Design and Tailoring of a Three-Dimensional Lithium Rich Layered Oxide-Graphene/Carbon Nanotubes Composite for Lithium-Ion Batteries

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Abstract: Poor rate capability and cycling performance are the major barriers to the application of lithium rich layered oxides as the next generation cathodes for lithium-ion batteries. In this paper, a novel tactics is applied to enhance the rate property and low temperature performance of lithium rich layered oxides materials by using graphene and multi-walled carbon nanotubes as the building blocks to form a hybrid 3D conductive network in the synthesized composites. Spray pyrolysis method is employed to obtain the target material. The hybrid 3D conductive network can decrease the reaction overpotential greatly, as well as reduce the cell resistance and enhance the lithium ion transportation in the bulk material, which are confirmed by cyclic voltammetry measurement and electrochemical impedance spectroscopy. The conductivity of the obtained composite is so high that no additional conductive agent is needed in the fabrication of electrodes. Our investigation further demonstrates that the conducting framework can efficiently alleviate the polarization of pristine lithium rich layered oxides material, leading to an outstanding enhancement in rate capability, low temperature performance and cycling stability.

Keywords: lithium rich layered oxides, hybrid conductive network, rate capability

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1. Introduction

Recently, lithium-rich layered materials with a general formula of $\text{Li}_2\text{MnO}_3 \cdot \text{LiMO}_2$ ($\text{M} = \text{Mn, Ni, Co}$) have attracted increasing interest, due to their high specific capacities (up to $250 \text{ mAh} \cdot \text{g}^{-1}$). [1, 2] However, the commercialization of those materials is currently hindered by some drawbacks the materials possessed, such as low rate capabilities [3], large voltage decay during cycling [4] and the irreversible capacity loss in the first charge/discharge process [5]. In particular, the poor kinetics is not only related to the Li_2MnO_3 component, lithium ion diffusion pathway, and interface reaction barrier, [2] but also associated with the electronic and ion conductivity of $\text{Li}_2\text{MnO}_3 \cdot \text{LiMO}_2$ ($\text{M} = \text{Mn, Ni, Co}$) and electrodes. [6] Thus improving the electronic and ion conductivity of the bulk material is an effective way to decrease the electrochemical and concentration polarizations in the electrodes, which will be also helpful to depress the side reactions and enhance Li^+ transportation during the charge/discharge processes. Consequently an enhanced cycling performance and better high-rate capability can be expected.

As is all known, carbon nanotube (1D) [7, 8] and graphene (2D) [9, 10] are appealing building blocks of conductivity network for the purpose of resolving the issues of sluggish electron transport kinetics and rate performances. Many types of composite materials consisting of graphene (GN) or carbon nano-tubes (CNTs) have been synthesized and used in LIBs to take advantage of their superior electrical conductivity and mechanical flexibility, such as $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, [11] LiFePO_4 , [12, 13] LiMO_2 , [14, 15] LiMn_2O_4 , [16] $\text{LiMnO}_3 \cdot \text{LiMO}_2$, [6, 17] and so on. Besides, hybridized

GN and CNTs which have 3D conductive network for active materials are also proposed to enhance the electrochemical performance and flexible of active materials.[18-20] However, it is difficult to form high effective conductive network when using these materials, while GN or CNTs could be only loosely wrapped on the surface of the second particles.[21] Most primary particles inside the second particles still show poor kinetics and high polarizations in the obtained materials, resulting in limited enhancement in electrochemical activity of the whole materials.[15, 22] Besides, GN can exhibit a steric hindrance effect for the Li^+ diffusion due to the planar structure.[23, 24] So the homogeneous dispersion and good contact design between nano-carbon and active material is the key point in this issue.

Spray pyrolysis is an effective one-step production technique with advantages of short production time and homogenous particle composition in the final products.[25, 26] Moreover, Spray pyrolysis is also an effective method in maintaining phase uniformity of the prepared materials due to the rapid evaporation of solvent in the synthesizing process, which is beneficial in forming isotropic capillary compression force to avoid the agglomeration of GN sheets and CNTs caused by van der Waals force.[26]

In this work, we designed and prepared $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$ (denoted as LR-NCM) composites with hybrid multi-walled CNTs and GN sheets conductive network by spray pyrolysis method. In our design, the LR-NCM primary particles were tightly wrapped with multi-walled CNTs and GN pieces (with the size of 1-3 μm) connect among particles of LR-NCM, as shown in Figure 1. Hereafter, for

simplification, we abbreviate the present double nano-carbon decorated LR-NCM composite as LR-NCM@CNT&GN, in which LR-NCM, CNTs and GN represent the LR-NCM primary particles, multi-walled carbon nano-tubes, and graphene sheets, respectively.

2. Experimental

2.1 Synthesis of LR-NCM

LR-NCM sample was synthesized by a Spray pyrolysis method combining with annealing. In a typical process, stoichiometric mixture of $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$ (5% excess) were grounded for 2h with de-ionized water as solvent. The resulting slurry was added into the spray drier machine by peristaltic pump with a speed of $1500\text{mL} \cdot \text{h}^{-1}$ and atomized at 220°C with atomizing pressure of 0.5MPa. The obtained hollow spherical precursor was heated at 500°C for 10h and then sintered at 850°C for 16h.

2.2 Prepared LR-NCM@GN&CNT

In preparing the LR-NCM@GN&CNT composite, the as-prepared LR-NCM particles were firstly dispersed by ball-milling method, the sample was milled at a planetary ball mill with a speed of 300 rpm for 2h using tungsten carbide vial and zirconium oxide balls. A ball to-mixture weight ratio was 30:1. Afterwards, 1600 g composite conductive aqueous solution NCL-O5 (GN:CNTs=3:7 with 5.7% solid content from BTR Nano Tech. Co., Ltd.) was dispersed in 1.5L water and, then 920g dispersed of LR-NCM was added to the suspension and magnetically stirred at 50°C for 4h. The resulting slurry was added into the spray drier machine by peristaltic

pump at $1500\text{ mL}\cdot\text{h}^{-1}$ and atomized at 220°C with atomizing pressure of 0.5MPa . The as-obtained mixture was dried overnight at 120°C .

2.3 Characterization

X-ray diffraction (XRD) measurements of the LR-NCM and LR-NCM@GN&CNT powder were performed using a Philips PW3710 with filtered Cu K α radiation (Rigaku D/max-2500). Raman measurements were carried out using a DXR Raman Microscope (Thermo Fisher Scientific Inc.) with a laser wavelength of 514.5 nm . The morphology, size and the microstructures morphology of the LR-NCM powder and the LR-NCM@GN&CNT composite were investigated by Scanning electron microscopy (SEM; Hitachi S-4800) with an operation voltage of 5 kV and transmission electron microscopy (TEM; JEM-2100HR). Thermogravimetric analysis (TGA) curves were collected by using a Netzsch system with a heating rate of $5^{\circ}\text{C}\cdot\text{min}^{-1}$ in air. The four-point probe resistivity measurement system is used to measure the electronic conductivities of the LR-NCM powder and the LR-NCM@GN&CNT composite.

2.4. Electrochemical measurement

Electrochemical measurements were performed using Swageloktype cells assembled in an argon-filled glove box. A mixture of LR-NCM@GN&CNT and poly(vinyl difluoride) (PVDF) with a weight ratio of 90:10 was pasted on an Al foil to prepare the working electrodes. As a comparison, the electrode of LR-NCM was prepared by mixing active material, carbon black(CB) and poly(vinyl difluoride) (PVDF) with a weight ratio of 80:10:10 and Al foil was used as the current collector.

The loading mass of active materials is about 10 mg cm^{-2} . Pure lithium foil was used as a counter electrode. Celgard 2502 (25 μm) was utilized as separator. The electrolyte consisted of a solution of 1 M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (3:7 in wt%) obtained from Guangzhou Tinci Materials Technology Co., Ltd. The cells were tested on a LAND-CT2001A battery test system (Jinnuo Wuhan Co., Ltd., P. R. China) with Galvano statically charged-discharged mode. Low temperature performance was tested in the voltage range of 2.0-4.8V under a constant current density of 0.2 C at various low temperatures (25, 0, -10 and -20°C). Here, it is noted that the cycling at -20 , -10 and 0°C was conducted in a household refrigerator with about $\pm 2^\circ\text{C}$ fluctuation. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on an Autolab PG302N at room temperature.

3. Results and discussion

Figure 2a shows the XRD patterns of LR-NCM and LR-NCM@GN&CNT samples. Both samples exhibit typical layered diffraction pattern, which could be indexed to the trigonal symmetry of layered LiMO_2 (M could be Ni, Co or Mn). The weak humps located between 20° and 23° are well-known as a consequence of the unique LiMn_6 ordering in transition metal layers.[27] This observation is accompanied by the existence of nano-domains of Li_2MnO_3 integrated into the compatible LiMO_2 structure. Any peaks for graphene and CNTs weren't observed from all the reflections due to its nanoscale size and low content. The Raman spectra recorded for the pristine material LR-NCM and LR-NCM@GN&CNT composite in

the range 200-2000 cm^{-1} is shown in figure 2b. The major peaks both pristine LR-NCM and LR-NCM@CNT&GN have been observed at 425, 485 and 595 cm^{-1} . The peaks at 485 and 595 cm^{-1} are attributed to the E_g and A_{1g} Raman-active modes for the M–O arrangements in the layered LMO_2 structure.[28] And the peak at 425 cm^{-1} should derive from the A_g and B_g modes of Li_2MnO_3 . [6, 29] For LR-NCM@GN&CNT, intense vibrations observed at 1340 and 1574 cm^{-1} correspond to the D and G bands of carbon nanostructures, respectively. The D band arises due to the disorder induced in sp^2 -bonded carbon, whereas the G band arises from the in-plane vibration of sp^2 carbon atoms of graphene, which is an indication of the existence of graphene and CNTs (CNTs is composed entirely of sp^2 carbon–carbon bonds) in the composite.

The size, morphology, and structure of the as-prepared samples were characterized by SEM. The low-magnification SEM image of Figure 3a reveals that the LR-NCM particles have a hollow spherical shape with a size of about 5-8 μm . The high-magnification SEM (Figure 3b) of the LR-NCM shows that LR-NCM primary particles with sizes of 200-300nm have smooth surface and highly crystalline. Interestingly, the LR-NCM@GN&CNT composite (Figure 3c) displays a Bird's nest-like shape with larger particle size of 10-30 μm . The Bird's Nest-like shape, is a kind of deformation of hollow spherical shape, may originate from the isotropic capillary compression force during the rapid evaporation of solvent in spray pyrolysis process. The high-magnification SEM (Figure 3d) indicates that the primary particle is embed in the three-dimensional(3D) net which interweaves by the GN and CNTs,

forming a well-connected microenvironment. Furthermore, the TEM image (Support Information 2) of LR-NCM@GN&CNT also displays the primary particles have been tightly enwrapped and interweaved by flexible graphene and CNTs. The unique hierarchical structure and electric contact microenvironment of the composites would be expected to provide a unique electronic conductivity and mass transfer kinetics, which are in turn responsible for the respective electrochemical performances.

In order to further clarify the structure of the hybrid 3D net wrapped between the LRNCM particles, we present the low magnification TEM images of LR-NCM@GN&CNT composite in Figure 4a. It is clear to observe a particle twining around several CNTs and connect with another particle by surrounded CNTs and GN, resulting in a conductive network to provide more effective and continuous pathways for electron transfer than single conductive addition such as black carbon, CNTs, GN and so on. The high resolution TEM image of LR-NCM@GN&CNT composite (Figure 4b) reveals the CNTs and GN are coating on the surface of LR-NCM primary particles and good connect among CNTs, GN and LR-NCM primary particles are formed in the composites. The electronic conductivities of the pristine LR-NCM and LR-NCM@CNT&GN are also tested (Figure 4c), LR-NCM@CNT&GN exhibits an electronic conductivity of $3.7 \times 10^{-1} \text{ S} \cdot \text{cm}^{-1}$, which is almost a six orders of the magnitudes increase than the pristine LR-NCM ($6.8 \times 10^{-7} \text{ S} \cdot \text{cm}^{-1}$). As we all know, the electronic conductivity of powder is not only related to its intrinsic properties but also is highly affected by the numbers of particle contacts. So the high electronic conductivity also means that the CNT&GN network in LR-NCM composites

contacted closely and interconnected.

Cyclic voltammetry (CV) is a useful technique for studying the phase transformation and ionic diffusion process during electrode reactions. Figure 5 show the initial two cyclic voltammetry (CV) curves of the LR-NCM and the LR-NCM@GN&CNT electrodes in the potential range of 2.0–5.0 V at a scan rate of $0.05 \text{ mV}\cdot\text{s}^{-1}$. Compared with the pristine LR-NCM material, the current intensities of oxidation and reduction peaks of LR-NCM@GN&CNT are obviously increased. The potential difference between these two peaks is smaller for the LR-NCM@GN&CNT electrode. Those results indicate that the LR-NCM@GN&CNT composite with optimized electrode kinetics and reversibility by the aid of CNT&GN network (as shown in Figure 4c), which are expected to endow an improved rate capability and cycle stability as the side reactions might be depressed with the significantly reduced overpotential.[14]

The rate performance is one of the important factors of in hindering the commercial applications of lithium rich layered materials. To evaluate the rate performances of the pristine LR-NCM material and the LR-NCM@GN&CNT composite, both of them were cycled from 0.1C to 12C ($1\text{C}=250 \text{ mAh}\cdot\text{g}^{-1}$) between the voltage limits of 2.0–4.8 V vs Li^+/Li (Figure 6a). While the LR-NCM electrode exhibits nearly no discharge capacity at 10C, the LR-NCM@GN&CNT composite can still deliver a discharge capacity of about $65.7 \text{ mAh}\cdot\text{g}^{-1}$. Furthermore, the LR-NCM@GN&CNT composite has a discharge capacity as high as $43.0 \text{ mAh}\cdot\text{g}^{-1}$ even at a very high rate of 12C. The marked improved rate performance is in good

agreement with the above CV tests. Another enhanced property for the LR-NCM@GN&CNT is its superior low temperature performance. Figure 6b displays the discharge curves of the pristine LR-NCM and LR-NCM@GN&CNT composite at various low temperatures under a 0.2 C rate with the same charging condition (25 °C, 0.2C rate). The discharge capacities of LR-NCM@GN&CNT are 286.2, 209.8, 173.4 and 135.5 mAh·g⁻¹ at 25, 0, -10 and -20 °C, respectively. It still displays 73.3% (0°C), 60.6% (-10°C) and 47.3% (-20°C) of the capacity gained at 25°C, while the pristine material can exhibit 67.8% (0°C), 55.6% (-10°C) and 40.3% (-20°C) of the capacity obtained at 25°C, respectively. Further, the discharge curves also reveal that the middle discharge voltage of LR-NCM@GN&CNT composite is obvious higher at various low temperatures than that of LR-NCM. According to the rate performance and low temperature testing data, coupled with the CV results and electronic conductivities, it can be deduced that the GN/CNTs conductive network plays an important role in improving the electrochemical properties of LR-NCM material. The main role of the GN/CNTs network can be summarized as follows. First, the network can afford an efficient electron pathway and provide better electrical contacts among electrochemical active particles, resulting in the decrease of the charge transfer impedance. Second, the GN and CNTs have huge specific surface area which is helpful for the electrolyte transport throughout the primary particles efficiently and disperse uniformly on the surface of each primary particle, which can not only enhance the possibility of Li⁺ diffusion in the electrode but also stabilize the interface effectively.

The cycling behavior and the corresponding coulombic efficiency profiles of LR-NCM@GN&CNT and LR-NCM are shown in Figure 7. As can be seen, LR-NCM@GN&CNT delivers a higher discharge capacity ($\sim 288 \text{ mAh}\cdot\text{g}^{-1}$) than that of LR-NCM ($\sim 250 \text{ mAh}\cdot\text{g}^{-1}$) at 0.2C with the voltage range of 2.0-4.8V at room temperature. The initial coulombic efficiency of the LR-NCM@GN&CNT ($\sim 81.2\%$) is also higher than that ($\sim 73.4\%$) of the LR-NCM. It is noted that both the discharge capacity and the initial coulombic efficiency of the LR-NCM@GN&CNT are higher than that of the LR-NCM. The results may be caused by the following reasons: First, the introduction of GN/CNTs network is beneficial for the promotion of the transformation reactions (the more $\text{Mn}^{4+}/\text{Mn}^{3+}$ transformation) at the $\sim 4.5 \text{ V}$ plateau during the first charging process of lithium rich layered oxides.[6] Second, building 3D GN/CNTs network among the LR-NCM materials can significantly reduce the polarization as shown in the CV curves (see Figure 5), which is helpful for depressing the irreversible side reactions in the initial charging. And third, the 3D GN/CNTs network can act as a bridge to increase the area that is simultaneously accessible to electrons and lithium ions, thus significantly reducing the inert zones and leading to high specific capacity. [15] As shown in Figure 7, the efficiencies of both samples maintain around 98% in all cycles except for the first one, indicating their good cycling behaviors. The capacity retention is above 88.9% after 50 cycles for the LR-NCM@GN&CNT composite, much higher than that for the pristine LR-NCM, which retention is only 83.0%. It can be seen that the cyclability of LR-NCM@GN&CNT material is better than that of LR-NCM. On one hand,

introducing 3D GN/CNTs network into LR-NCM material can not only reduce the polarization of electrode but also enhance the possibility of Li diffusion. On the other hand, the continuous and 3D GN/CNTs network provides well-developed porous structures, high mechanical strength, and superior flexibility to the LR-NCM@GN&CNTs composite, which is helpful for the composite to endure the volume changes during cycling.

To further understand the influences of the hybrid GN/CNT networks on the Li-rich cathode, EIS has been carried out to test the ionic conductivity of the pristine LR-NCM and LR-NCM@GN&CNT composite, respectively. The impedance spectra at open circuit condition under 50% SOC for the LR-NCM@GN&CNT and the pristine were measured, and the Nyquist plots (Z' vs. Z'') are shown in Figure. 8a. The plots consist of three regions, a semicircle in the high-frequency region as well as another one in the intermediate-frequency region and the Warburg-type element (the sloping line) in the low-frequency region. The first semi-circle can be attributed to the surface film resistance (R_f), whereas, the second one represents the charge transfer resistance (R_{ct}). The Warburg impedance in the low frequency refers to the Li^+ diffusion in the bulk of the electrode, which has been used to determine the apparent diffusion coefficient (D_{Li^+}) in the compound. As summarized in Table 1, the value of R_f is notable decreased from 254.3 to 92.0 m Ω and the charge transfer impedance (R_{ct}) is greatly decreased from 146.5 to 64.8 Ω . As we all known, during first charge and discharge process of LR-NCM, oxygen molecule loss and structure modification is involved. Meanwhile, a series of spontaneous reactions between the active materials

and the electrolyte solvents take place in this process, resulting in some depositions deposited on the materials surface, especially, at high voltage. Those depositions are the mainly reason of R_f . As mentioned above, 3D GN/CNTs networks can not only afford an efficient electron pathway and better electrical contacts among electrochemical active particles but also provide an unperturbed Li^+ supply for the primary particles by the efficient electrolyte transport. Therefore, the LR-NCM@GN&CNT with 3D GN/CNTs networks can effectively decrease polarization and depress the side reactions between the cathode active materials and the electrolyte solvents. The enhanced synergic effects of the electron and ionic transport lead to remarkable decrease values of R_f and R_{ct} .

In addition, the D_{Li^+} is calculated by the formula, $D_{\text{Li}^+} = \frac{0.5R^2T^2}{n^2F^4A^2C^2\sigma^2}$ where R is the gas constant, T the absolute temperature, C the concentration of Li^+ in the material, F the Faraday constant, A the surface area of the electrode, and σ the Warburg factor obeying the following relationship: $Z' = R_s + R_{ct} + \sigma\omega^{-1/2}$. Z' is the real part of impedance, thus σ can be obtained from the linear fitting of Z' vs. $\omega^{-1/2}$ in the low frequency range (Figure 8b). As be presented in Table 2, the calculated D_{Li^+} of the LR-NCM@GN&CNT and the pristine are $5.1 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ and $7.73 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively, which reveals a significantly enhanced the apparent diffusion (D_{Li^+}) for the LR-NCM@GN&CNT sample. The 3D GN/CNTs network which can supply enough Li^+ for the primary particles and has the ability to store and release a great quantity of charge rapidly. Therefore, the 3D GN/CNTs network imparts a beneficial effect in terms of improved kinetics of the Li^+ insertion/extraction process.

To get a deep understanding of how the hybrid conductive network performs, it is necessary to discuss the charge transfer process in such composites. By using tradition conductive addition such as SP (super-P), acetylene black, and so on, those particles are usually filled on the second particle surface and also particle corners. It is difficult to form continuities conductive network in three-dimensional (3D) unless massive conductive additive is added in the electrode which is easily result in energy density loss. Furthermore, during long term of charge and discharge process, more and more gap can be formed in the particles of LR-NCM,[30] which will lead to degradation of cycle performance due to the rapidly increasing charge transfer resistance (R_{ct}) as well as the overpotential. In sharp comparison, the high mechanical strength and flexible nature of the CNTs tightly interweaves around each primary particle and flexible graphene pieces exists among the LR-NCM@GN&CNT primary particles. This 3D network forms a well-connected microenvironment at 3D orientation as shown in Figure 9, which provides a superhighway for the electron as resulted in Figure 4c. The graphene sheets with planar structure can easily serve as ideal electrical "bridge" in linking the second particles, resulting in high quality contact between the current collector and the active materials, and the high conductivity of the material enables e^- to flow along the conductive plane to reach the active particles to react with Li^+ . Besides, the bird' nest-like shape and high specific surface area of GN&CNT network provide enough electrolyte for Li^+ faster transportation. As a result, the charge transfer process of electrode allowing a high flux of Li^+ to pass through in all directions, while its high conductivity enables e^- to

flow along the conductive plane to reach the composite for reaction with Li^+ .

4. Conclusions

In summary, LR-NCM@GN&CNT composite material with a hybrid GN/CNTs constructing 3D conducting networks was successfully prepared by a spray pyrolysis method combining with annealing. Compared with LR-NCM sample, the LR-NCM@GN&CNT composite displays better specific capacity, rate capability, low temperature properties, and long cycling stability. Those results can be ascribed to the improved ionic diffusion as well as the efficient electron transport and transfer in the electrode of LR-NCM@GN&CNT. Besides, the concept of material design and tailoring used in this study has many advantages: 1) the procedure is very simple and easy to mass manufacture; 2) with LR-NCM primary particles uniformly distributed in the hybrid GN&CNTs network, it is easy to achieve full utilization of the active material and to prevent polarization; 3) the continuous and 3D GN&CNTs network renders well-developed porous structures, high electronic conductivity, and superior capability of absorbing electrolyte. Therefore, this strategy may be a useful guidance to the future design and synthesis other electrode materials.

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Figure captions:

Figure 1 Schematic illustration of the preparation process and the micro-scale structure of LR-NCM@GN&CNT composite.

Figure 2. (a) XRD patterns and (b) Raman spectra of LR-NCM (black line) and LR-NCM@CNT&GN(red line) powders.

Figure 3. SEM images of LR-NCM material (a and b) and LR-NCM@GN&CNT (c and d)

Figure 4 (a) TEM and (b) HR-TEM images of the LR-NCM@GN&CNT materials which is corresponded to the area of the white rectangle 1 in (a); (c) Electronic Conductivity profiles of the pristine LR-NCM and LR-NCM@GN&CNT.

Figure 5 CV of the LR-NCM and LR-NCM@GN&CNT composite in the voltage range between 2.0-5.0V; scan rate $0.05 \text{ mV}\cdot\text{s}^{-1}$

Figure 6 (a) Rate performance of LR-NCM and LR-NCM@GN&CNT. (b) low temperature discharge curves at various low temperatures (25, 0, -10 and -20 °C) under a 0.2 C rate.

Figure 7 Cycling performance and Coulombic efficiency of the pristine LR-NCM and LR-NCM@GN&CNT composite with the voltage range of 2.0-4.8V at room temperature.(The discharge current of the First 3 cycles is 0.2C and then is 0.5C).

Figure 8 (a) The impedance spectra of pristine LR-NCM and LR-NCM@GN&CNT composite. (b) The relationship plot between Z' and $\omega^{-1/2}$ at low-frequency region.

Figure 9 Schematic diagrams of electrodes with conductive additives free mechanism.

Table captions:

Table 1. Impedance parameters of equipment circuit of samples

Item	R_s ($m\Omega$)	R_{sei} ($m\Omega$)	R_{ct} ($m\Omega$)	Z_w ($m\Omega$)
LR-NCM	8.63	254.3	146.5	1069.0
LR-NCM@GN&CNT	2.69	92.0	64.8	530.5

Table 2. σ values and the apparent diffusion coefficients of lithium ion for LR-NCM

and LR-NCM@GN&CNT obtained by EIS.

Samples	LR-NCM	LR-NCM@GN&CNT
A (cm^{-2})	1.13	1.13
C ($\text{mol}/\text{cm}^{-3}$)	0.001	0.001
σ	18.92528	7.33747
D_{Li} ($\text{cm}^{-2} \text{ s}^{-1}$)	7.7E-11	5.1E-10

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9