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# Carbon Nanotubes Coating on LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> as Cathode Materials for Lithium Battery

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The carbon nanotubes (CNTs) have been utilized as a coating for  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) synthesized by calcining Ni-Co-Al composite hydroxide as a strategy to improve the electrochemical performance of cathode. The samples coated with CNTs were characterized by X-ray diffraction (XRD), scanning electron microscopy, Raman spectroscopy, and elemental analyses. The CNTs coated  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (CNTs-NCA) exhibited an initial discharge capacity of 205.6 mAh g<sup>-1</sup> and a highly improved discharge capacity retention (91.7%) after 80 cycles between 2.8 and 4.3V (versus  $\text{Li/Li}^+$ ), compared with the pristine NCA (P-NCA), which presented an initial discharge capacity of 201.2 mAh g<sup>-1</sup> and relative lower discharge retention of 84.4%. In addition, CV and EIS analysis demonstrated the CNTs coating NCA improved the surface electrochemical stability and rate capability, whereas the pristine NCA formed a thick resistive solid electrolyte interphase film by enhancing the surface side reactions. The improve diectrochemical performance can be attributed to shorten the length of lithium transport path and improve the electronic conductivity of NCA.

**Keywords:** Lithium ion batteries; Cathode; LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>; Carbon nanotubes; Electrochemical performance

# **1. INTRODUCTION**

Lithium ion battery (LIBs) have been widely applied in electron devices such as mobile phone, electric camera. Especially in recently years, LIBs as the promising energy storage for the electric vehicles (EVs) and hybrid electric vehicles (HEVs) attract more attention [1-3]. However, in the actual application, compared with convention batteries, whatever EVs or HEVs, it requires much more energy, power density and longer cycle life [4-6]. At present, the various commercialized cathode

materials such as LiFePO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub> and Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> and other layer structure ternary cathode materials are widely considered as promising substitutions for LiCoO<sub>2</sub> due to their high reversible capacity and low cost [7-9]. The NCA have particularly attractive for its much higher specific capacity (220mAh g<sup>-1</sup>) than those of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (160mAh g<sup>-1</sup>) and LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> (170mAh g<sup>-1</sup>) in the operating voltage range between 2.8 V and 4.4 V. However, the unexpected rapidly capacity fading of NCA are hindering its application in EVs and HEVs [10-11].

Recent researches on the quickly fading capacity of NCA during the charge-discharge cycling have been conducted with various method. The rise of impedance is caused by the cation mixing layer which is the migration of Ni and Co into Li slabs due to their similar ionic radius during cycling process [13]. To address the above issues, coating a layer onto the surface of NCA particles have been widely adopted to suppress the side reactions with the electrode material, meanwhile, alleviate the transition of surface phase. The coating materials can be metal fluorides [14], metal phosphates [15-17] inactive metal oxides [18-20], and some electrochemically active materials with better cycling stability than NCA such as LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> [21] and LiCoO<sub>2</sub> [22]. These materials exhibit a certain degree oxidation resistance due to their strong ionic bonding, what's more, the strong ionic bonding decrease the electronic conductivity. In other words, at a certain degree, these coating layer would inevitably hinder the lithium diffusion and reduce the specific capacity of the original material.

Considering the above reasons, carbon based materials as conductive coating components not only rest on their abundance and inexpensive characteristics but also consist in their excellent electronic conductive. However, thermal treatment carbon-based materials is a conventional coating methods, which was limited in terms of utilizing in the coating the surface of oxide material. This limitation can be caused by the inevitable carbon thermal reduction that occur during the heat treatment, which always damage the structure of crystal materials. Therefore, the mechanized method for simple carbon coating has the advantage which need not require any extra heat treatment [23].

Carbon nanotubes is a promising candidate as conductive materials to resolve the limitation of NCA composites, compared with general carbon additives. High aspect ratio and excellent flexibility to entangle cathode material particle which can effectively prevent active particle separation with extended cycling. T.Hwang [24] provided the multi-walled carbon nanotubes (CNTs) as a coating materials for over-lithiated layer oxide to suppress the side reaction on the surface of layer oxide and enhance its electronic conductivity. To date, multi-walled CNTs have been predominantly investigated in cathodes; showing  $\sim 10\%$  improvement in the reversible capacity of the electrodes up to an equivalent of a 3C rate for LiCoO<sub>2</sub> compared to carbon black counterparts [25-26].

Herein, we present the CNTs-NCA can not only increase the average valence of the transition metals (cobalt and nickel) but also induce restructuring of the surface of the hydroxide precursor. In this study, the pristine and treated NCA have been fully characterized by various techniques. Electrochemical evaluation and deeply analysis of CNTs-coated NCA electrodes were performed for comparison with pristine NCA to reveal the influence of the carbon nanotubes as a coating material for cathode applications in LIBs.

# 2. EXPERIMENTAL

## 2.1. Preparation of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>

The spherical LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (P-NCA, for short) used in this experiment was combined with commercial Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub> (OH)<sub>2</sub> precursors and LiOH·H<sub>2</sub>O via a simple process. Specific steps were as follow: First, the commercial Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub> (OH)<sub>2</sub> precursors was uniform mixing with LiOH·H<sub>2</sub>O at a molar ratio of 1:1.05 in a mortar, then the mixture was calcined at 480 °C in the flowing oxygen atmosphere for 5h and finally heated to 750 °C for 15h.

#### 2.2. Pretreatment of the Multi-walled carbon nanotube

The Multi-walled carbon nanotube (S.MWNTs-1020, purity  $\geq$ 98wt %, 15 nm in diameter, 2 um in length, approximate surface area of 300 m<sup>2</sup> g<sup>-1</sup>) named as CNTs used in this experiment was provided by Shenzhen Nanotech Port Co. Ltd. CNTs were dispersed into concentrated nitric acid (65 wt%) very carefully under sonication. After filtered and then dried at 110°C for 8 h, the CNTs were calcined at 900°C for 6 h in the flowing Ar/5 wt%H<sub>2</sub> mixture gas (H<sub>2</sub> flow was 100 sccm) to remove impurity functional groups.

#### 2.3. Preparation of NCA/ CNTs

To modify the NCA cathode material with 0.5 wt% CNTs via the high-power ultrasonic stirring technology. Firstly, 0.05g CNTs were evenly dispersed in anhydrous ethanol under high-power ultrasonic stirring technology for 1h at room temperature, and then 9.95g prepared  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  slowly add to the above solution, and then ultrasonic stirring for 1h. Finally, the mixture was filtered and dried in a vacuum oven at 80°C. In the experiment, the prepared NCA/CNTs samples are marked as CNTs-NCA. For comparison, the unmodified NCA was named as P-NCA.



Figure 1. Illustration of the preparation procedure

#### 2.4. Materials characterizations

X-ray power diffraction (XRD, D/MAX-Ultima IV, Japan) patterns with Cu Karadiation in the  $2\theta$  range from  $20^{\circ}$  to  $80^{\circ}$  was used to test the pristine and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2/\text{CNTs}$  samples of Crystalline phases. Field emission scanning electron microscope (FESEM, S-3400N, Japan) was applied to characterize the morphology of the samples and the CNTs. Raman spectroscopy was measured with a laser Raman spectrometer (RS, Renishaw 2000) with 514 nm excitation (Ar ion laser).

#### 2.5. Electrochemical measurements

The electrochemical performances of the cathode materials were evaluated by assembling into CR2032 type half-cells with a positive electrode, a metallic lithium which used as counter-electrode, a microporous polypropylene membrane (Celgard 2400) and electrolyte at room temperature ( $25^{\circ}$ C). The electrolyte was 1 mol  $L^{-1}$  LiPF6 in ethylene carbonate (EC)/dimethyl carbonate (DEC)/ethyl methyl carbonate (EMC) (1:1:1 by volume). To prepare the positive electrode, 80 wt% active material, 10 wt% acetylene black (Super P) and 10 wt% polyvinylidene fluoride binder (PVDF) were dissolved to N-methylpyrrolidone (NMP, from Aldrich). After ultrasonic and stirring, the slurry was spread onto aluminum foil (20um thickness) by using applicator and then dried at 110  $^{\circ}$ C for 12h in a vacuum oven to get the electrode. The dried electrode was punched into circular disks with a diameter of 12 mm for assembling the coin half-cells, and then rolled into a film with a thickness of 32 mm. The cells were assembled in an argon-filled glove box with the contents of the water and the oxygen below 0.1ppm. After standing for 12h, the rate performance of the cells are charged by 0.2C (36 mA g<sup>-1</sup>), and discharged from 0.1 C to 5 C in the voltage range of 2.8-4.3V (versus Li/Li<sup>+</sup>) by using the Neware battery testing system at room temperature. Furthermore, the cycle performance of the cells is tested at charged to 4.3V at 0.2C and discharged to 2.8V at 2C. The Cyclic voltammetry (CV) measurements at a scan rate of 0.1 mV s<sup>-1</sup> between 2.8 and 4.3 V, and the electrochemical impedance spectroscopy (EIS) with amplitude of 5 mV at the frequency range from 0.01 Hz to 100 KHz were performed by an electrochemical workstation (CHI670D, CH Instruments).

### **3. RESULTS AND DISCUSSION**

The X-ray diffraction patterns of P-NCA and CNTs-NCA composite are shown in Fig. 2. Both samples have good crystallinity and correspond to an  $\alpha$ -NaFeO<sub>2</sub> structure with the R3m space group, without any peak weakening, peak shifting or peak broadening. Although the presence of CNTs was not confirmed from XRD pattern, the XRD analysis results revealed there were not any bulk change of the crystal lattice in the NCA materials during the process of CNTs coating.



Figure 2. X-ray diffraction patterns of P-NCA and CNTs-NCA

SEM images of the surface morphologies of the P-NCA and CNTs-NCA composite are shown in Fig. 3, respectively. The size of the NCA and morphological are observed, it displays an average aggregate NCA particle size of  $8\mu$ m In comparison, the cathode particles coated with CNTs are show in Fig. 3 (b) and (c), it presents the high purity CNTs are effectively dispersed in and throughout the entire composite with the shape of small bundles. In Fig. 3 (d), through the internal distance of NCA particles, it can be concluded that the interconnected electronic conductivity network provided by the high aspect ratio CNTs.



**Figure 3.** FE-SEM images of (a) pristine NCA, (b) the NCA coated by CNTs, (c) the internal particle of NCA coated by CNTs, (d) the surface morphology of NCA coated by CNTs at 200nm scale. The inset of (a) is the CNTs SEM image.

Raman microscopy can be used to investigate the surface structure and chemical composition at a micrometer-scale spatial resolution. Clearly, the broad peak at around 500 cm<sup>-1</sup> is shown the specific peak for P-NCA. Towards to CNTs-NCA, there are two specific peaks corresponding to the disordered carbon (D peak, 1350 cm<sup>-1</sup>) and ordered graphite (G peak, 1582 cm<sup>-1</sup>) of CNTs appeared in the Raman spectra [27]. The D peak is well known as a double-resonance peak, because it generated by disordered structure and defects in the CNTs, meanwhile, the G peak derived from in plane vibration between ordered graphene sheets and carbon atoms [28]. And the specific peak at around 500 cm<sup>-1</sup> for NCA is remain invariant, this demonstrates that the preparation process of electrode materials don't change the state of transition-metal elements. Meanwhile, the D/G value from CNTs of coated electrodes is similar with the D/G ratio of pure CNTs, this demonstrates the prepared process didn't deteriorate the physic-chemical properties of the CNTs. In other word, the CNTs still maintain relative highly conductive capacity after the coating process. It is very significant that the electrode should preserve high electronic conductive to play a role of the conductive coating. This result is good agreement with the above analysis.



Figure 4. Raman spectra of P-NCA and CNTs-NCA

In Fig. 5a, the initial charge-discharge curves of P-NCA and CNTs-NCA at 0.1 C are displayed, it can be seen the discharge capacity of CNTs-NCA (205.6 mAh  $g^{-1}$ ) is quite similar to that of P-NCA (201.2 mAh  $g^{-1}$ ). The cycling performance of P-NCA and CNTs-NCA at 2C in the voltage range of 2.8-4.3 V are shown in Fig. 5b. The coin batteries were activated at 0.1C during the before three cycle firstly, and then cycled at 2C for subsequent cycles. The cycling performance of CNTs-NCA and P-NCA were tested at 2C in the voltage range of 2.8-4.3V. In Fig.5. (b) , obviously, CNTs-NCA displays a much better cycling stability than P-NCA, CNTs-NCA exhibits a 158.4 mAh  $g^{-1}$  with a capacity retention of 91.7% after 80 cycles, compare with the P-NCA, which deliver a discharge capacity of 123.5 mAh  $g^{-1}$  with 84.4% capacity retention at the similar condition. The differences may be caused by the polarization of cathode during cycling increase more rapidly than that for CNTs-

NCA, the reason is that the serious side reactions on the surface of the cathode material, resulting in a clearly capacity fading furtherly.



**Figure 5.** (a) Initial charge and discharge curves of P-NCA and CNTs-NCA at 0.1 C, (b) Cycling performance of P-NCA and CNTs-NCA at 2C in the voltage range of 2.8-4.3 V

In Fig. 6, the charge-discharge curves during cycling of P-NCA and CNTs-NCA are exhibited, which reveal the polarization of the electrodes during the charging–discharging process. Toward to the P-NCA electrode, the working voltages decrease rapidly as the increase of cycle numbers, the main reason is that the cation disorder and material defects bring about the increasing polarization. However, the electrode exhibited more stable working voltage and a much better cycling stability than P-NCA while the NCA mixed with the 0.5% CNTs as conductive additive, the reason is that CNTs additive improve the percolation network and achieve higher composite conductivity at dramatically lower additive concentration (0.5%), which can make a higher percent of active electrode material to be used in the electrode, this results is consistent with the above SEM analysis.



**Figure 6.** Selected charge-discharge curves during cycling of (a) P-NCA and (b) CNTs-NCA in the voltage range of 2.8-4.3V, respectively.

In the voltage range of 2.8-4.3 V, the rate capabilities of the P-NCA and CNTs-NCA electrodes are shown in Fig. 7. The discharge capacities of both samples are nearly similar at relatively low current density. However, CNTs-NCA displays much higher capacities at relatively higher current densities than P-NCA. During a constant current charging process from 2.8 to 4.3 V, the discharging voltage of P-NCA has a sudden drop as the increase of C rates. Especially, CNTs-NCA displays a discharge capacity of 151.8 mAh  $g^{-1}$  at 5C rate, while P-NCA only has 116.3 mAh  $g^{-1}$ . At high rates, the discharge capacity of P-NCA differs considerably from that of CNTs-NCA. This excellent rate capability of CNTs-NCA is mainly caused by the CNTs, which provide sufficient electrical conductivity at a certain current density to achieve the expected reversible capacity, and increase the intrinsic conductivity and enhance the composite percolation network.



**Figure 7.** Charge-discharge curves during cycling of (a) P-NCA and (b) CNTs-NCA at 2C in the voltage range of 2.8-4.3V.

Figure. 8 shows the rate capacities of P-NCA and CNTs-NCA measured at various rate (0.1C, 0.5C, 1C, 2C and 5C) for every 5 cycles between 2.8 and 4.3V. Obviously, the discharge capacities of the both samples are decreased at relative high C rates condition, this can be attributed to the internal polarization of lithium extraction and intercalation reaction [29-30]. CNTs-NCA displays discharge capability of 205.6 mAh  $g^{-1}$ ,191.9 mAh  $g^{-1}$ ,183.5 mAh  $g^{-1}$ , 163.4mAh  $g^{-1}$  and 151.8mAh  $g^{-1}$  at a rate of 0.1C, 0.5C, 1C, 2C and 5C, respectively. On the whole, the rate capability of CNTs-NCA are better than the P-NCA prepared by the solid state reaction method, the main reason is that CNTs has excellent electronic conductivity, and the NCA coated by CNTs can effectively improve the conductivity of cathode.



Figure 8. Rate capabilities of the P-NCA and CNTs-NCA

The CV curves of the P-NCA and CNTs-NCA samples between 2.8 and 4.3 V with a scan rate of 0.1 mV s<sup>-1</sup> in Fig. 9. In the first cycle, there are only two peaks on the oxidation curves to observe clearly, the two peaks may correspond to the oxidation of Ni<sup>3+</sup> to Ni<sup>4+</sup> (about 4.16 V) and of Co<sup>3+</sup> to Co<sup>4+</sup> (about 4.22 V), respectively. However, the oxidation peaks can't correspond exactly to the reduction peaks, the main reason is that the irreversible phase transition during the initial charging process, leading to the relatively low initial Coulombic efficiency for nickel-based materials [31].



Figure 9. CV curves of the P-NCA and CNTs-NCA samples between 2.8 V and 4.3 V with a scan rate of 0.1 mV s<sup>-1</sup>.

However, in the subsequence cycles, there are three main peaks (3.78 V, 4.12 V, and 4.21 V) displayed in the oxidation curves. On the basic of Huang et al [32] and Han et al [33] research, the three peaks are attributed to three phase transitions from hexagonal to monoclinic, monoclinic to hexagonal, and hexagonal to hexagonal, respectively. A small peak around 3.9 V reveals the existence of a single-phase region of M. For the P-NCA sample, there are no obvious peaks to observe in the second and third curves, indicating the larger polarization in the charging-discharging process. Meanwhile, these results are consistent with the above results and analysis.



**Figure 10.** Nyquist plots for (a) P-NCA electrodes and (b) CNTs-NCA electrodes in a 50% charge state controlled by the median charge voltage of 3.5 V after the 1st, 40th and 80th cycles at a 0.5C rate between 2.8 and 4.3 V (c) equivalent circuit used for curve fitting

EIS curves were presented to better understand the kinetic behavior of the P-NCA electrodes (Fig.10 a) and CNTs-NCA electrodes (Fig.10 b). The Nyquist plots for both samples in a 50% charge state controlled by the median charge voltage of 3.5 V after the 1st, 40th and 80th cycles at a 0.5C rate between 2.8 and 4.3 V.

Usually, each of the impedance spectra displays two semicircles and a line inclined at a constant angle to the abscissa axis. On the basic of previous researches [34-35], the semicircle located in high-to-medium frequencies is ascribed to the resistance for Li<sup>+</sup> ions migrating through the film covered on the surface of cathode materials and film capacitance, the semicircle at a medium-to-low frequency range can be attributed to the charge-transfer resistance, and the inclined line at low frequencies named Warburg impedance reflect the process of lithium ion diffusion road through a solid state electrode. Towards to both samples, it can be seen the film resistance increases as the cycling number, the main reason is that the formation of an increasingly thicker film leading to side reactions with the electrolyte on the surface of cathode materials.

However, both the film and charge-transfer resistance of CNTs -NCA increase more slowly than those for P-NCA, which suggest that the CNTs can effectively shorten the lithium ion transport road and improve the conductivity of the electrode, and then bringing about remarkable improvements of the electrochemical properties of NCA cathode materials.

#### **4. CONCLUSION**

In this study, CNTs have been used as a coating material for NCA to shorten the length of lithium transport path and to improve the electronic conductivity of NCA. Cycling capability measurement shown the pristine NCA suffered capacity fading, the main reason is that the formation of SEI film during the mechanism process. The good rate performance of CNTs-NCA rather than pristine NCA have been demonstrated by experiment. The discharge capacity of the CNTs-NCA composite retained 151.8 mAh g<sup>-1</sup> at 5C, and presented stable cycling after 80 cycles, which is nearly 1.5 times higher than the value for NCA electrode, this reason is mainly result in CNTs effectively shorten the length of lithium transport path and improve the electronic conductivity of NCA. Consequently, the CNTs-NCA composite exhibited excellent electrochemical performance and recognized as a promise candidate for high performance lithium ion battery.

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