Int. J. Electrochem. Sci., 15 **(2020)** 11632 – 11642, doi: 10.20964/2020.11.45

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Ternary Cathode Materials $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with High Electrochemical Performances Synthesized by Hydrothermal Synthesis with the Aid of Surfactants

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Received: 27 July 2020 / *Accepted:* 3 September 2020 / *Published:* 30 September 2020

The ternary layered cathode materials $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCM) was successfully synthesized by hydrothermal process with the assistance of surfactant (sodium alkylbenzene sulfonate (SDBS), polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB)). The effects of surfactants on the morphology, structure and electrochemical properties of the materials were investigated in detail. The structure and morphology of the materials was characterized by XRD and SEM respectively, and the electrochemical properties of the materials including initial charge and discharge, cycle and rate performances, as well as electrochemical impedance spectroscopy (EIS) were studied by means of electrochemical workstation and battery comprehensive performance tester. The results showed that the material synthesized with the aid of SDBS had more uniform size, better dispersion and better crystallinity. In the voltage range of 2.5 ~ 4.6 V, the initial discharge specific capacity reached 184.66 mA·h/g, and the capacity retention rate remained at 87.03% after 100 cycles at 0.5 C. It indicated that our synthesized LNCM material had good morphology, structure and electrochemical performances. Therefore, choosing the ideal surfactant is a very effective method to assist the synthesis of high-performance cathode material.

Keywords: $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCM); Surfactant assisted synthesis; Hydrothermal; Electrochemical performances

1. INTRODUCTION

At present, the research and industrialization of new energy vehicles are widely encouraged and supported by the state, and the development of high energy density materials is the trend and urgent requirement for the development of power batteries in the future[1]. Among all the cathode materials, the high energy density ternary cathode materials have been particularly favored by researchers in recent years, and has become a research hotspot in the lithium battery industry[2-3]. Studies have shown that the morphology, structure and composition of materials have a very large impact on electrochemical performance[4-7]. Among them, sphericalization, nanocrystallization and porous structure are one of the most important means to improve the energy density of materials[8]. As we know, spheroidization can increase the tap density of the material, thereby increasing the energy density of the material and promoting the industrialization process of the material. The nanocrystallization may result in larger specific surface area and effectively shorten the diffusion path of lithium ions[9]. The porous structure can increase the contact area between the materials and the electrolyte, which is beneficial to the infiltration of the electrolyte. At high current density, lithium ions are more easily deintercalated on the surface of the materials[10]. Therefore, the goal of this research is to synthesize a ternary precursor with good spherical morphology, nanometer and porous structure, and finally produce a ternary lithium ion battery with good electrochemical performance.

Surfactant is a substance having a unique amphiphilic functional group, therefore, the addition of a surfactant is beneficial to promote compatibility between the components[11]. In addition, in the process of surfactant-assisted synthesis of various materials, the difference in composition and structure of surfactant will have different effects on the morphology and structure of the materials[12]. It is found that, in the process of hydrothermal and crystallization, the surfactant can play its role as a soft template, which can simultaneously change the crystal growth direction and microstructure of the primary and secondary crystal grains, and prevent the growth and agglomeration of the particles[13]. Obviously, surfactant-assisted synthesis is very advantageous and effective in the achievement of uniform morphology and nanostructured materials

In this paper, the $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ (NCM) precursor material was synthesized by hydrothermal method with the assistance of surfactant (SDBS, PVP, CTAB). The influence of different surfactants on the morphology and structure of the ternary precursor and the electrochemical performance of the corresponding ternary lithium ion battery had been systematically studied and analyzed by comparison.

2. EXPERIMENTAL DETAIL

2.1. Synthesis of NCM precursor

The precursor $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ (NCM) was synthesized following the steps below. According to molar ratio 1 : 1 : 1, 0.789 g $NiSO_4·6H_2O$, 0.8433 g $CoSO_4·7H_2O$, 0.507 g $MnSO_4·H_2O$ was dissolved in 40 mL deionized water, and 0.009 mol Na_2CO_3 and 0.001 mol surfactant (sodium alkylbenzene sulfonate (SDBS), or polyvinylpyrrolidone (PVP), or cetyltrimethylammonium bromide (CTAB)) were dissolved in 40 mL deionized water in another beaker. Then the evenly mixed Na_2CO_3 and surfactant solution was slowly dropped into the precursor solution, followed by hydrothermal treatment for 12 h under 170 ^{0}C, natural cooling process, and adequate filtration. After 12 h drying at 80 ^{0}C, then the pink precursor NCM was achieved.

2.2. Two-step sintering process

According to the molar ratio 1 : 1.05, the precursor NCM and LiOH·H_2O were thoroughly ground in a mortar, followed by a two-step sintering process in a muffle furnace. The pre-sintering was carried out at 550 ^{0}C for 5 h, and the subsequent sintering treatment was handled at 850 ^{0}C for 18 h with a heating rate 2 ~ 10 ^{0}C /min. Naturally cooled to room temperature, then ternary cathode material $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCM) was successfully synthesized.

2.3. Structure and morphology

The crystal structure of synthetic material was characterized by X'Pert Pro X-ray diffractometer (40kV, 40 mA, Cu target Kα radiation λ=1.5404 Å, 2θ=10°-80°, 5°/min of scanning speed, PANalytical), and the morphology of synthetic material was analyzed by FESEM (5 kV, SU5000, HITACHI)

2.4. Electrochemical measurement

Electrochemical experiments were carried out on CR2016 button batteries. According to mass ratio of 8 : 1 : 1, active materials, carbon black and poly vinylidene fluoride (PVDF) were mixed evenly, then N-methyl-2-pyrrolidone solvent was added to them to form electrode slurry. The slurry was coated evenly on the aluminum foil with a coater, then it was dried in a vacuum drying oven at 80°C for 12 h, followed by punching it into a circular sheet with an area of 1.131 cm^2 and average weight of 1.51 mg. Metallic lithium and celgard2400 polypropylene microporous membrane was used as anode and separator, respectively. The electrolyte was composed of 1M $LiPF_6$ in a mixture of dimethyl carbonate (DMC)/ethylene carbonate (EC) (volume ratio of 1 : 1). The CR2016 coin battery was assembled in a high purity argon glove box, in which the relative humidity was less than 0.1 ppm and oxygen pressure was less than 0.1 ppm. These assembled batteries were stand still for 12 h for activation, followed by electrochemical performance testes including charge and discharge, electrochemical impedance spectroscopy (EIS) and cyclic voltammetric (CV). The CV and EIS tests were performed on an electrochemical working station under room temperature conditions (Init E(V)=2.98, High frequency (Hz) = 1×10^5, Low frequency (Hz) = 0.1, CHI760e, Shanghai Chen Hua Co., Ltd., China). The charge and discharge tests including cycle and rate performance were carried out using the NEWARE batteries test system (BTS-4000, Shenzhen New will Co., Ltd., China).

3. RESULTS AND DISCUSSION

3.1. Influence of different surfactants on materials structure

It can be seen from Fig. 1 that the synthesized cathode material belonged to the hexagonal R3m space group and had a typical α-$NaFeO_2$ layered structure[14]. In all the diffraction patterns, there were only sharp diffraction peaks without any other impurity peaks, which meant that the synthesized material had a good crystallinity and a high purity. After the addition of the surfactant, the corresponding

(108/110) diffraction peak splitting was more pronounced, indicating that the synthesized ternary materials had a typical layered structure, and the surfactant can promote the improvement of the layered structure[15]. In the lattice constant, when the layer spacing c/a >4.9, the material has good layered structure, and the larger the ratio, the better the deintercalation of lithium ions between the layered structures[16]. The relevant parameters obtained by refining the XRD pattern were listed in Table 1. It can be found that the c/a value of 4.9647 belonged to the material without surfactant addition, but the c/a value higher than 4.97 corresponded to these materials added different surfactants, indicating that the unique properties of surfactants had an important influence on the layered structure of ternary materials. As a result, a good layered structure was beneficial to facilitate the migration of lithium ions, then further increasing the diffusion coefficient of lithium ions. The $R = I_{003}/I_{104}$ is the intensity ratio of 003 crystal plane to 104 crystal plane, reflects the crystallinity of the material and the degree of cation mixing of the material[17]. When R<1.2, the degree of cation mixing is serious, which will reduce the electrochemical performance. When R>1.2, the degree of cation mixing is slight, which is favorable for the stability of the layered structure and the improvement of electrochemical performance. Compared by the R values, it can be found that the addition of surfactant can effectively reduce the degree of cation mixing of the material. In addition, $(I_{006} + I_{102})/I_{101}$ is the intensity ratio of $(I_{006} + I_{102})$ crystal plane to 101 crystal plane, the value $(I_{006} + I_{102})/I_{101}$ is often used to judge the order of the hexagonal close-packed structure. In general, the value is ideal around 0.5. With the temperature increases, the value gradually decreases, and the order of the hexagonal close-packed structure gradually increases[18]. Therefore, our synthesized materials had an ordered close-packed hexagonal structures.

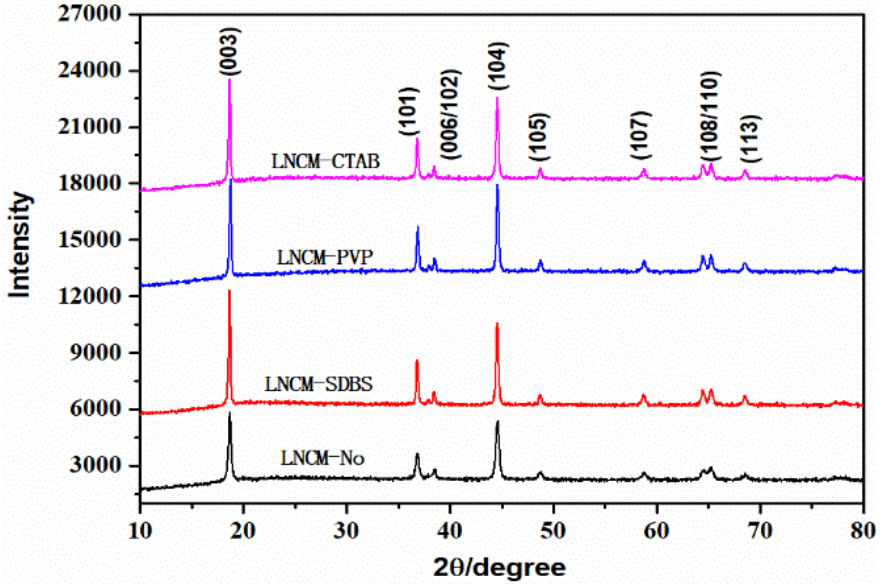

Figure 1. XRD patterns of the synthesized NCM materials

Table 1. Lattice structural parameters of cathode materials with different surfactan

Surfactant	a/nm	c/nm	c/a	V/nm^3	R=I_{003}/I_{104}	$(I_{102}+I_{006})/I_{101}$
None	2.8644	14.2209	4.9647	0.10063	1.11726	0.448908
SDBS	2.8582	14.2260	4.9773	0.10075	1.32021	0.473096
PVP	2.8586	14.2221	4.9752	0.10065	1.18005	0.448626
CTAB	2.8597	14.2264	4.9748	0.10072	1.22389	0.456932

3.2. Morphology analysis of cathode materials achieved by different surfactants addition

Fig. 2 showed SEM images of these samples achieved by different surfactants addition at different magnifications.

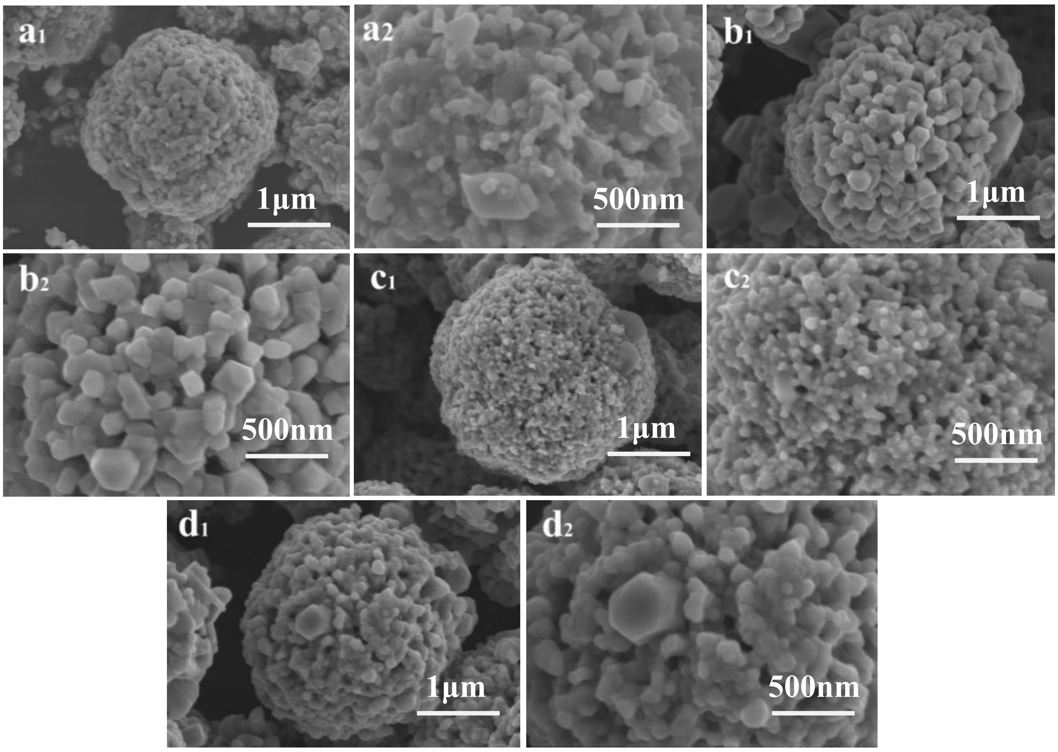

Figure 2. SEM images of synthetic NCM materials. (a_1, a_2) without surfactant, (b_1, b_2) with SDBS, (c_1, c_2) with PVP, (d_1, d_2) with CTAB

Compared with these samples without surfactant addition, the degree of agglomeration of surfactant-addition materials was effectively suppressed, and the particles with more uniform size, better dispersibility and crystallinity can be presented. In addition, the porous structure was beneficial to promote the penetration of electrolyte and the occurrence of electrochemical reactions. Due to its unique amphiphilic functional group and organic long-chain structure, the surfactant can be used as a soft template[19-20]. In the hydrothermal synthesis process of the precursor, the surfactant was evenly distributed in the precursor particles, thereby promoting the formation of particles with uniform size and good dispersion. Compared by the b1, b2, c1, c2, d1, and d2 in Fig. 2, it can be found that the effects of different surfactants were not exactly the same, and the synthetic material with the assistance of SDBS had better uniformity, dispersibility and crystallinity.

3.3. Electrochemical performance

3.3.1. Cycle, rate and initial charge and discharge curves

Fig. 3 showed the cycle performances of synthesized materials with different surfactants addition at 0.5 C, and the corresponding discharge specific capacity data was shown in Table 2.

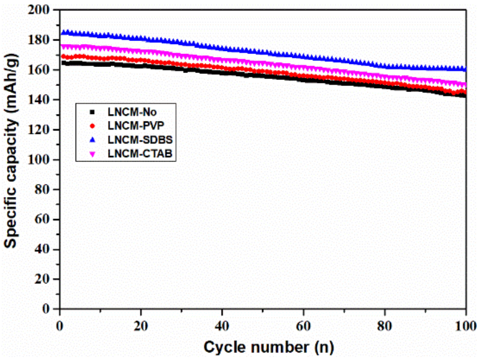

Figure 3. Cycle performance of cathode materials with different surfactants

Table 2. Electrochemical properties of cathode materials with different surfactants

Surfactant	Initial discharge specific capacity （mA·h/g）	Specific capacity after 100 cycles (mA·h/g)	Capacity retention rate (%)
None	164.81	141.55	85.88
SDBS	184.66	160.71	87.03
PVP	168.97	145.57	86.15
CTAB	175.67	151.55	86.27

The corresponding initial discharge specific capacity for these synthetic materials assisted by surfactants (SDBS, PVP and CTAB) was 184.66, 168.97, 175.67 mA·h/g respectively, it still remained 160.71, 145.57, 151.55 mA·h/g respectively after 100 cycles, and the corresponding capacity retention rates was 87.03%, 86.15%, and 86.27% respectively. Without surfactant addition, the initial discharge specific capacity was only 164.81 mA·h/g, and the specific capacity declined to 141.55 mA·h/g after 100 cycles, it had only 85.88% capacity retention rate. Therefore, the addition of surfactants can effectively improve the initial discharge specific capacity and cycle performance of LNCM materials. By comparison, SDBS was the most effective auxiliary material in improving the cycle performance of LNCM material.

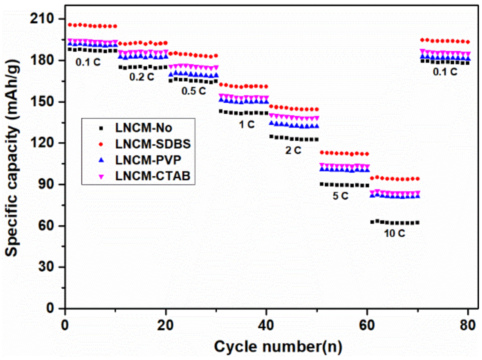

Figure 4. Rate performances of cathode materials with different surfactants

Fig. 4 showed the electrochemical performances of the synthesized materials at 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C, and 10 C rates, and the corresponding discharge specific capacities at different rates were listed in Table 3.

Table 3 Discharge specific capacity of cathode materials at different rate

Sample	Discharge Specific capacities at different rates（mA·h/g）						
	0.1 C	0.2 C	0.5 C	1 C	2 C	5 C	10 C
LNCM-No	187.9	174.9	165.2	142.9	124.7	87.1	52.7
LNCM-SDBS	205.8	192.3	184.7	162.3	146.6	113.2	86.6
LNCM-PVP	192.1	182.5	169.7	151.2	134.1	97.8	71.8
LNCM-CTAB	194.8	186.3	175.9	154.8	138.7	102.3	74.6

Combining the data of Fig. 4 and Table 3, it revealed that the addition of surfactants SDBS, PVP and CTAB effectively boosted discharge specific capacity in different degrees, especially at a high rate. Among the three surfactants, the effect of SDBS on discharge specific capacity was the most desirable. For example, the discharge specific capacity of LNCM-No material had only 87.1 mA·h/g at 5 C, but that of LNCM-SDBS material still retained 113.2 mA·h/g, which was 30% higher than that of LNCM-No material. Similarly, the discharge specific capacity of LNCM-No material sharply reduced to 52.7 mA·h/g at 10 C, but that of LNCM-SDBS material still maintained 86.6 mA·h/g, which was 64.3% higher than that of LNCM-No material. Obviously, surfactants can not only change the micromorphology, particle size, dispersibility and crystal structure, but also effectively improve the electrochemical performances of synthesized material[21-22]. The best cycle and rate performances enjoyed by LNCM-SDBS material may be attributed to the good morphology and structure resulted from the assistance of SDBS. The previous characterization and analysis of XRD and SEM had proved that the LNCM-SDBS material possessed better crystallinity and dispersibility of the particles, as well as an ideal layered structure, a smaller degree of cation mixing and a more ordered close-packed hexagonal structure.

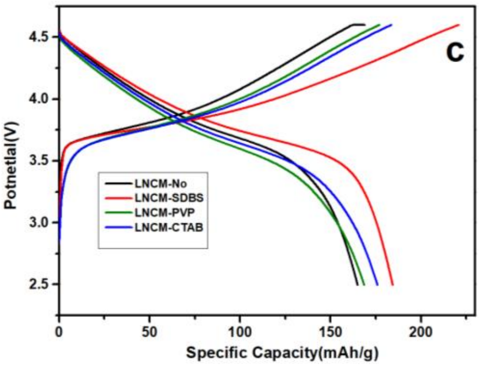

Figure 5 Initial charge and discharge curves of cathode materials with different surfactants at 0.5 C

The initial charge and discharge curves of cathode materials with the addition of different surfactants at 0.5 C were shown in Fig. 5, the initial discharge specific capacities of LNCM-SDBS, LNCM-CTAB, LNCM-PVP, and LNCM-No was 184.7, 175.9, 169.7 and 165.2 mA·h/g, respectively. Obviously, the initial discharge specific capacity of surfactant assisted material was higher than that of no surfactant addition. Especially, SDBS had the best effect on initial discharge specific capacity, which should be attributed to the special influence of unique organic chain of the surfactant SDBS on the morphology and structure of LNCM cathode material, thus significantly improving the electrochemical properties. Table 4 was a comparison of the rate performance and cycle performance of the LNCM-SDBS material with several pristine $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials in the reference. It can be found that the LNCM material synthesized with the assistance of the surfactant SDBS had more ideal electrochemical performance, which revealed the great significance of the reasonable selection of surfactants for the synthesis of high electrochemical performance electrode material.

Table 4. A comparison of the rate performance and cycle performance for several similar materials

Sample	Rate performance (mA·h/g)	Cycle performance after 100 cycles (mA·h/g)
LNCM-SDBS	86.6 (10 C)	160.71 (0.5 C)
References 14	56.5 (8 C)	139.9 (0.5 C)
References 17	69.7 (5 C)	140 (1 C)
References 25	~ 70 (10 C)	~80 (1 C)

3.3.2. Analysis of EIS and cyclic voltammetry curves

In the EIS curves, the larger the semicircle, the larger the interface impedance of the solid electrolyte; the larger the slope of the line, the faster the diffusion of lithium ions[23]. Fig. 6a showed that the semi-circle corresponding the surfactant added material was smaller than that of no surfactant addition, indicating that the addition of the surfactant can effectively reduce the interfacial impedance of the material during the electrode reaction. The linear slope corresponding the SDBS addition material was significantly larger than that of other materials, indicating that the pore channel between the particles became more smooth under the action of the surfactant SDBS, which was beneficial to the sufficient infiltration of the electrolyte, thereby accelerating the migration rate of lithium ions. The CV curves of several synthetic materials were shown in Fig. 6b. Obviously, all redox peaks were symmetrical, indicating that lithium ions had good reversibility of insertion and extraction[24]. Table 5 listed the peak potential of the oxidation peak and reduction peak, as well as the corresponding potential difference. By studying the data in Table 4, it can be found that the potential difference corresponding to the surfactant-assisted material was lower than that of the material with no surfactant addition. As known to us, the value of potential difference can reflect the degree of polarization of the material during charging and discharging.

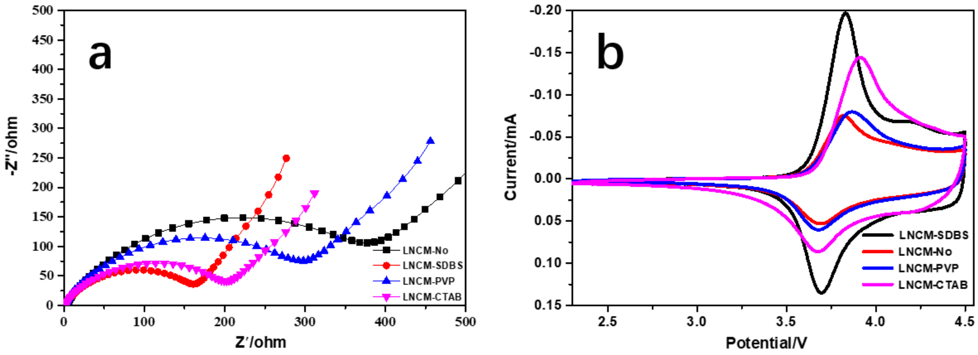

Figure 6. The EIS and CV curves of cathode materials with different surfactants addition

Table 5 Redox potentials of cathode materials synthesized with different surfactants

Sample	Oxidation peak potential (V)	Reduction peak potential (V)	Potential difference (V)
LNCM-No	3.86	3.68	0.18
LNCM-SDBS	3.83	3.74	0.09
LNCM-PVP	3.84	3.69	0.15
LNCM-CTAB	3.83	3.70	0.13

Among all data, the potential difference 0.09 V corresponding to the material synthesized by SDBS assistance was the smallest, which meant that the electrode polarization of the material was the slightest. In addition, the peak current was related to the lithium ion diffusion coefficient. The larger the peak current, the larger the lithium ion diffusion coefficient[25]. The material synthesized by SDBS assistance had the largest peak current, indicating the largest lithium ion diffusion coefficient. A series of electrochemical tests have demonstrated that surfactant SDBS can make LNCM material achieve the desired morphology, structure and electrochemical performance.

4. CONCLUSIONS

With the assistance of surfactants, LNCM material had been hydrothermally synthesized. The results showed that surfactant assistance synthesis can improve the dispersion of the particles, the uniformity of the size and the perfection of the crystal, then further effectively improve the electrochemical performance. Especially at high magnification, the improved effect of was more prominent. Among the three surfactant additive LNCM materials, the LNCM-SDBS material had the most outstanding electrochemical performance, including the largest initial discharge specific capacity, the best rate and cycle performances, which may be attributed to the unique organic chain of the surfactant SDBS on the morphology and structure of LNCM cathode material, thus resulting in the smallest polarization, the greatest lithium ion diffusion rate and the most prominent electrochemical properties. Therefore, it was a good way to use the unique organic structure of surfactant to assist the synthesis of high-performance lithium ion electrode materials.

ACKNOWLEDGMENTS
This work was financially supported by the characteristic innovation projects of universities in Guangdong province (Grant No.2019GKTSCX108), the Science and Technology Major Project of Guangxi (Grant No. AA19046001) and the Open Research Fund of Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials (Grant No. EMFM20181119)

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