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# Improving the Electrochemical Performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> Cathode Materials by Surface Coating with Cyclized Polyacrylonitrile for Lithium-Ion Batteries

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The spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (LNMO) is a promising cathode material for lithium-ion batteries due to its high working voltage. However, the capacity fading is a major problem of LNMO, especially at elevated temperatures. Surface coating is an effective method to solve this problem. In this paper, a conducting polymer, the cyclized polyacrylonitrile (cPAN), is applied to coat on the surface of LNMO by a simple heat-treatment method in air. The cPAN coating layer can prohibit the electrode materials from direct contacting with the electrolyte therefore reduce the amount of transition metal ions dissolved into the electrolyte. In addition, the cPAN coating layer can increase the conductivity of cPAN-LNMO. Compared to pristine LNMO, the electrochemical properties of cPAN-LNMO are significantly improved, especially at elevated temperatures. After 100 cycles at 55°C, the discharge capacity of cPAN-LNMO is 112.9 mAh g<sup>-1</sup> with the 95.2% retention, while that of pristine LNMO is only 104.7 mAh g<sup>-1</sup> with the 87.8% retention. These results indicate that the cPAN-LNMO composite is a competitive cathode material for practical application in high-voltage lithium-ion batteries.

**Keywords:** Cathode materials; Coating; LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>; Lithium-ion battery; Polyacrylonitrile

# **1. INTRODUCTION**

In recent years, increasingly prominent energy and environmental issues make the electric vehicles (EVs) become one of research hotspots [1-3]. The lithium ion battery (LIB) is the only candidate for EVs power sources, as the energy density is higher than for any other battery technology [1, 4]. However, common cathode materials such as  $LiCoO_2$  and  $LiFePO_4$  can not well meet the requirement of high energy density for EVs [1, 5-6]. To raise the energy density of LIB, increasing the

working voltage is an effective strategy [7]. The working voltage of LIB is mainly determined by the cathode materials since the working voltage of anode materials such as graphite is near to 0 V (vs Li<sup>+</sup>/Li). The spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (LNMO) is regarded as one of the most promising cathode materials allowing for a high energy density due to operation at high voltage (~ 4.7 V vs Li<sup>+</sup>/Li) and high specific capacity (147 mAh g<sup>-1</sup>). Besides, the elements Ni and Mn are more abundant and non-toxic compared with the element Co in LiCoO<sub>2</sub> [8-9].

However, some problems hindering the practical application of LNMO should be addressed. The capacity fading is the main issue of LNMO, especially at elevated temperatures. The impurity  $Mn^{3+}$  ions in LNMO are inclined to take disproportionate reaction into  $Mn^{2+}$  and  $Mn^{4+}$  due to the Jahn-Teller effect. While the Mn<sup>2+</sup> ions are easily dissolved into the electrolyte and deposited on the surface of anode with increasing the impedance of the cell as reported [10-12]. Besides, the working voltage of LNMO is higher than the stable potential of traditional organic electrolyte (~ 4.5 V), which causes the decomposition of the electrolyte and may produce detrimental substances on the surface of LNMO [7]. There are two effective methods to overcome the problem in materials aspect at present. One is doping, including the cationic doping with Fe [13], Cr [14] and Ru [15] etc. and the anion doping with F [16]. The other one is surface coating with inorganic materials or organic materials. The excellent coating materials should have three characteristics as the following: (1) they can form uniform coating layer on the surface of LNMO, (2) they are conductive rather than insulative, and (3) the coating process can not damage the structure of LNMO. Previously, the surface of LNMO is coated with many inorganic materials, such as ZnO [17], Al<sub>2</sub>O<sub>3</sub> [18] and Bi<sub>2</sub>O<sub>3</sub> [11] etc. Most of studies show improvement on the electrochemical properties of LNMO. However, the majority of inorganic materials are insulative and can not form continuous coating layer. Conducting polymers, such as polypyrrole (PPY), polyaniline (PANi), polythiophene (PTP) and poly (3, 4-ethylenedioxythiophene) (PEDOT) etc., can meet the basic requirements aforementioned and have been reported as the coating materials for some cathode and anode materials in recent years [19-23]. Wu et al. reported that the electrochemical performance of Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> is significantly improved after coating with PEDOT : PSS [21]. Gao et al. demonstrated that the PPY coating layer obtained by in-situ synthesis method can increase the electrical conductivity and reduce the impedance of the LNMO electrode [24].

Among the numerous polymers, the polyacrylonitrile (PAN) can be used as the matrix of the electrolyte polymer and the coating material in LIBs as reported recently. Piper et al. found that the cyclized polyacrylonitrile (cPAN) has intrinsic electronic conductivity after heat-treatment at 300 ~ 500°C in an inert environment and the nano-Si/cyclized-PAN composite reveals excellent performance [25]. Yang et al. reported that the cycling performance of LiCoO<sub>2</sub> was obviously improved after coating with the cross-linked PAN in air rather than inert environment [26]. Because the transition metal ions of cathode material will be reduced to a lower valence state upon heat treatment conducts in an inert environment [27]. In addition, the  $-C\equiv N$  group in the PAN chain has a strong polarity, which can adsorb on the surface of LNMO and form an uniform coating layer [28]. To the best of our knowledge, the effect of cPAN on the electrochemical performance of LNMO has not been reported yet. In this work, the cPAN layer was coated on the surface of LNMO by a simple heat-treatment in air. The influences of cPAN on the morphology, structure and electrochemical properties of LNMO have been systematically studied.

## 2. EXPERIMENTAL SECTION

#### 2.1 Material preparation

The co-precipitation method was used to prepare the plate-like precursor (Ni<sub>0.25</sub>Mn<sub>0.75</sub>)(OH)<sub>2</sub>. The MnSO<sub>4</sub>·H<sub>2</sub>O and NiSO<sub>4</sub>·6H<sub>2</sub>O with the Mn : Ni stoichiometric atomic ratio of 3 : 1 were dissolved in deionized water to prepare a 2 M transition metal solution, and the appropriate amount of NaOH and NH<sub>3</sub>·H<sub>2</sub>O were also dissolved in deionized water to prepare a mixed alkaline solution. The transition metal solution and alkaline solution were simultaneously pumped into a reactor (1 L) under constant stirring and nitrogen atmosphere. The stirring speed was set at 1000 rpm and the reaction temperature was 55°C. The pH of the reaction mixture was kept constant at 10.8 by controlling the pumping rate of alkaline solution. The resulting slurry was aged overnight at 55°C in N<sub>2</sub> atmosphere, then the slurry was collected and washed with deionized water and ethanol until the pH of the filtrate was 7.0. After drying at 80°C overnight, the precursor was mixed uniformly with LiOH H<sub>2</sub>O (5.0% excess to compensate for the volatilization of Li during high-temperature calcination) by ball milling (Pulverisette 14, Fritsch, Germany) at the speed of 150 rpm for 1 h. The mixture was pre-sintered at 480°C for 6 h, then calcined at 800°C for 20 h followed by annealing at 600°C for 10 h to compensate for oxygen vacancies caused by the high temperature calcination in air. After annealing, the mixture was naturally cooled to ambient temperature to obtain LNMO. To prepare cPAN-LNMO, 0.01 g PAN (Mw = 150,000 g mol<sup>-1</sup>. Sigma-Aldrich) and 1 g LNMO were added into N, N-dimethylformamide (DMF) and constant magnetic stirring for about 10 h to form a homogeneous mixture. After that, the mixture was stirred at 80°C until the DMF was completely evaporated. Finally, the mixture was heat-treated at 400°C for 1 h in air to gain the cPAN-LNMO composite.

## 2.2 Material characterization

The crystal structure of the samples was determined by the X-ray diffraction measurement (XRD, Rigaku miniflex 600, Japan). The field emission scanning electron microscopy (FE-SEM, S-4800, Japan) was used to observe the morphology of the samples. The transmission electron microscopy (TEM, JEOL-2100, Japan) was carried out to verify the surface of cPAN-LNMO. The surface elemental distribution of the particles was determined by energy-dispersive X-ray spectrometer (EDS). Thermogravimetric and differential scanning calorimetry (TG–DSC, STA 449 F3 Jupiter NETZSH, Germany) analysis was carried out in the temperature range of 35 ~ 800°C at the rate of 5°C min<sup>-1</sup> in air. The fourier-transformed infrared spectra (FT-IR, Nicolet iS5 Thermofisher, USA) were used to research the structure changes of PAN after heat treatment in air. The intrinsic electronic conductivity of cPAN was demonstrated by a microscopic Raman instrument (XploRA ONE Horiba, Japan).

#### 2.3 Electrochemical measurements

CR2016-type coin cells were used to evaluate the electrochemical performance of pristine LNMO and cPAN-LNMO. To prepare the cathode, 70 wt% active material, 5 wt% graphite, 15 wt%

acetylene black and 10 wt% polyvinylidene fluoride (PVDF) dispersed in N-methylpyrrolidinone (NMP) were well mixed to form a slurry. The slurry was uniformly casted on the current collector by the coating machine and dried overnight at 80°C in vacuum. The diameter of the electrode was 11 mm. The Celgard 2400 was used as the separator and the lithium foil was acted as the anode. The electrolyte was 1 M LiPF<sub>6</sub> dissolved in dimethyl carbonate (DMC) / diethyl carbonate (DEC) / ethylene carbonate (EC) with the volume ratio of 1 : 1 : 1. The coin cells were assembled in an argon-filled glovebox and charged / discharged by a CT-2001A cell tester (LAND, Wuhan, China) between 3.5 and 4.9 V (vs Li<sup>+</sup>/Li).

To evaluate the rate performance of pristine LNMO and cPAN-LNMO, the cells were charged at 1C then discharged at various rates. The CHI electrochemical workstation (Chenhua, China) was used for cyclic voltammetry (CV) measurement between 3.5 and 4.9 V (vs Li<sup>+</sup>/Li) at the scan rate of 0.1 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 100 kHz to 0.1 Hz using Autolab electrochemical workstation (PGSTAT302N Metrohm, Switzerland).

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

Figure 1 displays the XRD patterns of pristine LNMO and cPAN-LNMO composite. Both XRD patterns can be assigned to the spinel ordered structure (space group P43<sub>3</sub>2, JCPDS 80-2184). The impurity peaks of NiO or  $\text{Li}_{1-x}\text{Ni}_x\text{O}$  can not be observed, which indicates that the annealing process at 600°C can compensate for the oxygen vacancies formed during high temperature calcination [29]. The XRD pattern of cPAN-LNMO composite is similar to that of pristine LNMO, revealing that the coating process of cPAN does not damage the structure of LNMO.



Figure 1. XRD patterns of pristine LNMO and cPAN-LNMO.

The FT-IR spectroscopy is a useful technique to determine the functional groups on the material surface. Figure 2a presents the FT-IR spectra of pristine LNMO, cPAN-LNMO, PAN and cPAN. In the FT-IR spectrum of PAN, the characteristic peak at 2242 cm<sup>-1</sup> is attributed to the  $-C\equiv N$  stretching vibration [30]. For the sample heat-treated at 400°C, the characteristic peak of  $-C\equiv N$  disappears, indicating the damage or opening of  $-C\equiv N$  group and forming the conjugated -C=N group. Two broad bands around 1261 and 1593 cm<sup>-1</sup> are attributed to -C-N and -C=N/-C=C groups, respectively [30-31]. The bands width represents the degree of crosslinking and cyclization of PAN. For the cPAN-LNMO composite, the characteristic peaks of cPAN are fairly obvious, indicating that the LNMO and cPAN formed a composite.

In order to confirm that cPAN has intrinsic electronic conductivity, Raman measurements are performed on the samples heat-treated at different temperatures. Figure 2b presents the Raman spectra of PAN, cPAN-300°C, cPAN-400°C and cPAN-500°C. No Raman peaks can be observed in the case of PAN, while two obvious Raman peaks around 1360 cm<sup>-1</sup> and 1590 cm<sup>-1</sup> are shown for cPAN-300°C, cPAN-400°C and cPAN-500°C, which are consistent with D band and G band, respectively [25]. The D band represents the amorphous carbon and the G band stands for the graphitized carbon [32]. Like graphite, the Raman spectra of cPAN have the D band and G band which mean good electronic conductivity [33]. The intensity ratio of D band and G band denotes the degree of graphitization. The  $I_D/I_G$  values of cPAN-300°C, cPAN-400°C and cPAN-500°C are 2.58, 2.25 and 1.75, respectively. We can see that the  $I_D/I_G$  values of cPAN decrease with the increases of heat treatment temperatures [25, 34]. Considering the graphitized degree and residue of cPAN, 400°C is chosen as the heat treatment temperature.



**Figure 2.** (a) FT-IR spectra of pristine LNMO, cPAN-LNMO, cPAN and PAN. (b) Raman spectra of PAN, cPAN-300°C, cPAN-400°C and cPAN-500°C.

The TG–DSC is carried out to determine the content of cPAN in the composite. Figure 3a presents the TG-DSC curves of PAN between 35 and 800°C. There is an obvious exothermic peak at 318°C, indicating the cyclization of PAN. PAN begins to lose weight at about 270°C and finishes at around 690°C [34]. Figure 3b shows the TG curve of cPAN-LNMO composite ranging from 35 to 800°C. The evaporation of surface adsorbed water causes an obvious weight loss of about 0.17 wt%

between 35 and 200°C [34]. The inset in Figure 3b shows that pristine LNMO begins to decompose at about 690°C, so the weight loss about 0.35 wt% between 200 and 690°C results from the decomposition of cPAN. The designed value of PAN is 1.0 wt%. After heat treatment, the content of cPAN in the cPAN-LNMO composite is approximately 0.35 wt%.



Figure 3. (a) TG-DSC curves of PAN powder. (b) TG curve of cPAN-LNMO, the inset shows TG of LNMO.

Figure 4(a-d) show the FE-SEM images of precursor (Ni<sub>0.25</sub>Mn<sub>0.75</sub>)(OH)<sub>2</sub>, pristine LNMO, cPAN-LNMO and cPAN, respectively. The precursor  $(Ni_{0.25}Mn_{0.75})(OH)_2$  is composed of primary particles (Figure 4a), which aggregate to form sphere-like secondary particles with an average size of 5 µm. The pristine LNMO particles have a polyhedron shape with well-defined edges and smooth surfaces (Figure 4b), corresponding to good crystallinity of the LNMO particles. Compared with pristine LNMO, the morphology of cPAN-LNMO composite does not change significantly because of the thin coating layer. Figure 4d shows that the surface of cPAN is smooth. In order to prove that the cPAN is uniformly coated on the surface of LNMO, the EDS mapping is conducted. Figure 4(f-i) present the uniform elemental distributions of Mn, Ni, C and N in the cPAN-LNMO composite. The high resolution TEM (HR-TEM) images of pristine LNMO and cPAN-LNMO are demonstrated in Figure 5(a, b), respectively. The lattice fringes of the two samples are apparent in the HR-TEM images, indicating that the coating process did not damage the bulk structure of the LNMO. The interplanar spacing lattice of the two samples are both 0.45 nm. Figure 5b shows that an amorphous coating layer with the thickness of approximate3 ~ 5 nm is coated on the surface of the cPAN-LNMO composite. Based on the FT-IR and elements mapping data above-mentioned, it is supposed that the amorphous coating layer is the cPAN, indicating that cPAN is successfully coated on the surface of LNMO.



**Figure 4.** FE-SEM images of (a) precursor (Ni<sub>0.25</sub>Mn<sub>0.75</sub>)(OH)<sub>2</sub>, (b) pristine LNMO, (c) cPAN-LNMO and (d) cPAN. (e-i) SEM image and corresponding elemental distributions mapping of cPAN-LNMO.



Figure 5. HR-TEM images of (a) pristine LNMO and (b) cPAN-LNMO.

The charge and discharge tests are conducted to investigate the influence of the cPAN coating layer on the electrochemical performance of LNMO. Figure 6a presents the cycle performance of pristine LNMO and cPAN-LNMO at 1 C and 25°C. The initial discharge capacities of pristine LNMO and cPAN-LNMO are122.9 and 125.1 mAh g<sup>-1</sup>, respectively. The initial coulomb efficiency of cPAN-LNMO is 75.9%, which is slight higher than that of pristine LNMO (73%). After 300 cycles, the discharge capacities of pristine LNMO and cPAN-LNMO are 112.5 and 116.9 mAh g<sup>-1</sup>, respectively.

Figure 6b shows the capacity retentions of pristine LNMO and cPAN-LNMO, which are corresponding to their initial discharge capacities. The capacity retention of cPAN-LNMO is continuously higher than that of pristine LNMO. The discharge median voltage can be used to evaluate the polarization degree of the cell [35]. Figure 6c demonstrates the discharge median voltage curves of pristine LNMO and cPAN-LNMO. We can find that the discharge median voltage of pristine LNMO drops sharply, while that of cPAN-LNMO drops slowly, indicating that the cPAN coating layer is contributing to a reduction of the polarization of the cells. Figure 6d shows the rate performance of pristine LNMO and cPAN-LNMO at 0.2, 0.5, 1.0, 2.0, 5.0, 10 and 0.5 C. The cells were sequentially charged at 1C then discharged at various rates for five cycles and finally at 0.5 C. The discharge capacities of cPAN-LNMO are 118.7, 121.1, 121, 120.4, 118.2, 116, and 118.2 mAh g<sup>-1</sup> at 0.2, 0.5, 1.0, 2.0, 5.0, 10 and 0.5 C, respectively, which are much better than those of pristine LNMO. These results indicate that the cPAN is contributed to enhance the cycling performance and rate properties of LNMO, which is ascribed to the improved electronic conductivity of the cPAN [34].



**Figure 6.** Electrochemical performance of pristine LNMO and cPAN-LNMO: (a) cycle performance and coulombic efficiency at 1 C and 25°C; (b) capacity retention related to the initial cycle; (c) discharge median voltage; (d) rate performance.

Figure 7(a, c) demonstrate the charge/discharge curves of the 1st, 10th, 100th and 200th cycle of pristine LNMO and cPAN-LNMO, respectively. Both two samples exhibit a discharge plateau around 4.7 V of LNMO, corresponding to the reduction of Ni<sup>4+</sup> to Ni<sup>2+</sup>. Compared with pristine LNMO, the charge/discharge curves of cPAN-LNMO show better coincidence except the 1st cycle,

indicating that the cPAN can improve the reversibility of the LNMO cathode. Figure 7(b, d) show the CV curves of pristine LNMO and cPAN-LNMO, respectively. The cathodic and anodic peaks are observed at around 4.7 V for both pristine LNMO and cPAN-LNMO, which is associated with the oxidation/reduction of  $Ni^{4+}/Ni^{2+}$  [36]. The CV profile of cPAN-LNMO exhibits more reproducible than that of pristine LNMO.



**Figure 7.** Charge/discharge curves of (a) pristine LNMO and (c) cPAN-LNMO in different cycles between  $3.5 \sim 4.9$  V at 1.0 C. The CV curves of (b) pristine LNMO and (d) cPAN-LNMO between  $3.5 \sim 4.9$  V (vs Li<sup>+</sup>/Li) at the scan rate of 0.1 mV s<sup>-1</sup>.

Figure 8 shows the cycling performance of pristine LNMO and cPAN-LNMO at 55°C. To form a stable interface between the electrode and the electrolyte, the cells were pre-cycled at 1 C and 25°C for 3 cycles. Then the cells were cycled at 5 C and 55°C for 100 cycles. The initial discharge capacities of pristine LNMO and cPAN-LNMO are 119.2 and 118.6 mAh g<sup>-1</sup>, respectively. After 100 cycles at 55°C, the discharge capacity of cPAN-LNMO is 112.9 mAh g<sup>-1</sup> with the retention of 95.2%, while the discharge capacities of pristine is only 104.7 mAh g<sup>-1</sup> with the retention of 87.8%, indicating the superior cycling performance of cPAN-LNMO at elevated temperatures. Based on the results, it is assumed that a stable protecting layer of cPAN not only reduces the side reactions between the electrode and the electrolyte, but also increases the electronic conductivity of LNMO, leading to the improved cycling performance of cPAN-LNMO with other similar cathode materials at elevated

temperatures. It can be found that cPAN-LNMO exhibits excellent performance in both specific capacity and capacity retention.



Figure 8. Cycling performance of pristine LNMO and cPAN-LNMO at 5 C and 55°C.

Table 1. Comparison of	the cycling performance	e of the cPAN-LNMO	composite and	similar ca	athode
materials at eleva	ted temperatures.				

Material	Measurement condition (temperature / current density)	Cycle number	Specific capacity (mAh g <sup>-1</sup> )	Capacity retention (%)	Ref.
ZnO-LNMO	50°C/0.25 C	50	68.0	69.4	17
Al <sub>2</sub> O <sub>3</sub> -LNMO	55°C/0.5 C	100	116.0	90.0	18
Polythiophene- LNMO	55°C/1C	100	105.0	78.8	22
Polypyrrole- LNMO	55°C/1C	100	105.2	91.0	24
V <sub>2</sub> O <sub>5</sub> -LNMO	55°C/5C	100	116.2	92.0	37
cPAN-LNMO	55°C/5C	100	112.9	95.2	This work

In addition, the EIS is performed to investigate the effect of cPAN on the impedance of the cells. Figure 9a shows the typical Nyquist plots of pristine LNMO and cPAN-LNMO measured at the fully charge state of 4.9 V after 5 cycles at 25°C. Both the two cells display similar profile, consisting of an arc in the medium-high frequency range and a sloped line in the low-frequency range. The equivalent circuit model is presented in Figure 9b. The  $R_s$  is attributed to the electrolyte resistance in the cells, and the  $R_{ct}$  represents the charge transfer resistance. The  $W_s$  is ascribed to the diffusion of Li<sup>+</sup> in the active materials [37]. Figure 9c presents the fitting results, the  $R_{ct}$  of cPAN-LNMO is about half

of that of pristine LNMO, indicating the cPAN coating layer is beneficial for reducing the impedance of the LNMO electrode [34].



**Figure 9.** (a) EIS of pristine LNMO and cPAN-LNMO after 5 cycles at 1 C and 25°C; (b) the equivalent circuit for fitting; (c) the fitting values using the equivalent circuit of Figure 9b.



**Figure 10.** The mass percentage of Mn and Ni cations dissolved into the electrolyte after 50 cycles at 1 C and 25°C.

The dissolution of transition metal ions into the electrolyte is considered to cause the capacity fading of LNMO [38]. The amount of transition metal ions dissolved into the electrolyte was measured with the inductively coupled plasma (ICP). Figure 10 presents the mass percent of Mn and Ni cations of pristine LNMO and cPAN-LNMO dissolved into the electrolyte after 50 cycles at 25°C. The dissolved mass percent is calculated on the basis of the active materials. Compared to pristine LNMO, the dissolved mass percents of Mn and Ni cations are lower, indicating that the cPAN protective layer

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can reduce the dissolution of transition metal ions therefore enhance the electrochemical properties of LNMO.

## 4. CONCLUSION

In summary, the cPAN coating layer was uniformly coated on the surface of the spinel LNMO particles by a simple heat-treatment method. Compared to pristine LNMO, both the cycling performance and rate performance of cPAN-LNMO have been significantly improved, especially the cycling performance at elevated temperatures. The capacity retention of cPAN-LNMO is much higher than that of pristine LNMO at 5 C and 55°C. The cPAN coating layer not only can prevent the electrode materials from direct contacting with the electrolyte then reduce the amount of the transition metal ions dissolved into the electrolyte, but also increase the electronic conductivity of LNMO. Therefore, the high performance of cPAN-LNMO makes it a promising cathode material for high-voltage lithium-ion batteries.

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