



A core–shell structure spinel cathode material with a concentration-gradient shell for high performance lithium-ion batteries



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HIGHLIGHTS

- The spinel $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$ is synthesized via co-precipitation process.
- The $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$ exhibits excellent cycling performance at elevated temperature.
- The $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$ exhibits significantly improved rate capability.

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ABSTRACT

A novel spinel cathode material with an average composition of $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$, in which the LiMn_2O_4 core material is completely encapsulated by a stable spinel structure concentration-gradient shell (CGS), is successfully synthesized via co-precipitation process. The spherical LiMn_2O_4 core is encapsulated by CGS that increased continuously Ni and Co contents, and the composition of the outmost layer of the spherical $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$ is $\text{LiNi}_{0.45}\text{Mn}_{1.45}\text{Co}_{0.1}\text{O}_4$. The electrochemical properties of the $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$ compared to the LiMn_2O_4 are carefully investigated by galvanostatic charge–discharge, cyclic voltammetric and electrochemical impedance spectroscopy. It has been found that the electrochemical properties of the $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$ material are far superior to those of the alone LiMn_2O_4 core material. Besides, the $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$ sample exhibits excellent cycling stability at elevated temperature. It delivers a discharge capacity of 118 mAh g^{-1} between 3.0 and 4.4 V vs. Li/Li^+ with a retention of 96% over 200 cycles at a rate of 1 C (148 mA g^{-1}) at 55°C . In the same time, the $\text{LiMn}_{1.912}\text{Ni}_{0.072}\text{Co}_{0.016}\text{O}_4$ shows also a good rate capability. It can still deliver a high discharge capacity of over 110 mAh g^{-1} even at a rate of 5 C. Therefore, the core–shell structure spinel cathode material with CGS will be a promising cathode material for advanced lithium ion batteries.

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1. Introduction

Recently, the imperative of tackling environmental pollution and the exhaustion of fossil fuel reserves has rendered electric vehicles (EVs) of greater importance than ever before. Making these sustainable vehicles a reality still relies on the availability of suitable energy storage systems, and highly efficient lithium-ion batteries can in principle serve the purpose [1–3]. Indeed these batteries have achieved a leading role in the consumer electronics market where they are the power sources of choice of a series of

portable electronic devices. However, in their present version these batteries are unable to meet the requirements of electric vehicles, and thus making these systems suitable for application in the electric vehicle sector by the development of advanced, low cost, abundant availability, better safety, environmental compatibility and high-performance electrode materials is mandatory [4–7]. In this respect, LiMn_2O_4 has been extensively investigated as one of the most promising cathode materials for being used in Li-ion batteries for EV and HEV due to its low cost, non-toxicity, high safety and high power density [8–13]. However, the wide practical use of the LiMn_2O_4 electrode has so far been hindered by their severe capacity fading during cycling, especially when operating at elevated temperature. This limiting phenomenon is mainly due to the structural distortion via Jahn–Teller effect and Mn dissolution in the electrolyte [14–18]. Thus, the improvement in the

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electrochemical reversibility and stability of LiMn_2O_4 at elevated temperatures becomes more and more important. In order to solve the above problem, many methods such as fabrication of non-stoichiometric spinels [19], doping with foreign ions [20], application of coatings [21], or utilization of electrolyte additives or different electrolytes have been investigated to improve the cyclability of LiMn_2O_4 [22].

On the other hand, the core–shell structure is becoming a hot research direction because it can produce a synergetic effect from both the core and the shell [23–25]. For example, Myung et al. reported a core–shell $\text{Li}[(\text{Li}_{0.05}\text{Mn}_{0.95})_{0.8}(\text{Ni}_{0.25}\text{Mn}_{0.75})_{0.2}]_2\text{O}_4$ spinel [7], which showed pretty excellent cyclic performance, because this $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -shell material protects the $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ -core material from HF attack during the cycling effectively. However, the conductivity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is relatively low. Furthermore, the interface composition of the transition metals between the core and shell changes rather sharply, which would cause a different shrinkage ratio during the high-temperature calcinations process. In that case, the interface between the core and shell could act as a barrier to Li^+ diffusion, thereby resulting in poor electrochemical properties of the materials [26–28]. Hassoun et al. reported that the $\text{LiNi}_{0.45}\text{Mn}_{1.45}\text{Co}_{0.1}\text{O}_4$ spinel material exhibits excellent cycling stability and rate capability [6]. The Co-doped $\text{LiNi}_{0.45}\text{Mn}_{1.45}\text{Co}_{0.1}\text{O}_4$ had significantly improved cycling stability and rate capability, probably due to the enhanced electronic conductivity and structural stability due to the stronger bonding character of Co–O in the structure. Therefore, the $\text{LiNi}_{0.45}\text{Mn}_{1.45}\text{Co}_{0.1}\text{O}_4$ can serve as a good protective shell for the core material. Furthermore, according to previous reports [1], concentration-gradient structure can compensate for the shortcomings of core–shell structure.

Based on the above consideration, a new scheme has been designed. The advantages of the LiMn_2O_4 and Co-doped $\text{LiNi}_{0.45}\text{Mn}_{1.45}\text{Co}_{0.1}\text{O}_4$ are just the right combination together for the first time. A novel cathode material with long cycle life and high rate capacity has been prepared. The material has a bulk LiMn_2O_4 core to deliver high capacity, and the CGS made of a concentration-gradient of the transition metals (Ni, Co and Mn) can enable smooth Li ions diffusion and yield a protective layer. Furthermore, the physicochemical and electrochemical performances of this cathode material have been studied in detail.

2. Experimental

2.1. Synthesis of spherical core-CGS cathode material

To prepare the spherical core-CGS precursor particle, it is necessary to synthesize firstly the spherical MnCO_3 as the core precursor, and then grow a concentration-gradient of Ni, Co, and Mn in the shell layer by a co-precipitation method. Encapsulation of the MnCO_3 by a concentration-gradient carbonate resulted in the coexistence of three carbonates in the product. At the beginning of the process, the 1.6 mol L^{-1} of MnSO_4 solution (aq) was pumped into a continuously stirred tank reactor at the feeding rate of 1 mL min^{-1} . At the same time, the 1.6 mol L^{-1} Na_2CO_3 solution (aq) as precipitant and the 0.5 mol L^{-1} $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (aq) as chelating agent were also separately fed into the reactor at the feeding rate of 1.03 mL min^{-1} and 0.2 mL min^{-1} , respectively. The pH of the reaction mixture (about 7.3), the operation temperature (about 45°C) and the stirring speed (about 800 rpm) in the reactor were carefully controlled. When only remained 40 mL MnSO_4 solution (aq), 60 mL, the 1.6 mol L^{-1} of mixture aqueous solution of NiSO_4 , MnSO_4 and CoSO_4 (cationic ratio of Mn:Ni:Co = 1.45:0.45:0.1) was continuously pumped into the stock solution containing the starting MnSO_4 solution at the feeding rate of 0.6 mL min^{-1} , after which the homogeneously mixed solution

was continuously fed into a continuously stirred tank reactor to form the $[\text{Mn}_x(\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z)_{1-x}]\text{CO}_3$ ($0.725 < x < 1$, $0 < y < 0.225$, $0 < z < 0.05$) core-CGS precursor. After that, the core-CGS precursor particles were then filtered, washed, and dried at 110°C . The prepared carbonates were fired at 480°C for 6 h in air to convert the carbonates into oxides. Finally, the resulting powders were thoroughly mixed with appropriate amount of lithium carbonate and the mixture was calcined at 780°C for 20 h in the air to form $\text{Li}[\text{Mn}_x(\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z)_{1-x}]_2\text{O}_4$ ($0.725 < x < 1$, $0 < y < 0.225$, $0 < z < 0.05$) core-CGS material. For comparison, the spherical LiMn_2O_4 sample was also prepared in the same conditions.

2.2. Materials characterization

The phase identification of the samples were performed with a diffractometer (D/Max-3C, Rigaku, Japan) using Cu $K\alpha$ radiation ($\lambda = 0.154178 \text{ nm}$) and a graphite monochromator at 40 kV, 40 mA. The scanning rate was 4° min^{-1} and the scanning range of diffraction angle (2θ) was $10^\circ \leq 2\theta \leq 80^\circ$. The morphologies and structures of the materials were characterized by scanning electron microscopy (SEM, JSM-5600LV), transmission electron microscopy (JEOL JEM 2010). The tapping density was tested by centrifugation of the sample at 8000 rpm for two hours. The two samples were examined by adsorption experiments of nitrogen, and adsorption/desorption isotherms of nitrogen were measured at 77 K (JW-BK112) after the prepared samples were degassed at 110°C overnight. The estimation of Brunauer–Emmett–Teller (BET) specific surface area, was carried out according to the Brunauer–Emmett–Teller (BET) equation. The local composition of the samples was obtained with an energy-dispersive X-ray spectroscope (EDXS) (JSM-6100LV, JEOL, Japan). The chemical compositions of the resulting powders and the dissolved Mn element content were analyzed by atomic absorption spectroscopy (Vario 6 Analytik Jena AG, Jena, Germany).

2.3. Electrochemical test

To fabricate the positive electrode, the as-prepared materials were mixed with Super P and polyvinylidene fluoride (80:10:10) in *N*-methylpyrrolidone. The obtained slurry was coated onto Al foil and roll-pressed. The loading mass of the active material is $4\text{--}5 \text{ mg cm}^{-2}$. The electrodes were dried overnight at 110°C in a vacuum before use. The 2025 coin cells in the test used lithium foil as the counter electrode, polypropylene microporous membrane as the separator and 1 M LiPF_6 dissolved in ethylene carbonate (EC)–dimethyl carbonate (DMC) (1:1, v/v) as the electrolyte. The cells were assembled in an argon-filled glove box. The cells were charged or discharged galvanostatically at a rate of 1C using the Newell battery test system BTSXWJ-6.44S-00052 (Newell, Shenzhen, China) in a voltage range of 3.0–4.4 V or 3.0–4.9 V. In addition, the rate capability was measured at different current densities from 0.2 to 5C between 3.0 V and 4.4 V. The cyclic voltammetric (CV) tests were carried out on an electrochemical workstation (VersaSTAT3, Princeton Applied Research, USA) at different scan rates in a range of 3.0–4.4 V. The electrochemical impedance spectroscopy (EIS) of the cells was measured on a VersaSTAT3 electrochemical workstation (Princeton, America) in the frequency range of 10 kHz to 10 mHz with an AC voltage of 5 mV.

3. Results and discussion

Fig. 1a shows a scheme for the formation sequence and the architecture of the concentration-gradient electrode formulation. Based on this novel idea, the spherical precursor particle with an inner MnCO_3 -core and a CGS layer was properly synthesized via co-

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