# Enhancing the electrochemical performances of $LiNi_{0.5}Mn_{1.5}O_4$ by $Co_3O_4$ surface coating

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## ARTICLE INFO

## ABSTRACT

A $Co_3O_4$ coating is formed on the surface of $LiNi_{0.5}Mn_{1.5}O_4$ particles via an ethanol mediated precipitation method. The existence of the uniform $Co_3O_4$ coating is clearly observed by scanning electron microscopy and transmission electron microscopy. The results of electrochemical performance testing prove that the $Co_3O_4$ coating can greatly enhance the cycling stability and rate performance of $LiNi_{0.5}Mn_{1.5}O_4$. The optimal sample 5% $Co_3O_4$-coated $LiNi_{0.5}Mn_{1.5}O_4$ delivers a discharge capacity 126 mAh $g^{-1}$ at 1 C rate with a capacity retention 96.8% after 300 cycles and a high discharge capacity 97.5 mAh $g^{-1}$ at 10 C rate. The causes to the improvement are discussed based on elemental analysis, X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy.

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## 1. Introduction

The spinel-type $LiNi_{0.5}Mn_{1.5}O_4$ with a high energy density of 640 Wh $kg^{-1}$ and a theoretical specific capacity of 147 mAh $g^{-1}$ is a promising cathode material for the electric vehicles and hybrid electric vehicles [1—6]. However, its relatively low first-cycle columbic efficiency (75—85%), poor cycling and rate performances (especially at elevated temperatures), and cell gassing problem have seriously hindered its commercial applications [4,7,8]. The main mechanisms to cause poor cycling and rate performances are the dissolution of manganese and the decomposition of the electrolyte, both of which take place at the interface between the particle surface and the electrolyte. Therefore, to construct a stable coating layer on the surface of $LiNi_{0.5}Mn_{1.5}O_4$ is universally demonstrated to be an effective way to improve the electrochemical performance. In recent years, carbon [9—13], metal oxides [14—23], lithium compounds [2,24—26] and other active electrode materials [27] are widely adopted to modify the surface of $LiNi_{0.5}Mn_{1.5}O_4$ particles. Wang et al. reported a carbon coated

$LiNi_{0.5}Mn_{1.5}O_4$/C composite directly synthesized at high temperature (800 °C without air-supply) with improved rate capability [10]. Hwang et al. prepared the oxidized carbon nanotube-coated $LiNi_{0.5}Mn_{1.5}O_4$ via a mechano-fusion method which presented a highly enhanced discharge capacity retention (95.5%) and a columbic efficiency of 99.9% after 80 cycles [13]. Tao et al. adopted a $TiO_2$ coating layer to modify the surface of $LiNi_{0.5}Mn_{1.5}O_4$ and obtained a suppressed manganese dissolution and largely improved electronic conductivity [20]. Chong et al. fabricated a uniform and continuous $Li_3PO_4$ coating on $LiNi_{0.5}Mn_{1.5}O_4$ particles and effectively avoided the direct contact between the cathode materials and the electrolyte. Additionally, Zhu et al. developed a sol-gel method to prepare $Li_4Ti_5O_{12}$ (LTO)-coated $LiNi_{0.5}Mn_{1.5}O_4$ with much improved fast charge-discharge properties [27]. To our best knowledge, a fairly uniform coating layer of an appropriate material is highly desirable to improve the electrochemical properties of $LiNi_{0.5}Mn_{1.5}O_4$.

In this work, we adopt $Co_3O_4$ coating to modify the surface of $LiNi_{0.5}Mn_{1.5}O_4$ because it is easy to fabricate and has good electronic conductivity. Recently, it has been successfully used to coat other cathode materials such as $Li_2MnO_3$ [28], $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ [29], $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ [30], $LiMn_2O_4$ [31], and $0.4Li_{4/3}Mn_{2/}$

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$3O_2\cdot0.6LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [32]. Additionally, $LiCoO_2/Co_3O_4$ composite has been used to modify the surface of $LiNi_{0.5}Mn_{1.5}O_4$ particles and it is found that the rate capability of $LiNi_{0.5}Mn_{1.5}O_4$ is improved [33]. In this study, we synthesize $Co_3O_4$-coated $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials via a facile chemical precipitation coating method and its rate capability is even better than that of the $LiNi_{0.5}Mn_{1.5}O_{4@}LiCoO_2/Co_3O_4$ composite. Thus, the singly modified sample is better electrochemical properties than the doubly-modified sample $LiNi_{0.5}Mn_{1.5}O_{4@}LiCoO_2/Co_3O_4$. .

## 2. Experimental

Pristine $LiNi_{0.5}Mn_{1.5}O_4$ (LNM) sample was synthesized by a thermopolymerization method as described in our previous work [34]. Lithium nitrate ($LiNO_3$, 5% excess), nickel nitrate ($Ni(NO_3)_2\cdot6H_2O$) and manganese acetate ($Mn(CH_3COO)_2\cdot4H_2O$) were dissolved in distilled water with stoichiometric molar ration of 1:0.5:1.5. Then acrylic acid (AA) was added to form a mixed AA-$H_2O$ (1:2, v/v) solution. The solution was then placed in an oven at 150 °C for 10 h to undergo the thermopolymerization reaction and obtain a fluffy powder product. The powder was first calcined at 500 °C for 5 h and then grinded into a fine powder to obtain the intermediate product, which was sintered at 900 °C for 15 h and subsequently annealed at 700 °C for 48 h. All these heat treatment processes were carried out in ambient conditions/atmosphere.

We use a precipitation method to prepare $Co_3O_4$-coated LNM samples as depicted in Fig. 1. Cobalt acetate ($Co(CH_3COO)_2\cdot4H_2O$) was dissolved in an ethanol−water (volume ration = 1:1) mixed solvent, then poured into a suspension comprised of the as-prepared LNM powder and oxalic acid ($H_2C_2O_4$) with also the ethanol−water mixed solvents as the dispersing agent. The mixtures were stirred for 5 h with the precipitation process to form cobalt oxalate ($CoC_2O_4$) on the surface of LNM. After filtering and drying, the final X wt% $Co_3O_4$-coated LNM (X = 1, 3, 5, 7) powders were obtained by the subsequent calcination at 500 °C for 6 h.

X-ray diffraction (XRD) measurement was performed with Rigaku X-ray Diffractometer (Cu K-alpha radiation) with a scanning rate of 10° min$^{-1}$. The microstructures and morphologies of the prepared samples were observed by a scanning electron microscope (SEM, JSM-6390LA, JEOL) and transmission electron microscopy (TEM, JEM-2100F). The elemental composition was analyzed by energy dispersive X-ray spectroscopy (EDS) attached to the SEM instrument. The average oxidation state of Co was determined by the X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo-VG Scientific). A Nicolet 8700 infrared spectrometer (Thermo Scientific Instrument Co. USA) was employed for Fourier transformed infrared (FTIR) study.

For the electrochemical testing, the active materials (LNM, X wt % $Co_3O_4@LNM$), acetylene black and PVDF (80:10:10, w/w/w) with

N-methyl-2-pyrrolidone were mixed together to form the homogenous slurries, which were separately casted on an aluminum foil by a doctor blade and dried at 70 °C overnight. The loading density of the electrodes was about 2.27 mg cm$^{-2}$. The CR2032 half cells were assembled in an argon-filled glove box (MBraun Labmaster 130) with the electrolyte of 1 M $LiPF_6$ solution in ethylene carbonate (EC) − dimethyl carbonate (DMC) (1:1 w/w, Guotai Huarong New Chemical Materials Co.). The galvanostatically charged-discharged tests were performed on a multi-channel battery cycler (Neware BTS2300, Shenzhen) in the voltage window from 3.5 to 4.9 V at room temperature (25 °C, RT).

The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) of the cells were carried out on a CHI 604A electrochemical workstation with the frequency range from 0.01 Hz to $10^6$ Hz and a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 3.0−5.1 V, respectively. To evaluate the electrical conductivity of 0% and 5% $Co_3O_4$-coated LNM samples, the powders of LNM and $CoC_2O_4$-coated LNM samples were separately pressed to discs with a diameter of 14 mm by the tablet press, then sintered at 900 °C for 15 h. The sintered pellets were coated with the conductive adhesive on both of their top and bottom sides, and then tested on the CHI 604A electrochemical workstation in the same frequency range to measure their impedance.

## 3. Results and discussion

### 3.1. Crystal structures and particle morphology

Fig. 2 shows the SEM images of the pristine LNM and $Co_3O_4$-coated LNM samples. Compared with the pristine LNM with a clear well-crystallized octahedral morphology and smooth surface, $Co_3O_4$-coated samples show roughly the same average particle size but the particle surfaces are not very smooth. Instead, the surface of all the coated samples is surrounded by lots of small particles which are presumably $Co_3O_4$.

We can further observe the coated samples with TEM, as a representative example, 5% $Co_3O_4$-coated LNM is shown in Fig. 3. Compared with the smooth surface of uncoated LNM sample, the surface of 5% $Co_3O_4$-coated LNM sample is uniformly surrounded by a fluffy porous coating layer with a thickness 20−30 nm. Note that, this fluffy porous coating layer is available to supply the rapid diffusion path for lithium ions. Fig. 3c exhibits a complete octahedral LNM particle surrounded by amounts of small $Co_3O_4$ particles which construct an incomplete coating layer. As can be seen from Fig. 3d, the HRTEM image of 5% $Co_3O_4$-coated LNM shows the lattice fringes with the measured $d_{hkl}$ of ~0.47 nm and ~0.234 nm, which are separately corresponding to the (111) plane of LNM and the (311) plane of $Co_3O_4$. This confirms that $Co_3O_4$ particles with a good crystallinity have been successfully formed on the surface of
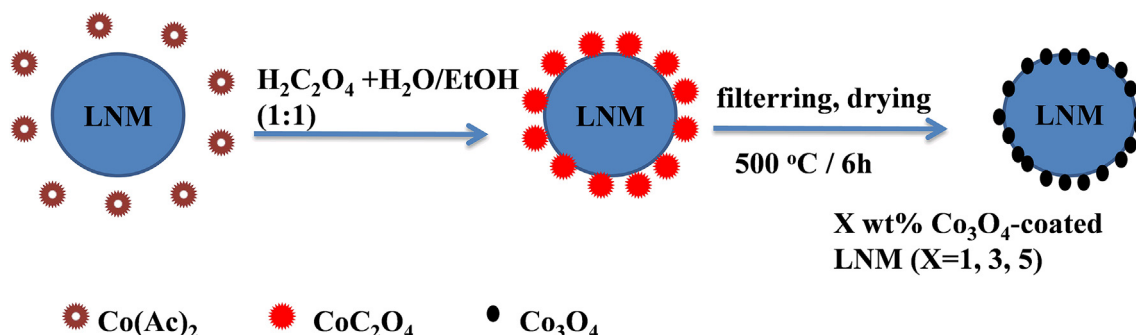


**Fig. 1.** Illustration of ethanol mediated precipitation coupled with subsequent calcination for the formation of X wt% $Co_3O_4$-coated LNM (X = 1, 3, 5).