high residual Li components ($\text{Li}_2\text{CO}_3/\text{LiOH}$) on the particle surface occurred during synthesis deteriorate the electrochemical properties [2,6–8]. In addition, the highly delithiated cathode materials at high voltage arising from the presence of highly reactive Ni^{4+} in cathode are easy to suffer from the attack of the electrolyte, which leads to the dissolution of transition metals and the surface structure degradation [7,9–12]. Meanwhile, the generation of the microstrain coupled with secondary particle breakdown due to the lattice changes during the delithiation/lithiation process further accelerates the uncontrolled side-reactions [13–16]. All of those factors deteriorate the electrochemical properties of Ni-rich cathodes, especially at high voltage. To solve those problems, a great number of strategies, such as surface modification [17,18], ion substitution [3,19] and particle architecture design (core-shell structure [20]), have been explored.

As previously reported, surface coating has been proved to be an effective way to improve the batteries' electrochemical performances due to the "firewall" effect. In past decades, a variety of coating materials, including metal oxides (MoO_3 [21], ZrO_2 [22], TiO_2 [23]) phosphates (FePO_4 [24], AlPO_4 [25]), fluorides (AlF_3 [26]), high Li^+ ion conductivity materials (LiAlF_4 [27], Li_3PO_4 [8], $\text{Li}_2\text{O-B}_2\text{O}_3$ [18]) and electronic conductivity materials (Y_2O_3 [28,29]), have been investigated to improve the interfacial properties of the bulk materials. However, most of those coating materials are generally detrimental to both lithium ion and electronic conductivities, which is unfavorable to the electrochemical performance, especially the rate performance. Reports on foreign partial substitution with Na [19], F [30], Zr [3,31] and Mo [32] etc. have suggested that the electrochemical properties could be improved effectively. The substitution effect can not only alter the valence states of both oxygen and transition metals through charge compensation mechanisms, but also modify the distance of both lithium ion and transition metals layers, leading to enhanced electronic and ionic conductivities of the bulk materials [3]. The ionic/electronic conductivity of the cathode has been identified as the rate-limiting process upon charging/discharging rates [9]. In previous reports, the electronic conductivity is determined by the metallic and film resistances in aluminum, carbon and surface resistance of active materials, while those for ion conductivity are the ion resistance in electrolyte and solid state diffusion in active materials [33]. CdO is an n-type semiconductor with the electrical resistivity of $10^{-2} \sim 10^{-4} \Omega \text{ cm}$ due to its oxygen vacancies and high carrier concentration [34,35]. Previous reports point out that the oxygen vacancies in cathode materials play a significant role on the electrochemical properties [36–38]. Furthermore, the positive effects of Cd-modification on the electrochemical performance of some cathode materials (i.e., LiFePO_4 [39], LiCoO_2 [40] and $\text{Li}_2\text{FeSiO}_4$ [41]) have been confirmed in previous studies, but the effects on layered $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode are lack of reports, especially at high cut-off voltage.

Herein, a cadmium oxide coating layer and partial Cd atoms inlaying were employed on the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials by a chemical precipitation method followed by post-calcination. Benefitting from the protection of cadmium oxide coating layer and the surface structural stability after Cd inlaying with gradient distribution, the modified $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) cathode material exhibits excellent electrochemical performances at high cut-off voltage (3.0–4.5/4.6 V).

2. Experiments

2.1. Material synthesis

The pristine NCM622 was obtained from Xiamen Tungsten Industry Co., Ltd. The Cd-modified samples were achieved by the following process. Firstly, cadmium acetate dehydrate was dissolved in anhydrous alcohol to obtain a certain concentration of Cd^{2+} solution. Secondly, the pristine NCM622 materials were added into the measured Cd ethanol solution based on the Cd/NCM622 mass ratio with 1000 (Cd-1000) and 3000 ppm (Cd-3000). Then the mixtures were stirred vigorously for 2 h with the 0.05 mol/L ammonia solution to control the pH at 6.5–7.5. Finally, the suspensions were dried at 100°C overnight and then calcined at 750°C for 4 h to obtain the Cd-modified materials (Cd-NCM).

2.2. Material characterization

Particle morphologies were characterized by scanning electron microscope equipped with an energy dispersive spectrometer (SEM/EDS, JEOL JSM-6360LV, Japan) and transmission electron microscopy (TEM, Tecnai G12, 200 kV). The crystallographic information of the samples were characterized by X-ray powder diffraction (XRD, Rigaku D/max-2500 diffractometer equipped with a $\text{Cu K}\alpha$ radiation source) with a scan speed of $2^\circ/\text{min}$. Rietveld refinement was performed with the GSAS/EXPGUI program [42,43]. The cycled cells were disassembled in the high-purity argon glove box (LS800S, DELLIS, Chengdu, China) and the obtained electrodes were subjected to a washing process with the high purity dimethyl carbonate (DMC) to remove the residual electrolytes, and then dried in a vacuum chamber at 90°C for 10 h prior to analysis. X-ray photoelectron spectroscopy (XPS, VG Multilab, 2000) was performed to investigate the elements' compositions on the surface of the samples. The pH characterization was measured by the following steps: first, 5.000 g of the sample was added into 50 mL ultrapure water with vigorously stirring for 30 min, and then standing for 30 min to make it solid-liquid separated. Finally, the PHS-3C (Shanghai Precision & Scientific Instrument Co. Ltd) was employed to measure the pH value of the solution.

2.3. Electrochemical testing

The pristine NCM and Cd-NCM cathode slurries, containing the active material, polyvinylidene fluoride PVDF binder and acetylene black with 80:10:10 mass ratio using N-methyl-2-pyrrolidone (NMP) as the solvent, were pasted on to Al foil which serves as the current collector and dried at 120°C overnight. And then, the plate was punched into discs of 14 mm in diameter as cathode electrode. CR2016 type coin cells were assembled in the high-purity argon glove box (LS800S, DELLIS, Chengdu, China) with the metallic lithium as anode electrode and Celgard 2400 as separator. 1 M LiPF_6 was dissolved in EC: DMC: EMC (1:1:1 vol ratio) as the electrolyte. The charge/discharge tests were investigated at various rates ($1 \text{ C} = 165 \text{ mAh g}^{-1}$) at high cut-off voltages ranging from 3.0 to 4.5 V/4.6 V at 25°C using a Land Test System (CT2001A, Wuhan Jinnuo Electronic Co., Ltd., Wuhan China). Cyclic voltammetry (CV) tests were carried out over 3.0–4.6 V at a scan rate of 0.1 mV s^{-1} . Galvanostatic intermittent titration technique (GITT) data was collected at a pulse of 0.1 C for 10 min and with a time interval of 50 min between each pulse after 3 cycles at 0.1 C rate. The electrochemical impedance spectroscopy (EIS) of the electrodes were conducted at various cycling stages (1st and 50th at charge states) over the frequency range of 0.01 Hz–100 kHz with an AC signal of $\pm 5 \text{ mV}$ amplitude.

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