

Preparation of spherical $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with core-multilayer shells structure by co-precipitation method and long cycle performance

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Abstract. As a promising cathode material for lithium ion battery of high voltage, spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has attracted interest due to its high discharging voltage at 4.7 V and high energy density of 610 Wh kg^{-1} . In this work, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with a new core-multilayer shells structure (LNMO-900) is synthesized successfully by co-precipitation method and shows a better electrochemical performance. The formation of the core-multilayer shells structure is related to the Kirkendall effect, the shell maintains structural stability, and improves long cycle performance. Core-multilayer shells structure is also beneficial for transmission of lithium ion, increasing rate performance. The effects of sintering temperature on the performance of LNMO were further investigated. Core-multilayer shells $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is synthesized successfully at 900 °C for 12 h uniquely. From the integral calculation of XPS spectra, a higher content of Mn^{4+} is observed in the outer shell of LNMO-900 compared with other homogeneous solid particles. The discharge specific capacity of LNMO-900 is 129.3 mAh g^{-1} at 1 C which is superior to others, and after 1000 cycles, LNMO-900 shows capacity retention of 87.9%. The initial capacity of LNMO-900 is 104.9 mAh g^{-1} at 5 C.

1. Introduction

Lithium-ion batteries are widely used as secondary batteries because of their high energy density, long cycle life and environmental friendliness for electrochemistry fields. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as cathode material of lithium-ion batteries has a theoretical discharge capacity of 146.7 mAh g^{-1} . $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is better than other commercial cathode materials in terms of energy density, safety and production cost in materials science fields [1]. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has three-dimensional lithium ion diffusion channels, it has excellent rate performance and can be used in the load-leveling utility application of rapid charge and discharge [2,3]. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material can offer much higher energy density (650 Wh Kg^{-1}) than other cathode material, such as LiCoO_2 (540 Wh Kg^{-1}), LiMn_2O_4 (500 Wh Kg^{-1}) and LiFePO_4 (500 Wh Kg^{-1}) [4]. The electrochemical performance can be improved by lattice and surface doping [5]. It can improve performance directly through designing special $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ structure [6-10].

Various synthesis routes producing $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with different morphologies and particle sizes have been reported [11,12]. Changing the transport rate of lithium ion through preparing special structure, thereby improving $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrochemical performance. The intrinsically fast Li^+ diffusion within the three-dimensional spinel structure leads to a good rate capability and cycling stability, making $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

attractive for vehicle applications [13,14]. Core-multilayer shells structure $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has the three-dimensional lithium ion diffusion channels, three-dimensional lithium ion diffusion channels contribute to high capacity, long cycle life and superior rate performance by increasing the contact area of the electrode/electrolyte, exposing a large number of active sites, as well as facilitating electron/ Li^+ ions diffusion channel [15-17].

In this work, we have prepared the better performance $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with core-multilayer shells structure. Precursor was synthesized from $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ solution. The pH value and the temperature of the solution as well as the droplet acceleration of the two salts should be adjusted [18-21]. Oxygen deficiency during the high temperature calcination will reduce Mn^{4+} to Mn^{3+} in the core [22]. In general, the core can deliver a high capacity, whereas the shell maintains structural stability. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ of spherical core-multilayer shells structure is formed by both $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ and Li_2CO_3 at 900 °C for 12 h. The formation of the core-multilayer shells structure is related to the Kirkendall effect [23]. The valence of Mn is nearly 4+ in the shell and most Mn^{4+} in multilayer shells can maintain the stability of structure. Core-multilayer shells structure can effectively improve the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Compared with other structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ made from co-precipitation, its cycle capacity retention rate has better advantages [24,25]. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ of core-multilayer shells

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structure is better than core-single shell and double-shelled hollow structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in some electrochemical performances^[26,27].

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with a new core-multilayer shells structure was synthesized successfully. Then the effects of sintering temperature on the performance of LNMO were further investigated. In all samples, the sample calcined at 900 °C with core-multilayer shells structure is the most obvious and the performance is the best. The initial capacity of LNMO-900 is 129.3 mAh g⁻¹ at 1 C, which can retain 87.9% capacity retention after 1000 cycles. The initial capacity of LNMO-900 is 104.9 mAh g⁻¹ at 5 C.

2. Materials and Methods

2.1. Characterization and Preparation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

All reagents were analytical grade without further purification. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.5 mol/L) and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (1.5 mol/L) were dissolved evenly in deionized water at a molar ratio Ni: Mn = 1: 3 stoichiometric ratio. Na_2CO_3 (2 mol/L) was dissolved in deionized water evenly. And appropriate amount of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%) was added to the Na_2CO_3 solution. A four-necked flask with 300 mL deionized water and NaHCO_3 (0.03 mol/L) were placed in a constant temperature water bath (55 °C). The sulfate solution and Na_2CO_3 solution were dumped into the four-neck flask by peristaltic pump at rate of 30 drops per minute and 25 drops per minute respectively. The continuous reaction was controlled at 55 °C and a constant pH of 7.6. After the complete addition of sulfate, the temperature of water bath was increased to 60 °C and a stirring speed of 1200 rpm/min to obtain carbonate precursor ($\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$). The obtained precursors were washed with deionized water and then dried at 120 °C. Finally the prepared precursor was mixed thoroughly with appropriate amount Li_2CO_3 . Mixture was sintered at 500 °C for 6 h with subsequent sintering by 850, 900 and 950 °C respectively for 12 h. They were labeled LNMO-850, LNMO-900, LNMO-950, respectively.

The surface images and energy dispersive spectrometer of the powders were captured by Scanning Electron Microscope (SEM) (PHENOM, Phenom Pro X, China) with an accelerating voltage of 25 kV. Powder X-ray diffraction (XRD) measurement is performed to identify crystal structures of the materials on a Rigaku MultiFlex Diffractometer (D/max-2500, Japan) using $\text{Cu K}\alpha$ -radiation at 20 kV and 4 mA. The scanning range of 2θ is from 10° to 80°. X-ray photoelectron spectroscopy (XPS) measurement were captured by Thermo Scientific Escalab Xi+. X-ray photoelectron spectroscopy were used to observe the particle valence changes. The C 1s peak of 284.6 eV was used as a reference to correct all bonding energies.

2.2. Electrochemical measurements

To prepare working electrodes, the prepared samples, Super P and a binding agent (PVDF) were mixed evenly with a ratio of 8: 1: 1. It was uniformly coated on an aluminum foil and then dried at 120 °C for 12 h in a vacuum. Finally, punching it into a 10 mm diameter disk to form working electrodes, the mass loading of active materials is about 2.37 mg/cm². Assembly work was carried out in an argon-filled glove box, and all prepared electrodes and lithium electrodes were installed into CR2025 button cells for later electrochemical testing. The electrolyte was 1 mol/L LiPF_6 solution with ethylene carbonate and diethyl carbonate in a 1:1 volume ratio as a solvent. A LAND BTS automatic battery test system (Shenzhen Xinwei Electronics Co, Ltd) is used for charging/discharging. The cells were activated by constant current charging /discharging after 3 cycles at 0.2 C (1 C=146.7 mA g⁻¹) and cycling performance was tested at 1 C. Cyclic voltammetry (CV) and EIS were performed on a CHI650D Electrochemical Workstation (Shanghai Chenhua Instruments Co., Ltd). CV tests were recorded at 2.0-4.8 V with a scanning rate of 0.1 mV/s. EIS tests of all samples adopted a range of frequency from 0.01Hz to 100 kHz.

3. Results & Discussion

XRD of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at different calcination temperature are shown in Fig. 1. According to the standard XRD-PDF card, XRD of the samples are matched with the cubic spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (JCPDS: 80-2162). It can be seen that there are weak impurity peaks at 37.5°, 43.5° and 67.3°. These impurity peaks correspond to $\text{Li}_x\text{Ni}_{1-y}\text{O}$ [28,29], which is a common impurity in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ materials. From Fig. 1, it can be seen that the samples are almostly pure spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

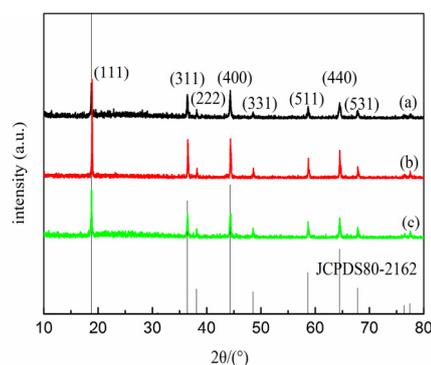


Fig. 1. X-ray diffraction patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$: (a) LNMO-850; (b) LNMO-900; (c) LNMO-950.

The SEM photographs of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ precursor microspheres are exhibited in Fig. 2a-c. It can observe directly the structure of the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ precursor and its cathode material of spherical structure. The spherical structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ maintains the spherical structure of carbonate precursor.

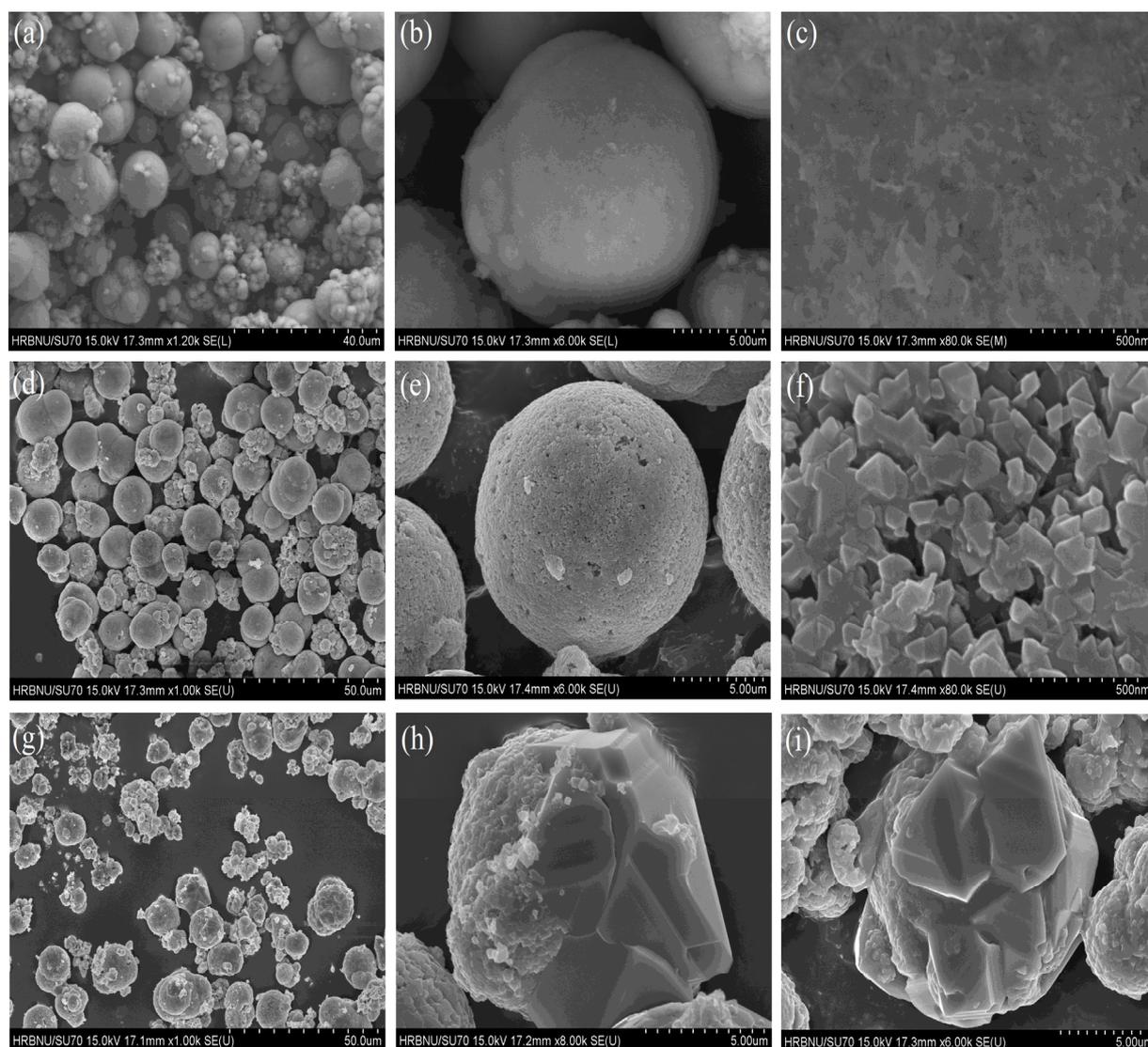


Fig. 2. (a), (b), (c): SEM images of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ microspheres, the inset shows the outer surface of the microsphere; (d), (e) SEM image of LNMO-850; (f) a high magnification 500 nm SEM image of LNMO-850 surface morphology; (g), (h), (i) SEM image of LNMO-950 microsphere.

Fig. 2 displays the SEM of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 850 oC and 950 oC. The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particle size is about 6 μm in Fig. 2e, retaining the porous spherical structure of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$. There are some holes in the shell of the product, which are probably caused by the emission of CO_2 gas during the calcination process. These pores can serve as channels for electrolyte penetration, which is beneficial for the reduction of internal resistance and improving rate capability for lithium ion batteries. The primary spinel of LNMO-850 are small and irregular in Fig. 2f, which length is about 100 nm. The SEM photographs of LNMO-950 is exhibited in Fig. 2g-i. As the temperature of calcination rises, primary particles begin to agglomerate into large spinel of polyhedrons, microsphere begin to agglomerate into polyhedrons and the core-multilayer shells structure disappear gradually. Fig. 2g-i show two morphologies for LNMO-950, it contains two kinds of particles, microsphere and polyhedron. Because the calcination temperature is high, primary spinel particle of

microsphere crystallizes to big particle, sphere structure crystallize to polyhedron morphology.

The spherical structure of LNMO-850 is not core-multilayer shells structure. As the calcination temperature rises from 850 oC to 900 oC, the crystallinity of small spinel particles grows larger, and the core-multilayer shells structure is formed. The primary $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles in Fig. 3b has more regular spinel morphology, the microsphere with core-multilayer shells structure is more obvious. The LNMO-900 in Fig. 3a-c are spherical core-multilayer shells structure, in which the inner and outer shells are composed of spinel with a size of 200-400 nm.

EDS mapping of Fig. 3 is performed to analyze the composition of element for LNMO-900. Ni and Mn are distributed uniformly in both core and shell, indicating that core and shell in LNMO-900 have the same chemical formation. The EDS results perform on the cross-section of single microsphere, it confirms further that the microsphere of LNMO-900 contain Mn and Ni.

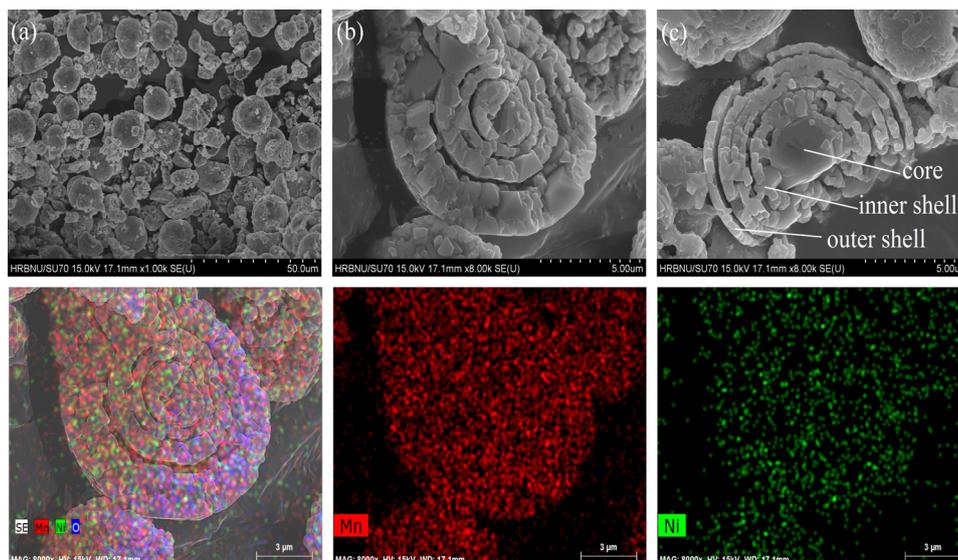


Fig. 3. (a), (b), (c): SEM image of LNMO-900 microsphere, the core, inner shell and outer shell are indicated. EDS mapping of Mn and Ni of LNMO-900 for core-multilayer structure.

We design and prepare core-multilayer shells microspheres of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ microspheres as self-templates without any additional templates or surfactants[30,31]. The nano-building blocks with short diffusion distance facilitate the Li^+ ions rapid diffusion, and the porous structure allows penetration of the electrolyte into the whole microspheres, both contributing to better rate capability. The void and space between the inner and outer shells can buffer against volume changes during Li^+ ions insertion/extraction processes, alleviate the problem of pulverization and reduces the charge transfer

resistance (R_{ct}), leading to the improved long-term cycling stability[24,32].

XPS spectra of Mn 2p, Ni 2p, C 1s and Li 1s are collected to further research the impact of the valence of manganese ion in the electronic environment. Fig. 4 displays the survey spectra of the samples, and the clear peak of Mn 2p in Fig. 5 further proves the maximum Mn^{4+} in the shell of LNMO-900. Mn^{2+} in the precursor outer shell of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is oxidized to Mn^{4+} , Mn^{2+} in the core will be oxidized to Mn^{3+} and core contains Mn^{3+} which improves the discharge specific capacity of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

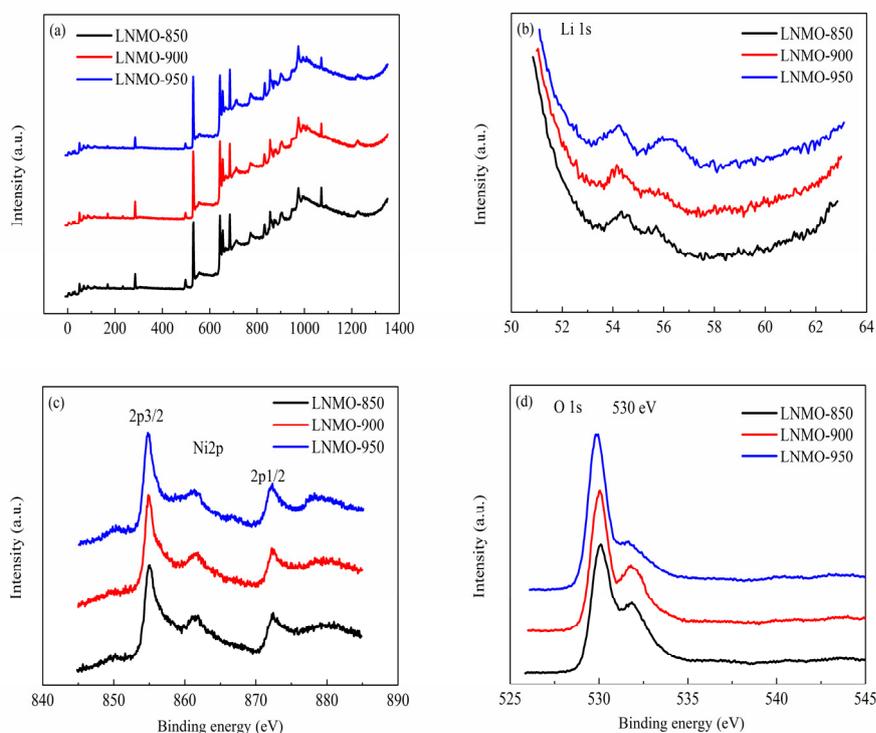


Fig. 4. XPS spectra of LNMO-850, LNMO-900 and LNMO-950: (a) XPS survey, (b) Li 1s, (c) Ni 2p, (d) O 1s.

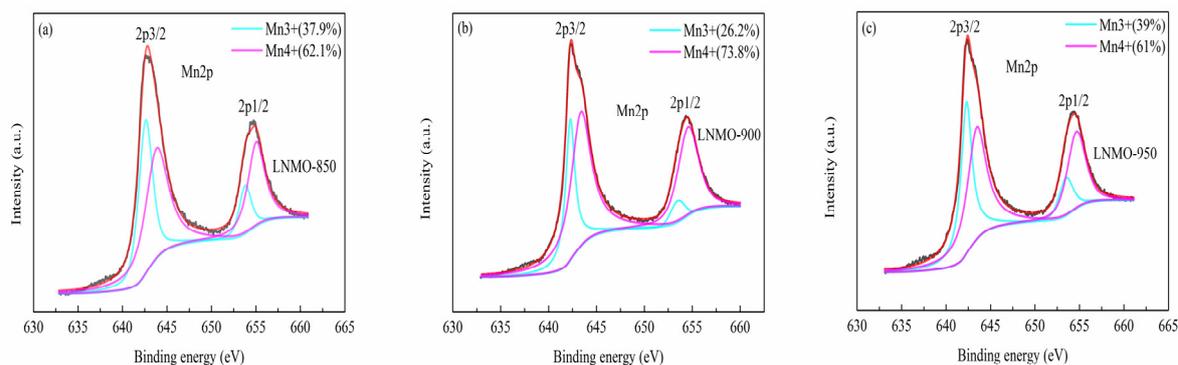


Fig. 5. XPS spectra and fitting results of survey for Mn 2p: (a) LNMO-850, (b) LNMO-900, (c) LNMO-950.

XPS spectra indicates that spectra of $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ do not increase the intensity of peak and shift the position of electron binding energy except for spectra of Mn. It is further proved that the content of manganese ions with different valence in the shell has a significant effect on the electrochemical properties of the material. The integral calculation gives the contents of $\text{Mn}^{4+}(\text{Mn}^{3+})$ as 62.1%(37.9%) for LNMO-850, $\text{Mn}^{4+}(\text{Mn}^{3+})$ as 73.8%(26.2%) for LNMO-900 and $\text{Mn}^{4+}(\text{Mn}^{3+})$ as 61%(39%) for LNMO-950 in Fig. 5. This indicates that different calcination temperature acts on the electronic environment of the surface structure of the particles. Fig. 5 indicates that shell of LNMO-900 contains the most Mn^{4+} , LNMO-900 with core-multilayer shells structure which keeps the large amount of internal Mn^{3+} and the higher discharge specific

capacity. The shell contains the most Mn^{4+} which reduce the Jahn-Teller effect of Mn^{3+} , this also suppressing structural damage[26,27], therefore maintain a high cycle capacity retention rate. XPS spectra indicate that valence of oxygen is - 2 valence, lithium is + 1 valence, and nickel is + 2 valence. The valence of manganese for all samples include + 3 valence and + 4 valence, and the average valence state of manganese is below + 4 valence, so there is oxygen defect in spinel crystal structure. Thereby also improving the discharge specific capacity effectively.

Initial charge/discharge profile of $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ at 1 C are tested in Fig. 6a. The discharge specific capacities of LNMO-850, LNMO-900 and LNMO-950 are 128.8 mAh g⁻¹, 129.3 mAh g⁻¹ and 128.6 mAh g⁻¹ respectively.

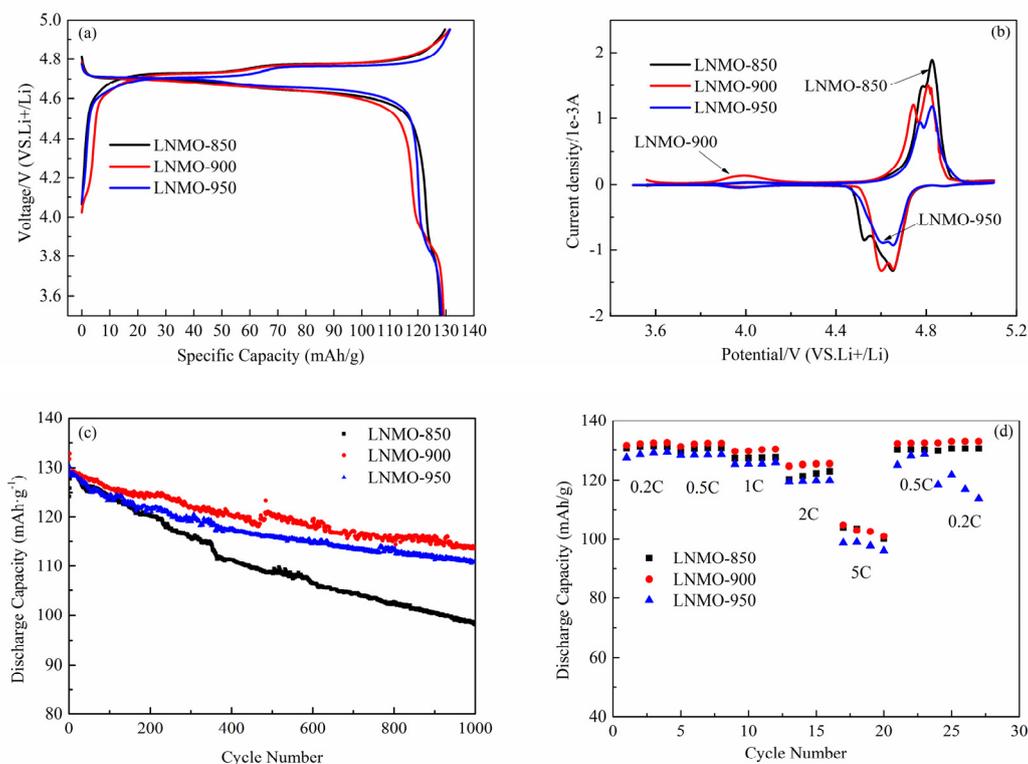


Fig. 6. (a) initial charge/discharge profile of LNMO-850, LNMO-900 and LNMO-950 at 1C; (b) CV of different samples; (c) cycle performances of different samples at 1 C; (d) rate performance of different samples for increasing rates of 0.2, 0.5, 1, 2, 5 C.

As can be seen from Fig. 6a, the discharge capacity for all samples appears on the discharge platform of 4.7

V potential (vs. Li^+/Li), which corresponds to $\text{Ni}^{4+}/\text{Ni}^{3+}$, $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox pairs[33]. In Fig. 6a, there

is an apparent discharge platform of 4.0 V potential (vs. Li⁺/Li), this platform is due to the reaction of Mn⁴⁺ to Mn³⁺, the discharge platform near 4.0 V can qualitatively analyze the content of Mn³⁺ in LiNi_{0.5}Mn_{1.5}O₄[34]. Fig. 6a shows that LNMO-900 has a relatively long 4.0 V potential platform, indicating that LNMO-900 contains more Mn³⁺ resulting from oxygen defect. The discharge capacity of LNMO-900 is the highest at 1 C, and the initial discharge capacity is 129.3 mAh/g. Fig. 6b shows cyclic voltammety curves at different calcination temperature. All samples have an obvious current peak near 4.7 V, which corresponds to Ni⁴⁺/Ni³⁺ and Ni³⁺/Ni²⁺ redox pairs. There is a weak current peak at 4.0 V, which corresponds to the redox pair of Mn⁴⁺/Mn³⁺[35], the current peak is formed at the 8a position of Li⁺ embedded in Fd_{3m} LiNi_{0.5}Mn_{1.5}O₄ of spinel octahedron, it results in area of 4.0 V peak[36]. 4.0 V peak area shows that core of LNMO-900 has the more Mn³⁺.

Fig. 6c displays a cycle performance curve for 1000 cycles at different calcination temperature. All samples are activated by 0.2 C after three cycles and then tested at 1 C condition. It can be seen from the Fig. 6c that LiNi_{0.5}Mn_{1.5}O₄ synthesized by co-precipitation has a high cyclic capacity retention rate. The discharge specific capacities of LNMO-850, LNMO-900 and LNMO-950 in the first cycle at 1 C are 128.8 mAh g⁻¹, 129.3 mAh g⁻¹ and 128.6 mAh g⁻¹ respectively. The discharge specific capacities after 1000 cycles are 98.2 mAh g⁻¹, 113.7 mAh g⁻¹ and 110.9 mAh g⁻¹ respectively, the capacity retention rates are 76.2%, 87.9% and 86.2%. The 1 C capacity of LNMO-900 is the highest.

XPS spectre of Mn 2p indicates that outer shell surface of LNMO-900 contains the most Mn⁴⁺. Shell of LNMO-900 has the most Mn⁴⁺ after high temperature calcination, which can better alleviate structure corrosion during high voltage charge-discharge cycle. The spherical LiNi_{0.5}Mn_{1.5}O₄ has a high cycle capacity retention rate because the spherical shell have most Mn⁴⁺[37,38]. It can be seen that spinel LiNi_{0.5}Mn_{1.5}O₄ with core-multilayer shells structure has excellent cyclic capacity retention rate and residual capacity after cycling. The discharge specific capacity of LNMO-900 after 1000 cycles is 113.7 mAh g⁻¹, and the capacity retention rate of LNMO-900 is 87.9%.

LiNi_{0.5}Mn_{1.5}O₄ is tested at different rate of 0.2 C to 5 C. As shown in Fig. 6d, with the increasing rate from 0.2 C to 5 C, its discharge capacity decreases gradually. The initial capacity of LNMO-850, LNMO-900 and LNMO-950 are 104.1 mAh g⁻¹, 104.9 mAh g⁻¹ and 98.9 mAh g⁻¹ at 5 C respectively. The 5 C capacity of LNMO-850, LNMO-900 and LNMO-950 are 77%, 76.2% and 74.2% of that 0.2 C respectively. The presence of the void between the hierarchically multilayer shells could serve as a reservoir for the electrolyte and allow much easier penetration of the electrolyte into the inside of the microspheres, thereby resulting in the facilitation of electrochemical insertion/extraction of Li⁺ and inhibiting the structural damage. The compact solid irregular particles is not beneficial to the transfer speed of lithium ion, LNMO-950 is compact solid structure, there is no good ion transport channel. It results in bad rate performance and large electric charge transfer resistance (R_{ct})[39]. The capacity of LNMO-950 is the lowest at 5 C.

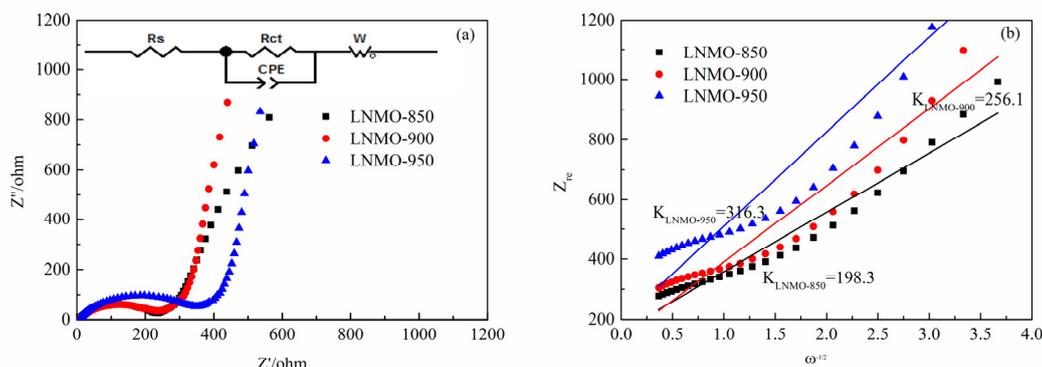


Fig. 7. (a) Nyquist plots of LiNi_{0.5}Mn_{1.5}O₄ after activation of three cycles and equivalent circuit used to fit the EIS; (b) $Z_{re}-\omega^{-1/2}$ relation of LiNi_{0.5}Mn_{1.5}O₄ material in Low frequency zone.

Fig. 7 shows the electrochemical impedance spectra of all samples and $Z_{re}-\omega^{-1/2}$ relation of LiNi_{0.5}Mn_{1.5}O₄ in Low frequency zone. Table 1 shows the parameters of EIS data that are fitted by Zview and

Li⁺ diffusion coefficient. Li⁺ diffusion coefficient is based on the following formula[40]:

$$D_{Li^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 (C_{Li})^2 \sigma^2}$$

Table 1 Electric charge transfer resistance (R_{ct}) and Li⁺ diffusion coefficient (D_{Li⁺}) of LiNi_{0.5}Mn_{1.5}O₄.

samples	R _{ct} / Ω (after activation)	D _{Li⁺} / cm ² ·s ⁻¹ (after activation)
LNMO-850	235.3	4.11532x10 ⁻¹⁷
LNMO-900	211	2.46735x10 ⁻¹⁷
LNMO-950	310.3	2.27682x10 ⁻¹⁷

The electric charge transfer resistance (R_{ct}) of LNMO-900 is fewer than that of LNMO-850 and LNMO-950. Firstly, core-multilayer shells structure of

LNMO-900 has a better three-dimensional lithium-ion diffusion path, three-dimensional lithium-ion diffusion path indicates that lithium ions can diffuse through

multiple paths and not just surface lithium layer. Secondly, XPS spectra of Mn 2p shows the absence of oxygen element in LNMO-900. The oxygen defect in spinel can cause oxygen defect in crystal lattice, resulting in oxygen defect. Oxygen vacancy is filled by electrons which conductivity is higher than that of ions, the oxygen defect in spinel helps lithium ion diffusion. Two advantages of spinel morphology for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can increase the diffusion coefficient of lithium ions and reduce electric charge transfer resistance (Rct). A variety of conditions are known to alter the transition metal oxidation state, such as the generation of oxygen vacancies[41-43]. The crystallinity of LNMO-850 is not enough large, the primary spinel is too small to form core-multilayer shells, so the electrochemical impedance of LNMO-850 is higher than that of LNMO-900. LNMO-950 particles aggregate into spinel of polyhedral without multilayer shells structure. Large polyhedral spinel particles without multilayer shells structure increase electrochemical impedance[44-46], large polyhedral spinel particles is against for lithium ion diffusion by decreasing the contact area of the electrode/electrolyte[47]. Multilayer shell structure has a low electrochemical impedance resulting from good diffusion coefficient of lithium ion[48,49]. The electric charge transfer resistance (Rct) of LNMO-900 is the lowest in table 1.

4. Conclusions

In summary, we have successfully designed and synthesized core-multilayer shells microspheres of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ microspheres as self-templates without any additional surfactants. We prepare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with core-multilayer shells structure, study the particle morphology and electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at different calcination temperature. Core-multilayer shells $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is synthesized successfully at 900 oC uniquely, which displays the highest capacity retention rate and the best rate performance. The multilayer shells structure can alleviate structural degradation during insertion/extraction of lithium ion, leading to improved long-term cycling stability. The hierarchical multilayer shells structure has shown potential to enhance electrochemical performance for cathode materials, and design of the core-multilayer shells structure will be a new and effective approach to high-performance electrode materials.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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